

Institut français du pétrole publications

Alain CHAUVEL

Professor, École Nationale Supérieure du Pétrole et des Moteurs

Deputy Director, Economics and Information Division

Institut Français du Pétrole

Gilles LEFEBVRE

Senior Engineer, Institut Français du Pétrole

Foreword by

Pierre LEPRINCE

Director, Institut Français du Pétrole

PETROCHEMICAL PROCESSES

TECHNICAL AND ECONOMIC CHARACTERISTICS



**MAJOR OXYGENATED, CHLORINATED
AND NITRATED DERIVATIVES**

Translated from the French
by Nissim MARSHALL

1989

EDITIONS TECHNIP 27 RUE GINOIX 75737 PARIS CEDEX 15

technip

AMONG OUR BOOKS

Publications in English

- Catalytic Cracking of Heavy Petroleum Fractions.
D. DECROOOCQ
- Methanol and Carbonylation.
J. GAUTHIER-LAFAYE, R. PERRON
- Principles of Turbulent Fired Heat.
G. MONNOT
- International Symposium on Alcohol Fuels. VIIth International Symposium, Paris, October 20-23, 1986.
- Applied Heterogeneous Catalysis. Design. Manufacture. Use of Solid Catalysts.
J. F. LE PAGE
- Chemical Reactors.
P. TRAMBOUZE, H. VAN LANDEGHEM, J. P. WAUQUIER

Translation of
"Procédés de pétrochimie
Caractéristiques techniques
et économiques
Tome 2. Les grands intermédiaires
oxygénés, chlorés et nitrés"
A. Chauvel, G. Lefebvre, L. Castex
© Éditions Technip, Paris 1986
(2nd Edition)

© 1989 Éditions Technip, Paris

All rights reserved. No part of this publication may be reproduced or
transmitted in any form or by any means, electronic or mechanical,
including photocopy, recording, or any information storage and retrieval
system, without the prior written permission of the publisher.

ISBN 2-7108-0561-8 (édition complète)
+ ISBN 2-7108-0563-4 (tome 2)

Printed in France
by Imprimerie Nouvelle, 45800 Saint-Jean-de-Braye

FOREWORD

Since 1971,¹ when the first edition of this book appeared, the petrochemical industry has experienced the upheavals resulting from the two oil crises and the economic recession which has struck most nations, to different degrees and at different times. Accordingly, the petrochemical industry has witnessed a rise in the prices of its raw materials as well as changes in its markets.

Raw materials

The 1960s were marked by two guidelines concerning the choice of raw materials. It was routine at the time to assert that the United States had built its petrochemical growth on ethane. Indeed, the tapping of the huge fields of natural gas required to satisfy its needs furnished a by-product, ethane, at attractively low cost, which was ideal for the production of ethylene.

By contrast, Europe and Japan, which had minimal natural gas resources, had based their petrochemical development on naphtha, which was then considered as a by-product of crude oil refining. At the time, demand for heavy petroleum fractions, and chiefly heavy fuel oil, for electric power production, left over large quantities of naphtha, which was unable to find sufficient outlets in the production of gasoline. Hence the price of naphtha was close to that of the fuel, \$18/t in April 1971. Thanks to this favorable economic context, the European and Japanese petrochemical industries underwent spectacular growth, not only for ethylene derivatives, but also those of propylene, butadiene and benzene, co-products of naphtha steam cracking. This situation led to a sharp increase in petrochemical consumption, so that, as of 1972 and early 1973, naphtha became so widely sought after that its price rose substantially: \$42/t in April 1972 on the Rotterdam market and \$65/t in July 1973. The rise was accentuated by the oil crisis in the fall of 1973, and the price of naphtha climbed rapidly to \$130/t at the end of 1974, and is \$240/t today.

Even considering inflation, which caused prices to double between 1971 and 1984, this period saw the price of naphtha triple in real value. This situation encouraged the petrochemical industry to search for other raw materials that could offer a more appropriate economic adequation to market needs. Accordingly, since 1971 the trend was established to use heavier fractions produced by oil refining, such as atmospheric gas oil and even vacuum gas oil. More recently, due to the higher recovery of associated gases in the Middle East oil fields, and that of gas condensates in gas fields (North Sea, Indonesia), the European and Japanese petrochemical industries moved towards the use of propane/butane, often blended with naphtha, and even ethane for the North Sea riparian states. However, since the availability and price of these new raw materials, gasoil as well as liquefied petroleum gas, were uncertain and liable to market fluctuations.

this led to the development of flexible steam crackers, capable of treating, in a single unit, different raw materials which the operator selected according to prices and the needs of downstream units. Finally, the trend towards vertical integration among the oil and gas producing countries, which manufactured finished products, resulted in the construction of new facilities for the production of ethylene by ethane cracking and the production of methanol from associated gas, especially in the Middle East. Since the capacities of these plants outstrip domestic needs by a wide margin, their products, enjoying the benefit of a cheap raw material, are liable to compete with the products of the industrial countries.

A similar situation also risks arising with the progressive production of the vast natural gas fields of eastern Canada. This development, whose effect is still slight today, could give rise in the future to a gradual shift of the production centers of basic petrochemical commodities.

Thus, although Europe and Japan are still net exporters, they could become importers of ethylene derivatives by the 1990s.

Markets

During the 1971/1984 period, world markets were deeply disturbed by the economic recession and by the steep rise in production costs, resulting from the increase in the prices of petroleum raw materials.

This increase in costs had a powerful effect on the markets of major intermediates in the developing countries. In the 1960s it was felt that the low cost of petrochemical derivatives, chiefly fertilizers and polymers, would, by the end of the century, become a decisive factor in the industrial growth of these countries. The predictions made at the time are increasingly illusory. This can be attributed primarily to the weight of the raw material price in the final product cost: it accounts today for 85 per cent of the operating costs of a steam cracker, whereas in 1973 it only represented 48 per cent. Moreover, for the same period, investments were multiplied by a factor of 4 in current value and by 1.6 in constant value. For these countries, this meant that petrochemical derivatives lost part of their character of cheap products, susceptible to widespread circulation.

In the industrial countries, the burden of the economic crisis resulted in a decline in consumption, so that production capacities showed a large surplus over needs, jeopardizing the financial equilibrium of manufacturing companies.

Techniques

Despite this discouraging situation, the 1970s witnessed a constant improvement and adaptation of manufacturing techniques. This included improvements which were often decisive in the economic context of petroleum products: yields were boosted and energy consumption reduced. The area which saw the most significant development was that of catalysts, whose performance was constantly improved thanks to advances in the knowledge of their action mechanisms.

Thus, in ammonia synthesis, mixed oxide base catalysts allowed new progress towards operating conditions (lower pressure) approaching optimal thermodynamic conditions. Catalytic systems of the same type, with high weight productivity, achieved a decrease of up to 35 per cent in the size of the reactor for the synthesis of acrylonitrile by ammonoxidation. Also worth mentioning is the vast development enjoyed as catalysts by artificial zeolites (molecular sieves). Their use as a precious metal support, or as a substitute for conventional silico-aluminates, led to catalytic systems with much higher activity and selectivity in aromatic hydrocarbon conversion processes (xylene isomerization, toluene dismutation), in benzene alkylation, and even in the oxychlorination of ethane to vinyl chloride.

The industrial development of homogeneous rhodium base catalysis, of which the synthesis of acetic acid by methanol carbonylation is the most spectacular example, still has considerable potential today. Even if the marketing of new processes (direct production of ethylene glycol from a synthesis gas, homologation of alcohols) remains hampered by a still unfavorable economic situation, significant progress can undoubtedly be anticipated, benefiting the production of many oxygenated petrochemical intermediates.

In the 1971/1984 period, technological innovations led to substantial gains : they were the outcome of a new optimization between energy expenses, raw materials consumption and capital investment. One of the most striking examples is the drop in natural gas consumption recorded in the production of ammonia ($28 \cdot 10^6$ kJ/t against $34 \cdot 10^6$ kJ/t) and methanol ($32 \cdot 10^6$ kJ/t against $37.5 \cdot 10^6$ kJ/t).

Improvements in existing processes accompanied by new techniques. The first edition of this book presented 70 processes. It now discusses 140. Admittedly these are not all innovations. Many of them are different versions of the same chemical reaction or of an already existing separation method. Others, more innovative, only made headway slowly; their industrial penetration was hindered by the slowdown in economic expansion : new solvents in extractive distillation for benzene production, metathesis of olefins (Shell), olefins for oxo synthesis (Dimersol, Institut Français du Pétrole), adiponitrile by direct hydrocyanation of butadiene (Du Pont de Nemours), or by the conversion of 1,6-hexanediol (Celanese), lauryllactam from cyclododecane (ATO, Hüls).

Simultaneously, separation and purification techniques for products obtained by chemical conversions gained increasing importance, in so far as new purity requirements became necessary for intermediate compounds to improve the properties of finished products, especially polymers. New techniques were developed to respond to this trend: extraction of paraxylene and 1-butene (Universal Oil Products, Torar) by selective adsorption on molecular sieves, hydrogen purification by permeation or by solid adsorption (Union Carbide, Linde), production of carbon monoxide by adsorption in a solvent (Tenneco). Cryogenics, hitherto reserved for specific cases (steam cracking effluent air distillation) was extended to separations of industrial gases, following progress achieved in low temperature heat transfers.

Also worth mentioning besides these processes, which apply to high tonnage intermediates, is the development of products already known in 1971 but which, owing to new applications, have become essential petrochemical derivatives : 1-butene, a co-

monomer in the manufacture of low density polyethylene, tertiary butanol, a by-product of propylene oxide manufacture, which is popular as a gasoline additive, and 1,4-butane-diol and dimethylcyclohexane for the manufacture of specialty polyesters.

This broad review highlights the innovative dynamism of the petrochemical industry which, despite the crisis, has succeeded in improving its techniques to adapt them to the economic circumstances. While this remark is optimistic, the difficulties of the future must not be underestimated: the shift of the centers of production to the oil producing countries, the absorption of surplus production capacity, market redistribution, and the development of new products.

In this context, investment decisions will require a sound knowledge of the technical and economic value of the available technologies.

I believe that this book, which the authors have striven to make both complete and precise, offers an outstanding guide for engineers in their technical and economic analyses of new petrochemical projects.

P. LEPRINCE
Director
Institut Français du Pétrole

Chapter 7

ETHYLENE AND PROPYLENE OXIDES

7.1 ETHYLENE OXIDE

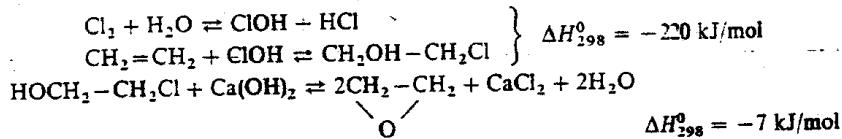
Ethylene oxide ($d_4^{20} = 0.8697^{(1)}$, bp_{1,013} = 10.7°C), which was synthesized for the first time by Wurtz in 1859, was only manufactured industrially in 1925 by *Union Carbide*. It subsequently witnessed considerable development, and US production, which was 7000 t/year in 1930, exceeded 2500,000 t/year in 1984.

Two processes were employed to manufacture ethylene oxide in the 1970s:

- Indirect oxidation of ethylene, with chlorohydrin as an intermediate.
- Direct oxidation by air or oxygen.

7.1.1 The ethylene chlorohydrin process

This method is now rarely used to synthesize ethylene oxide, but is still employed to manufacture propylene oxide. The main reactions involved in the process are the following:



Hypochlorous acid (ClOH) produced by the action of chlorine on water is added to ethylene. The chlorohydrin obtained is then treated with lime to form ethylene oxide. Despite a high molar yield in relation to ethylene (80 per cent) and relatively low investment, this process suffered from major drawbacks:

- Corrosion due to the use of chlorine, incurring high maintenance costs.

(1) Specific gravity, 68.0.39.2

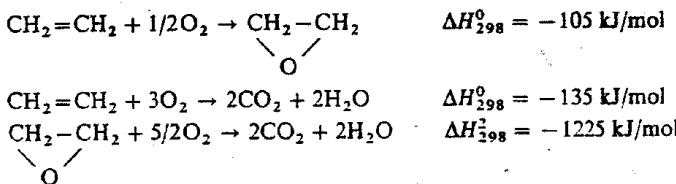
- (b) High operating costs, with a large share due to the price of chlorine.
- (c) The inevitable production of largely useless calcium chloride, and, to a lesser degree, that of another by-product, 1,2-ethylene dichloride.

7.1.2 Direct oxidation processes

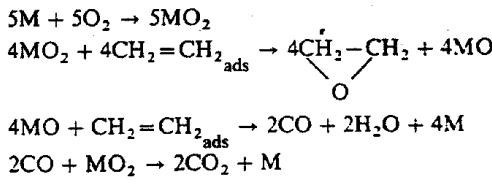
Ethylene oxide was first manufactured industrially by this route in 1938 by *Union Carbide*, which acquired the patents published by Lefort in 1931 concerning the synthesis of ethylene oxide by direct oxidation. Two years later, in 1940, this type of process accounted for 10 per cent of total installed capacity at the time in the United States, and, since 1973, the process is employed by nearly all plants in operation or planned throughout the world.

7.1.2.1 Theoretical considerations

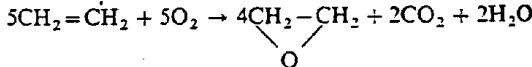
The main reactions involved are the following:



All these reactions and especially the latter two, which correspond to the complete combustion of ethylene and of its oxide, are highly exothermic and complete in the operating conditions of ethylene oxide synthesis. To guide the transformation in the direction of the first reaction, the operations require the presence of a metallic catalyst. The catalyst is generally considered to act according to the following reaction mechanism:



giving the overall reaction:



This transformation presumes the adsorption of ethylene on the metal surface, together with that of the oxygen, which is partly or completely dissociated into atoms. It also provides a maximum theoretical molar yield of 80 per cent, which may explain the apparent mediocrity of the performance achieved by commercial processes.

A. Catalysts

All present industrial catalyst systems are based on silver deposited on a slightly porous solid. The most widely used support is α -alumina, but silica-alumina and carbonium can also be employed. The specific surface area of the support, its porosity, and the pore size exert a considerable influence on the metal distribution at the surface, and consequently on catalytic activity. Several techniques are also available for fixing the silver, either by impregnation from a solution, or by deposition from a suspension. An initiator, usually consisting of alkaline earth or alkaline metals, can be added to the catalyst, but other metallic additions have also been recommended. Certain halogenated organic derivatives, such as dichloropropane, may increase selectivity in trace amounts (10 ppm in the feed), by reducing combustion side reactions.

Despite the variety of the catalyst systems proposed, none of them offers an ethylene oxide molar selectivity better than 70 per cent, with the liberation of heat at the rate of 500 kJ/mol of converted ethylene.

B. Raw materials

The degree of purity of the ethylene feed does not impose any particular constraints, as long as the acetylene, sulfur and carbon monoxide contents do not exceed 2 ppm each. Ethylene currently produced by steam cracking is perfectly satisfactory.

Air or oxygen can be used as the oxidizing agent, but it appears that economic advantages can be procured by using pure oxygen, thus avoiding an excessively high material loss in the off-gases, so that nearly all modern plants employ pure oxygen.

C. Operating conditions

The temperature must be kept between 260 and 290°C to obtain the optimal yield. This value must not be exceeded to avoid combustion reactions, which are by far the most exothermic. Temperatures higher by 20 to 40°C are recorded at the catalyst surface.

Although thermodynamic calculations show that the pressure has no effect on conversion at the reaction temperatures, operations are conducted at 1 to $3 \cdot 10^6$ Pa absolute to facilitate the subsequent absorption of ethylene oxide in water. Yield per pass reaches a maximum with increased residence time, but, to maintain high selectivity, this is limited to between 1 and 4 s in industrial plants.

The ethylene oxidation rate is proportional to the oxygen concentration. This means that the air-to-ethylene ratio has a predominant influence on the conversion and yield. For practical purposes, however, the optimal ethylene concentration is determined by the flammability limits of the mixtures with oxygen or air, and by the olefin loss in the off-gases.

Hence, in ambient conditions, the air/ethylene mixture exhibits an auto-ignition range between 2 and 28.6 per cent volume ethylene. The lower limit is substantially the same with rising temperature, while the upper limit is increased. For mixtures of air and ethylene oxide, the lower limit is 2.5 to 3 per cent volume oxide, and the upper limit approaches 100 per cent. To remain below 3 per cent volume in both cases, it is necessary to use inert diluents. The presence of carbon dioxide, which may also result from the recycling of the products of combustion reactions, can help to reduce the flammability

zone. Increasing use is now being made of processes using oxygen with a hold-up of methane, whose heat capacity and thermal conductivity are greater than those of nitrogen.

7.1.2.2 Industrial manufacture

As a rule, industrial plants operate with a silver-based catalyst in a fixed bed, with recycle of unconverted ethylene. They comprise two main sections, ethylene oxide synthesis and purification.

The earliest processes employed air as the oxidant (*Distillers, IG Farben, Scientific Design, Union Carbide*). Modern plants are nearly all supplied with oxygen (*Chemische Werke-Hüls, Japan Catalytic, Scientific Design second version, Shell, SNAM Progetti: Societa Nazionale Metanodotti*). The main concern of all these installations is the effective removal of the heat produced during the reaction. This is achieved by operation with a low ethylene conversion rate, cold product recycle, and external cooling of the catalyst bed.

A. Industrial schemes

The feed mixture (ethylene, oxygen and inert) is fed to a series of tubular reactors mounted in parallel, after being preheated by heat exchange with the exit gases. The tubes, of which several thousand may exist per shell, are of stainless steel. They range from 12 to 50 mm in inside diameter and are up to 12 m long. Kerosene or tetrailin flows around them and removes the heat liberated by the reaction. The condensation of the vapors of this coolant fluid in an external boiler helps to make maximum use of the heat recovered by the production of steam.

The reactor gaseous output is cooled in heat exchangers and undergoes countercurrent treatment in absorption columns with deionized water, filled with Raschig rings and operating under pressure. A large part of the gas leaving the top of the absorption column and containing unconverted ethylene is recycled. Continuous purge serves to prevent the accumulation of inert gases (mainly carbon dioxide).

The aqueous solution rich in ethylene oxide is sent to purification. It passes through a stripping column, which operates under vacuum and separates the ethylene oxide at the top. The aqueous effluent leaving at the bottom is recycled to the absorption stage. It can be treated in an auxiliary unit to recover the glycol it contains. The top effluent which, in addition to carbon dioxide, contains acetaldehyde and hydrocarbon traces, is sent to two distillation columns in series, one for dehydration (≥ 20 trays), and the second for purification (≥ 50 trays). These columns produce high-purity ethylene oxide with a very low acetaldehyde content. The product is stored in liquid form in tanks under nitrogen pressure.

The main processes display the following characteristics.

B. Shell process (Fig. 7.1)

In this technique commercialized since 1958, the raw materials are oxygen in a purity of 95 to 100 per cent volume and ethylene which may contain up to 10 per cent volume of methane. It accounts for about 35 per cent of all installations in operation today. The molar ratio between these two components may vary from 7 to 1, and the feed gases

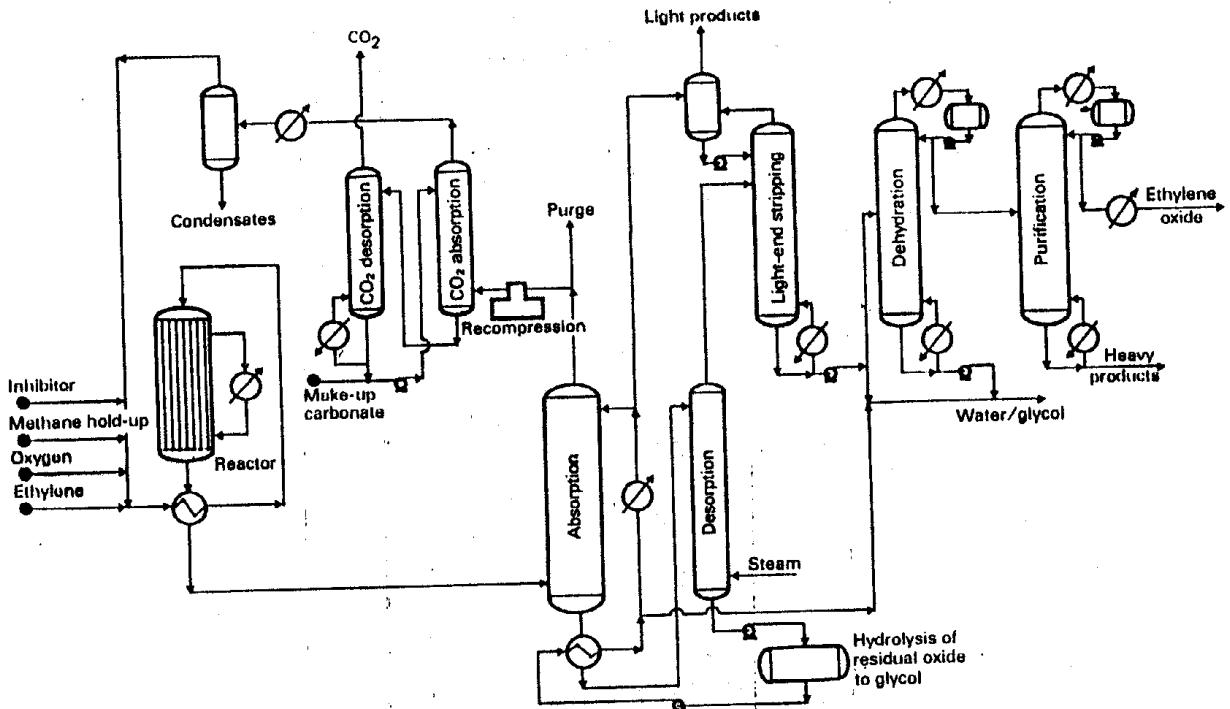


Fig. 7.1. Ethylene oxide production by oxygen oxidation. Shell process.

contain 10 to 40 per cent ethylene. This high olefin content produces a reaction mixture which is always above the upper flammability limit in the operating conditions.

The temperature is about 250 to 270°C, and the operating pressure about $1.2 \cdot 10^6$ Pa absolute. Molar selectivity is as high as 72 per cent with a once-through conversion rate of 18 per cent, and total yield is around 65 molar per cent. The presence of a moderator (ethylene dichloride added at the level of 5 ppm in the feed) helps to achieve this performance.

The reactors are supplied with a mixture of ethylene, oxygen and recycle gas acting as diluents. The recirculation stream is dissolved in a potassium carbonate solution to reduce the carbon dioxide content. In this process, which features closed-circuit circulation of inert gases, purge and hence ethylene losses (0.5 per cent of the amount introduced) are minimal.

C. Scientific Design process (Fig. 7.2)

The need to operate in the presence of diluents suggests the use of air as an oxidant. However, after the reaction stage, this method requires discharging all the inert introduced in a purge, causing a significant loss of unconverted ethylene (4 to 4.5 per cent). To reduce this useless waste of raw material, *Scientific Design*, whose first unit went on stream in 1953, carried out the oxidation in two series of reactors, with the reactors placed in parallel in each of them.

The first series is fed with a mixture of air and ethylene in a molar ratio of 10/1, and with recycle gases which lower the proportion of air to C₂H₄ plus inert in the feed gas to 7 to 8/1. These reactors operate at a low conversion rate (25 to 30 per cent) and hence with high molar selectivity (70 per cent). The output, which contains up to 2 per cent volume of oxide and 2 to 3 per cent ethylene, are cooled to 40°C by heat exchange with the recycle gases. After passage through the primary absorber, 60 per cent of the reactor output is recycled. The remainder, to which air is added to bring the air to ethylene ratio to 8/1, is sent to the second series of reactors, the so-called purge series, which operate at a high conversion rate (75 to 80 per cent) and low molar selectivity (50 per cent). A second absorber is used to extract the ethylene oxide with water.

The reactor temperatures range from 200 to 315°C, and the pressure from 0.85 to $1.2 \cdot 10^6$ Pa absolute. The total molar yield is 60 to 65 per cent. *Scientific Design* also offers another version of its process using oxygen, which is similar to the Shell technology described above. These two systems account for 55 per cent of all units currently in operation today.

D. Other processes

Other processes employing similar techniques have enjoyed less industrial development. The main license holders are *Japan Catalytic Chemical Company*, *Chemische Werke-Hüls*, *SNAM Progetti* and *Union Carbide*. *Dow* and *Montecatini* have their own processes.

All the current technologies suffer from the drawback presented by the low yield in relation to ethylene, of which about 30 per cent is degraded in the form of CO₂ and water. Attempts have been made to improve selectivity by modifying the catalyst, but none of these appears to have obtained industrial success. It has also been proposed (*Scientific Design*, *Vulcan Atlantic*) to use a fluidized bed catalyst to favor the removal of the heat of reaction, but this method has not yet gone beyond the pilot plant stage.

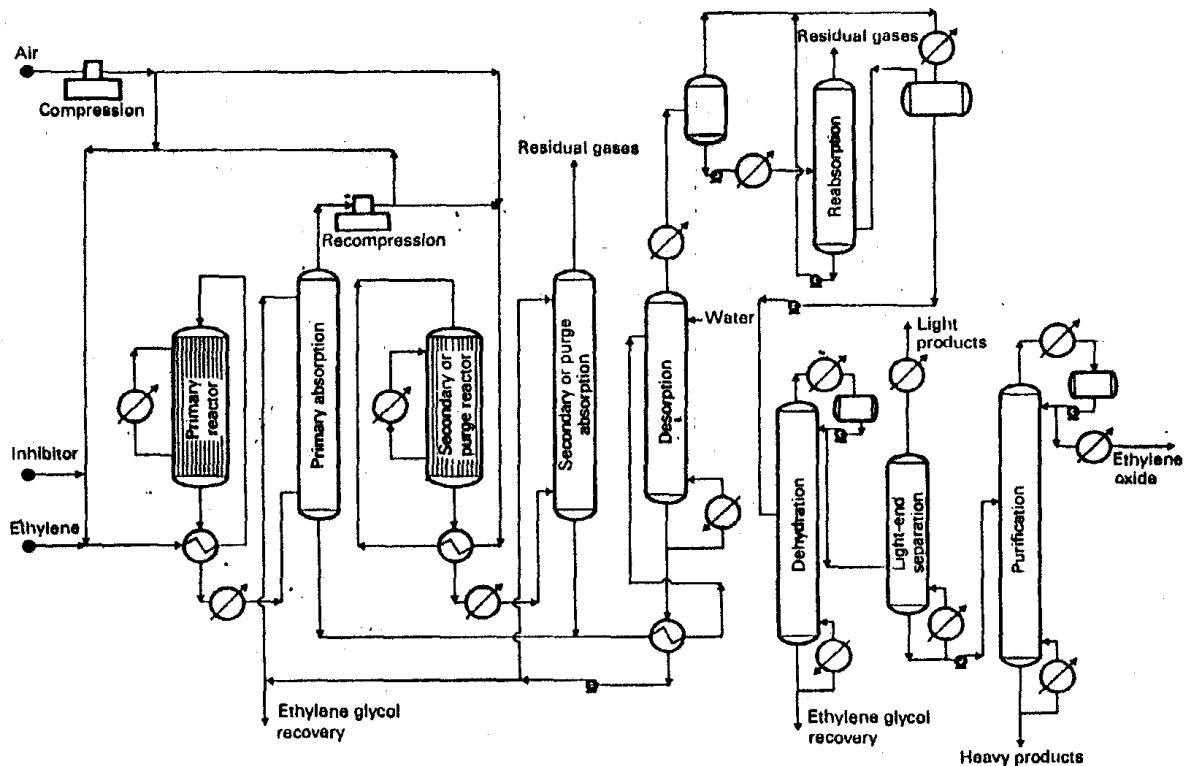


Fig. 7.2. Ethylene oxide production by air oxidation, Scientific Design process.

7.1.2.3 Economic data

Table 7.1 summarizes the economic data concerning processes for manufacturing ethylene oxide employing oxygen and air.

TABLE 7.1

ETHYLENE OXIDE PRODUCTION BY DIRECT OXIDATION OF ETHYLENE. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 140.000 t/year

Oxidant	Oxygen	Air
Typical technology	Shell/SD	Scientific Design
Battery limits investments (10^6 US\$)	58	85
Consumption per ton of ethylene oxide		
Raw materials		
Ethylene (t)	0.88	0.96
Oxygen (99.5 %) ⁽¹⁾ (t)	1.15	—
By-products		
Ethylene glycol (t)	0.04	0.04
CO ₂ (t)	0.88	—
Utilities		
Steam (t)	(-) 1.5	(-) 4.5
Electricity (kWh)	510	860
Cooling water (m ³)	250	270
Process water (m ³)	1.5	1.5
Labor (Operators per shift)	6	7

(1) At $1.8 \cdot 10^6$ Pa absolute

TABLE 7.2

AVERAGE COMMERCIAL SPECIFICATIONS OF ETHYLENE OXIDE

Characteristics	Values
Purity (% Wt) min.	99.9
Acidity (acetic acid) (ppm) max.	20
Aldehydes (acetaldehyde) (ppm) max.	10
Acetylenics (ppm) max.	None
Carbon dioxide (ppm) max.	100
Water (ppm) max.	300
Non-volatile residue (g/100 ml) max.	0.05
Color (Pt/Co) max.	10

7.1.3 Uses and producers

Table 7.2 gives the average commercial specifications of ethylene oxide. Its main uses in 1984 are listed in Table 7.3 for Western Europe, the United States and Japan. Production capacities and consumption for these three geographic areas are also given.

TABLE 7.3
ETHYLENE OXIDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Ethanolamines	10	8	6
Ethyleneglycol	45	61	58
Glycolic ethers	11	6	6
Surfactants (non-ionic)	21	12	21
Miscellaneous ⁽¹⁾	13	13	9
Total	100	100	100
Production (10^3 t/year)	1,515	2,585	530
Capacity (10^3 t/year) ⁽²⁾	1,780	2,950	620
Consumption (10^3 t/year)	1,505	2,580	530

(1) Acetal copolymer resins, arylethanolamines, choline, ethylene chlorohydrin, ethyleneglycols (di, tri, tetra-polyethyleneglycols), hydroxyethyl cellulose, hydroxyethyl starch, polyether-polylols...

(2) In 1984 the worldwide production capacity of ethylene oxide was $7.6 \cdot 10^6$ t/year and in 1986, $7.7 \cdot 10^6$ t/year with the following distribution:

United States	2.8	Western Europe	1.8	Middle East	0.4
Canada	0.4	Eastern Europe	0.9	Japan	0.6
Latin America	0.3	Africa	-	Asia and Far East	0.5

7.2 PROPYLENE OXIDE

Propylene oxide ($d_4^{20} = 0.830$ ⁽²⁾, $bp_{1.013} = 35^\circ\text{C}$, $mp = -112^\circ\text{C}$) has witnessed considerable industrial development in the past fifteen years, leading to its present level of world output, exceeding 2,300,000 t/year. This expansion is essentially connected with that of polyurethane foams, which consume about 60 per cent of the propylene oxide produced and with that of polyester resins, which use about 20 per cent.

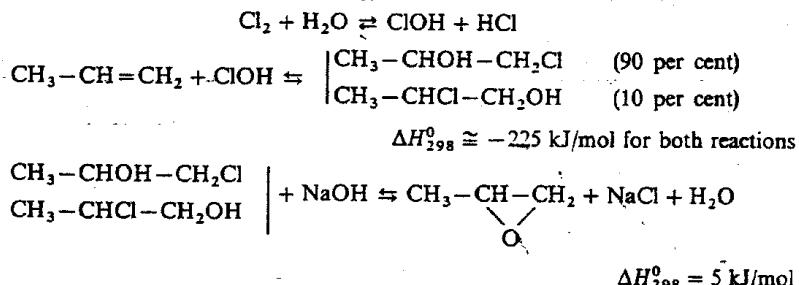
Until 1969, the only method for producing propylene oxide was the chlorohydrin process, using a technique similar to that used to synthesize ethylene oxide, and most of the production units were converted ethylene oxide plants.

(2) Specific gravity, 68.0-39.2.

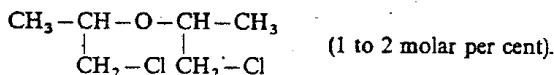
Several attempts have been made to achieve direct oxidation of propylene, but they have all failed industrially. This is because, in the case of propylene, the methyl group is the most easily oxidized, leading to a substantial drop in oxide selectivity and the production of a large number of oxygen products that are difficult to separate. The latest techniques circumvent the problem by using oxygen carriers such as hydroperoxides and peracids instead of oxygen, or an electrochemical process.

7.2.1 The propylene chlorohydrin process (Fig. 7.3)

This process is similar in principle to the ethylene oxide synthesis process. The main reactions involved are the following:



Selectivity in relation to propylene is 94 molar per cent. By-products formed are 1,2 dichloropropane (4 to 5 molar per cent) and chlorinated diisopropyl ether:



The association of a chlorine plant makes the process more profitable (see Section 11.2.5).

The chlorine, produced directly by electrolysis cells, is added to the recycle chlorohydrin, in which it dissolves before the injection of cooled water. Chemical grade propylene containing 8 per cent volume of propane is added to the chlorohydrin/chlorine/water mixture before it enters the reactor. The reactor is an unpacked tower in which the hypochlorous acid addition reaction takes place around 40°C. Chlorine conversion is practically complete. A gas phase and a liquid fraction are separated at the reactor outlet, by passage through an absorption column. The gas phase is recycled after a purge designed to remove the propane, on which supplementary adsorption treatment is used to recover traces of entrained chlorinated compounds. The aqueous solution, which contains 4 to 5 per cent weight of chlorohydrin, is sent to the dehydrochlorination reactor, where it reacts with a basic solution from the electrolysis cells, whose NaOH and NaCl content is 13 per cent weight for each of these two components. The propylene oxide is stripped as it is formed at the top of the hydrolyser. Chlorohydrin conversion per pass is practically total (99 per cent) and the propylene oxide molar yield as high as 96 per cent. The remaining solution is a brine that is recycled to the electrolysis unit.

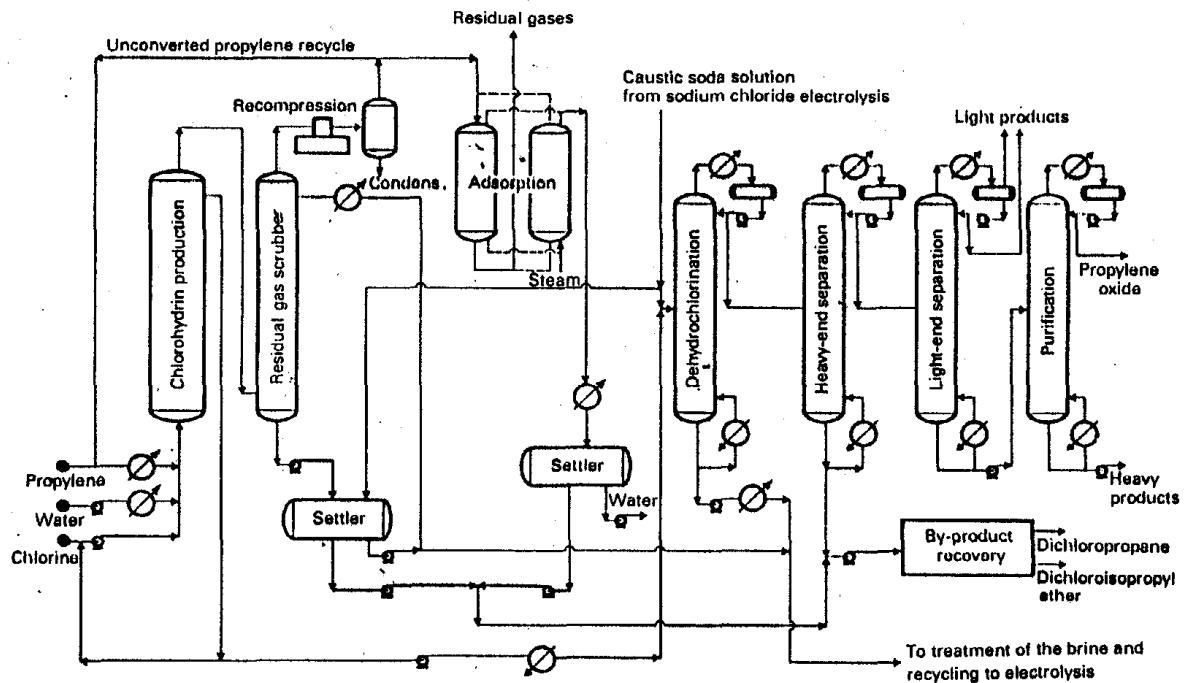


Fig. 7.3. Propylene oxide production, Chlorhydrin process.

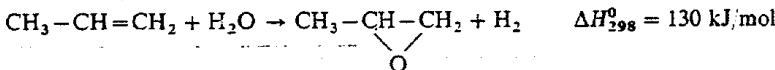
The integration of such an installation eliminates all the problems formerly raised by the use of lime to hydrolyse the chlorohydrin. Each ton of propylene oxide produced was formerly accompanied by the production of about 40 tons of a solution containing 5 to 6 per cent weight of calcium chloride.

The hydrolyser effluent is then purified, after having been rid of the different chlorinated by-products. This operation is performed in a series of three distillation columns, a heavy end separation column (25 trays), a light end separation column (15 trays) and a third column to adjust the product to specifications (35 trays). The final product is propylene oxide with a purity of 99.9 per cent weight.

A variant of the chlorohydrin method consists in causing chlorine and caustic soda to react simultaneously with *t*-butyl alcohol to form *t*-butyl hypochlorite, which can act on propylene to regenerate *t*-butyl alcohol and produce chlorohydrin. This is then hydrolysed in the presence of caustic soda to produce the final propylene oxide (Lummus process).

7.2.2 Electrochemical processes

The use of electrochemistry to convert propylene to the oxide was researched in particular by *Bayer* and *Kellogg*. In this method, propylene is injected in the neighborhood of the anode of a sodium chloride electrolysis cell with a mercury cathode (see Section 11.2.5.2.B). The hypochlorous acid formed with the chlorine liberated at the anode is added to the propylene. The chlorohydrin obtained is hydrolysed at the cathode by the caustic produced by the action of water on the amalgam. Propylene oxide is separated from the mixture by stripping, while the sodium chloride is returned to the electrolyser. The overall reaction is as follows:



Despite the variety of the patented systems, these processes have not yet enjoyed industrial development, chiefly because of the high capital expenditure and high energy consumption, associated with the low electrical efficiency and the high cost of recovering propylene oxide from dilute solutions.

7.2.3 Direct oxidation processes

The direct oxidation of propylene by molecular oxygen is a low-selective reaction. The propylene oxide yield can be raised by limiting the conversion rate to a low value, about 10 to 15 per cent, by using more selective catalysts, or by achieving co-oxidation with a more oxidizable compound than propylene (acetaldehyde, isobutyraldehyde etc.). Many patents have been filed concerning this process, but without any industrial implementation. Among them is the liquid phase oxidation of propylene on a rare earth oxide catalyst deposited on silica gel (USSR), or in the presence of molybdenum complexes in chlorobenzene or benzene (IFP: Institut Français du Pétrole, Jefferson Chemical), vapor phase oxidation on modified silver catalysts (BP: British Petroleum, IFP), or on

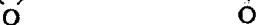
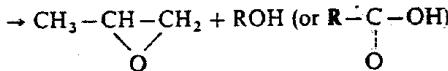
gold clusters obtained from cetenides (*Bryce Smith*). Co-oxidation in the presence of acetaldehyde has been proposed by *Union Carbide* and the USSR. In the *Union Carbide* process, oxygen is introduced into a mixture of propylene and acetaldehyde in solution in acetonitrile and xylenes, with operation at 110°C and $2.7 \cdot 10^6$ Pa absolute. For a once-through conversion of 10 per cent, molar selectivity of propylene oxide is 92 per cent, and 0.7 mol of acetic acid is co-produced per mol of propylene oxide.

7.2.4 Oxidation processes using peroxide compounds

7.2.4.1 Action mechanism of these compounds

The difficulties encountered in obtaining propylene oxide by direct oxidation, with high yields and acceptable purity, led to the search for more selective means of oxygen input and fixation. This led to the use of hydroperoxides ($\text{R}-\text{OOH}$) and peracids ($\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OOH}$),

which yielded excellent performance. For the manufacture of the epoxide, however, the use of a co-reactant, in amounts close to stoichiometry, causes the simultaneous production of a co-product (alcohol or acid), whose tonnage is necessarily high according to the following reaction:



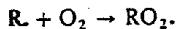
Although many peroxide compounds are suitable for this reaction, for economic reasons their choice is restricted to *t*-butyl and ethylbenzene hydroperoxides for the first type of co-reactant, and to peracetic and perpropionic acids for the second.

The hydroperoxides are obtained from the corresponding hydrocarbon and result from a chain auto-oxidation involving free radicals according to the following mechanism:

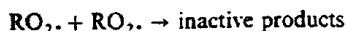
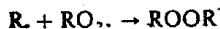
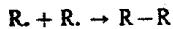
(a) Initiation



(b) Propagation



(c) Recombination



where A is the initiator. The reaction is exothermic and, in the case of isobutane, $\Delta H_{298}^0 = -109$ kJ/mol.

The peracids are obtained by the oxidation of the corresponding acids or aldehydes with hydrogen peroxide.

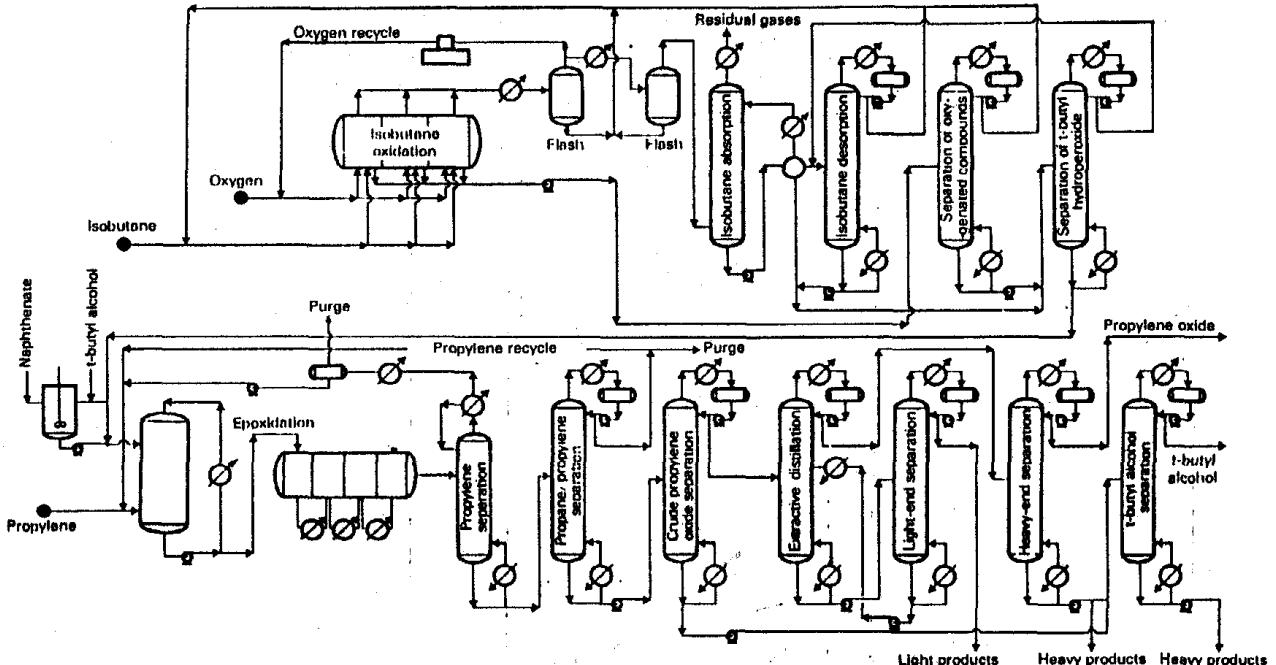


Fig. 7.4. Propylene oxide production by oxidation with peroxide compounds: ARCO Chemical (Oxirane) process; isobutane version.

7.2.4.2 Techniques employing hydrocarbons

These techniques were developed independently by *Halcon International* and *Atlantic Richfield Co.* (*ARCO*), who then cooperated to develop the *Oxirane* (now *ARCO Chemical*) process.

Since the conditions are not identical, the same unit cannot treat isobutane and ethylbenzene. As an example, this technique can be illustrated for the oxidation of propylene by *t*-butyl hydroperoxide (Fig. 7.4). Two main stages can be distinguished:

- (a) Production of the hydroperoxide.
- (b) Epoxidation of propylene.

A. *Oxidation of isobutane to t-butyl hydroperoxide and t-butyl alcohol*

The reaction takes place by oxygen in the liquid phase in several series of agitated reactors, each series laid out in parallel in the same horizontal shell. The reaction takes place without catalyst, but the continuous injection of small amounts of citric acid helps to prevent the formation of by-products in excessive quantities. As for the operating conditions, the temperature is 110 to 130°C, pressure 3 to $3.5 \cdot 10^6$ Pa absolute, and residence time about 7 h for a once-through isobutane conversion of 35 per cent. The total yield of hydroperoxide and alcohol is 94 molar per cent, and the molar ratio of these two products is approximately 1.2.

The make-up and recycle oxygen are introduced into the reactor with fresh and recycled isobutane in a proportion such that the oxygen concentration is kept at less than 8 per cent volume. It is essential to ensure that this concentration remains below the lower flammability limit. Make-up inert gas may be required to control this concentration.

The heat liberated by the conversion is removed by the vaporization of part of the reaction medium, consisting essentially of isobutane, which is recondensed and recycled directly after cooling and flash in two stages. The off-gas from high pressure flash, mainly containing oxygen, is returned to the oxidation reactors after recompression. The off-gas from the second flash, at lower pressure, is rid of the residual isobutane it contains in two columns, placed in series (35 and 20 trays), operating at $3 \cdot 10^6$ Pa absolute by absorption in the presence of ethyl acetate, followed by desorption by stripping.

The isobutane dissolved in the liquid stream drawn off from the reactors is also recovered at the top of a distillation column, at $0.15 \cdot 10^6$ Pa absolute (15 trays). The oxygenated compounds obtained at the bottom of this third column and of the desorption column are then fractionated (10 trays) at pressure less than $0.5 \cdot 10^6$ Pa absolute. The distillate, consisting of solvent, residual isobutane, and a little *t*-butyl alcohol, is sent to the desorption stage. The drawn-off stream essentially contains hydroperoxide and *t*-butanol.

This method serves to concentrate the reaction stream by minimizing the thermal decomposition of the peroxidic components, and by avoiding the need for cooling cycles, which require large investments and are big energy consumers, to condense the isobutane.

B. *Epoxidation of propylene*

Epoxidation takes place in the liquid phase. The catalyst employed for the purpose is generally a 5 per cent weight solution of molybdenum naphthenate in a mixture of

t-butyl hydroperoxide and alcohol. The metal concentration in the reaction medium is about 0.05 per cent weight. Operations take place between 80 and 110°C, at 3 to 4 . 10⁶ Pa absolute, in a series of staged reactors, in the presence of excess propylene (peroxide/alcohol/propylene molar ratio 1/1/3). Residence time ranges from 0.5 to 1 h per stage, and total residence time is about 2.5 h. It is about 1 h in the first stage and 50 per cent of the hydroperoxide reacts. Once-through conversion of propylene reaches 15 per cent, and that of the hydroperoxide 90 to 95 per cent. Molar selectivities of propylene oxide and alcohol amount to 85 and nearly 95 per cent respectively in relation to the peroxide. The heat of reaction ($\Delta H_{298}^{\circ} = -225 \text{ kJ/mol}$) is removed for the first reactor, by cooling a sideward stream that is recycled and, in the remaining four reactors, combined in a single shell, by intermediate cooling. In each stage, the temperature is 80°C at the inlet and 100°C at the outlet.

The stream from the reaction section is first distilled to remove unconverted propylene, whose recycle, added to the make-up, represents the feed of the first epoxidation stage. Excess propane is also removed by distillation ($\cong 50$ to 60 trays) to prevent its buildup in the synthesis loop. The heavy end of the first column is sent to the purification train for products for which the temperatures cannot exceed 100°C to avoid undesirable degradation. On account of the boiling points at standard pressure of the components present, this makes operation under vacuum necessary. Crude propylene oxide is collected at the top of the first distillation column (50 trays), and *t*-butyl alcohol at the bottom, with some hydroperoxide, the catalyst, propylene glycol, aldehydes, esters etc. This stream is sent to a *t*-butyl alcohol separation column (35 to 40 trays), where the alcohol is recovered at the top.

The crude propylene oxide is subjected to extractive distillation by means of a hydrocarbon (octane for example) in a set of two columns, one for extraction (30 trays), and the second for solvent regeneration (15 trays). The extract is rid of light products (50 trays) and heavy products (75 to 80 trays) to yield propylene oxide meeting commercial specifications.

The *t*-butyl alcohol, co-product produced at the rate of 2.5 t/t⁽³⁾ of propylene oxide, depending on whether or not a market is available, is utilized as such or dehydrated to isobutene (200°C, atmospheric pressure, titanium oxide base catalyst). If the isobutene is itself unusable, it can be hydrogenated to isobutane, which is recycled. The good anti-knock properties of *t*-butyl alcohol currently make it a highly popular additive for automotive gasolines. In addition, certain recent processes (*Mitsubishi Rayon, Nippon Shokubai, Oxirane*) can be used to convert the *t*-butyl alcohol to methacrylic acid (see Section 11.2.3.2).

The oxidation of propylene by ethylbenzene hydroperoxide was discussed in Section 6.4.2.2. In this case, the co-product is 1-phenyl ethanol, which is dehydrated to styrene. About 2.5 t of this co-product is formed per ton of propylene oxide.

(3) This ratio may vary from 2.1 to 2.5 according to the operating conditions. ARCO Chemical (formerly Oxirane) has developed a process derived from the propylene oxide *t*-butyl alcohol technology for the direct oxidation of isobutane to raise the proportion of alcohol.

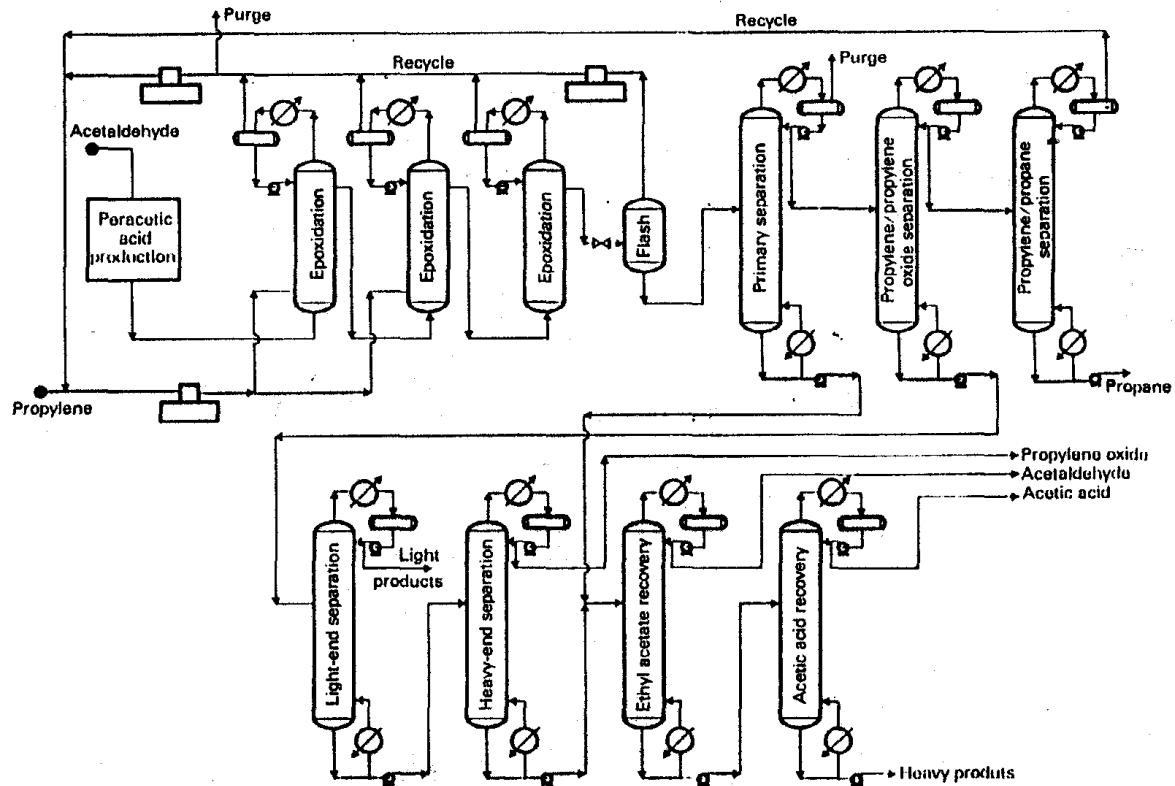


Fig. 7.5. Propylene oxide production by oxidation with peroxide compounds. Daiel process.

7.2.4.3 Techniques employing peracids and hydrogen peroxide

The two main peracids proposed are peracetic acid and perpropionic acid.

A. The Daicel process

The only process in use today is the one developed by *Daicel Chemical Industries* in Japan with a 12,000 t/year plant at Ohtake. It operates in two steps. The first consists of the production of peracetic acid by the oxidation with oxygen of acetaldehyde in solution in ethyl acetate, at room temperature and between 2.5 and $4 \cdot 10^6$ Pa absolute, in the presence of an acidic catalyst. The peracid formed is concentrated to about 30 per cent weight.

In the second step (Fig. 7.5), the propylene, peracetic acid and a solution of 10 to 15 per cent weight of acetic acid in ethyl acetate, containing a stabilizer, are introduced continuously into three reactors mounted in series. Epoxidation takes place between 50 and 80°C , and 0.9 to $1.2 \cdot 10^6$ Pa absolute. For a residence time of 2 to 3 h, once-through conversion of peracetic acid is 97 to 98 per cent, and the molar yield of propylene oxide is 90 to 92 per cent. The reaction products are distilled (35 trays) at between 0.15 and $0.5 \cdot 10^6$ Pa absolute. A mixture of propylene and its oxide is collected at the top, and a cut at the bottom consisting chiefly of ethyl acetate and acetic acid. The distillate is condensed by cooling and compression, and sent to a column (15 trays) operating between 1.2 and $1.5 \cdot 10^6$ Pa absolute, which produces propylene at the top, recycled to the first reactor, after separating the propane (70 trays) if necessary. The crude propylene oxide obtained at the bottom is then subjected to light end separation (30 to 35 trays) and then heavy end separation (50 trays) to meet commercial specifications. Its purity can also be improved by extractive distillation. The ethyl acetate/acetic acid cut and the bottoms from the propylene oxide heavy end separation column are sent to two final distillations (20 to 25 trays each), where ethyl acetate and acetic acid are separated in succession. The acetate is recycled to the peracetic acid synthesis reactor, and the acid is marketed.

B. Other industrial techniques

- In the Propylox process, developed in Belgium, peracetic acid is obtained by the action of hydrogen peroxide on acetic acid at about 40°C . in the presence of catalytic traces of sulfuric acid. The water formed in the reaction is removed by stripping or azeotropic distillation with ethyl acetate.
- The use of perpropionic acid as an epoxidation agent for propylene has been proposed by *Bayer/Degussa*, *Interox* (*Carbochimique*, *Laporte*, *Solvay*) and *Ugine Kuhlmann*. The perpropionic acid is produced by the oxidation of propionic acid with hydrogen peroxide, in the presence of sulfuric acid. The propylene is epoxidized between 0.5 and $1.4 \cdot 10^6$ Pa absolute, at about 60 to 80°C , in the *Bayer/Degussa* process, which operates in the presence of benzene, and at 100°C in the *Interox* process, which uses 1,2-dichloropropane as a solvent.
- Among the other processes using peracids, *Asahi Chemical* employs perisobutyric acid, *Metallgesellschaft* employs perbenzoic acid, and *Mitsubishi* perparatoluic acid, obtained by the oxidation of paratoluic aldehyde, itself produced by the carbonylation of

toluene. In this case, the para-toluic acid by-product can be oxidized subsequently to terephthalic acid.

• Direct epoxidation by hydrogen peroxide has sparked considerable research (IFP, Naphthachimie, PCUK : *Produits Chimiques Ugine Kuhlmann, Shell, Union Carbide*), and several catalyst systems have been proposed (compounds of molybdenum, tungsten, arsenic), but although the propylene oxide selectivities are as high as 85 to 95 molar per cent, the conversions never exceed 50 per cent, making the process uneconomic (large volume of reactors, cost of recycling, high price of hydrogen peroxide).

Remark. Among other methods under development are the following:

- Catalytic decomposition of propylene glycol hydroxyacetate, obtained by the acetoxylation of propylene (Chem-Systems process).
- Enzymatic conversion of D-glucose to D-fructose and propylene oxide (Cetus process) or directly of propylene in the presence of methane monooxygenase (Exxon process).

TABLE 7.4
PROPYLENE OXIDE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/year

Process (intermediate chemical compound)	Chlorohydrin	<i>t</i> -butyl hydroperoxide
Typical technology	Integrated electrolysis	ARCO Chemical ⁽¹⁾
Battery limits investments (10 ⁶ US\$)	88	102
Consumption per ton of propylene oxide		
Raw materials		
Propylene (t)	0.88	0.90
Sodium chloride (t)	0.15	—
Isobutane (t)	—	2.35
Oxygen (t)	—	1.00
By-products		
Dichloropropane (t)	0.11	—
Chloroether (kg)	25	—
<i>t</i> -butyl alcohol (t)	—	2.45
Miscellaneous (acetone, etc.) (t)	—	0.25
Utilities		
Steam (t)	9.0	9.5
Electricity (kWh)	4,500	400
Fuels (10 ⁶ kJ)	(—) 11.5	(—) 4.0
Cooling water (m ³)	250	380
Process water (m ³)	50	—
Chemicals and catalysts (US\$)	30	25
Labor (Operators per shift)	20	12

(1) Economic data concerning the variant of the ARCO Chemical (formerly Oxirane) process for the co-production of propylene oxide and styrene are given in Table 6.11 in Section 6.4.2.4.

TABLE 7.5
AVERAGE COMMERCIAL SPECIFICATIONS OF PROPYLENE OXIDE

Characteristics	Values
Purity (% Wt) min.	99.5
$d_{4}^{25}(1)$	0.829-0.831
Acidity (acetic acid) (ppm) max.	20
Aldehydes (propionaldehyde) (ppm) max.	50
Water (ppm) max.	500
Chlorides (chlorine) (ppm) max.	40
Non-volatile residue (g/100 ml) max.	0.002
Color (Pt/Co) max.	5

(1) Specific gravity, 77.0-77.0.

TABLE 7.6
PROPYLENE OXIDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Polyether-polyols	69	62	75
Propylene glycols	24	23	16
Miscellaneous ⁽¹⁾	7	15	9
Total	100	100	100
Production (10^3 t/year)	885	895	210
Capacity (10^3 t/year) ⁽²⁾	1,025	1,350	275
Consumption (10^3 t/year)	850	830	195

(1) Glycerin, glycol ethers, hydroxyethyl cellulose, isopropylamines, propylene carbonate, surfactants...

(2) In 1984 the worldwide production capacity of propylene oxide was $2.9 \cdot 10^6$ t/year and in 1986, $3.0 \cdot 10^6$ t/year with the following distribution:

United States	1.36	Western Europe	1.08	Middle East	—
Canada	0.07	Eastern Europe	0.14	Japan	0.24
Latin America	0.10	Africa	—	Asia and Far East	0.01

7.2.5 Economic data

Table 7.4 gives economic data on the synthesis of propylene oxide by chlorohydrin processes and by indirect oxidation passing through *t*-butyl hydroperoxide.

7.2.6 Uses and producers (Table 7.6)

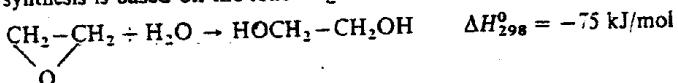
Table 7.5 lists the average commercial specifications of propylene oxide. Table 7.6 presents the main uses in 1984, as well as the production, capacities and consumption figures for Western Europe, the United States and Japan.

7.3 ETHYLENE GLYCOL

Monoethylene glycol, which is more routinely called glycol, $\text{OHCH}_2-\text{CH}_2\text{OH}$ ($d_1^{20} = 1.115^{(4)}$, $\text{bp}_{1,013} = 197^\circ\text{C}$), is the principal application for ethylene oxide, from which it is obtained by hydration. Despite many developments under way designed to produce it directly from ethylene or synthesis gas, this method is practically the only one employed industrially at the present time.

7.3.1 Ethylene glycol synthesis by hydration of ethylene oxide (Fig. 7.6)

This synthesis is based on the following exothermic reaction:



Industrial plants carry out this conversion according to the following scheme:

The ethylene oxide feed is first diluted by a quantity of water such that the $\text{H}_2\text{O}/\text{oxide}$ molar ratio is 20 to 25/1, in order to favor the production of monoethylene glycol and to minimize that of its higher homologues, particularly di- and triethylene glycol. The mixture obtained is initially raised to 150°C by heat exchange with the condensate from the final stage of a series of evaporators used further downstream, and then by means of steam, and is then introduced into the reactor. This operation takes place at about $1.5 \cdot 10^6 \text{ Pa}$ absolute and a temperature ranging from 150°C at the inlet to between 200 and 210°C at the outlet, in the absence of catalyst, and with a residence time of 45 min to 1 h. In these conditions, the molar selectivities are as follows: 88.5 per cent for ethylene glycol, 10.5 per cent for diethylene glycol, and 0.5 per cent for triethylene glycol.

The aqueous solution of crude glycols thus produced is then concentrated in a series of four evaporators operating at a pressure which decreases progressively from 0.6 to $0.01 \cdot 10^6 \text{ Pa}$ absolute. The steam leaving the top of a stage preheats the next stage. The condensate from the last evaporator, after being used to raise the feed to temperature, feeds the circulation of process water for the unit. The mixture of glycols produced by this operation undergoes final dehydration, achieved by vacuum distillation (10 kPa, 10 to 15 trays), followed by fractionation in a series of three columns also operating under vacuum. Separated in succession at the top of these columns are monoethylene glycol (3 to 4 kPa, 15 to 20 trays), diethylene glycol (3 kPa, 15 to 20 trays), and triethylene glycol (1 kPa, 12 to 15 trays).

(4) Specific gravity, 68.0 39.7

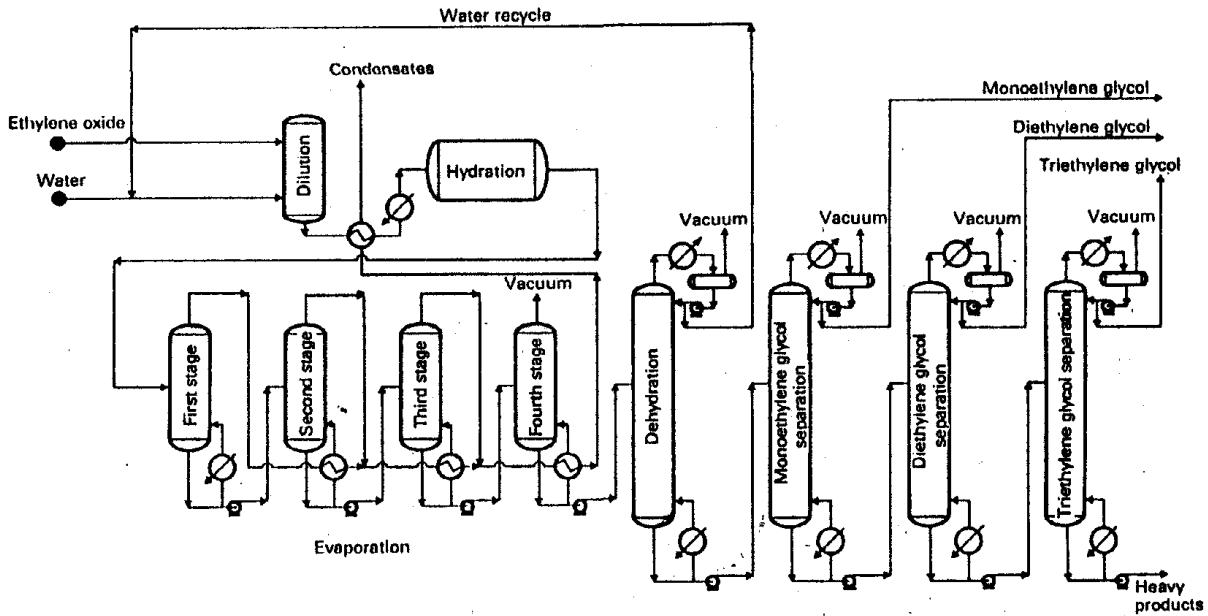
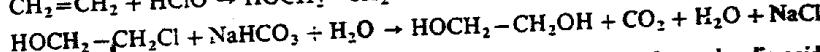
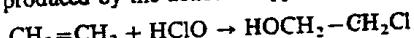


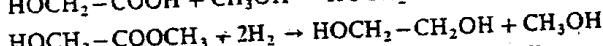
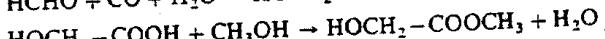
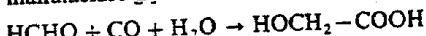
Fig. 7.6. Ethylene glycol production by ethylene oxide hydration.

7.3.2 Other processes for manufacturing ethylene glycol

The old process, by which sodium bicarbonate was used to hydrolyse the chlorohydrin produced by the action of hypochlorous acid on ethylene, has been abandoned:

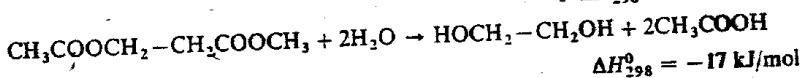
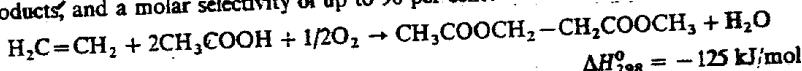


Similarly, the method based on the carbonylation of formaldehyde to glycolic acid, whose ester was then hydrogenolysed, is no longer practised by *Du Pont*, who only continue to manufacture glycolic acid in small amounts:



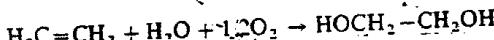
Recent processes are designed for the more direct production of glycol, either from ethylene or from synthesis gas:

- The acetoxylation of ethylene to glycol mono- and diacetates which are then hydrolysed, although comprising two stages, offers the advantage of not producing any by-products, and a molar selectivity of up to 98 per cent:



This method is developed in particular by *Halcon International* and *ARCO Chemical*, who use a homogeneous catalyst based on tellurium and bromine, or a mixture of manganese acetate and potassium iodide. Other processes based on acetoxylation have been proposed by *Du Pont*, *Celanese*, *ICI (Imperial Chemical Industries)*, *Kuraray* etc.

- It is now planned to synthesize glycol in a single step from ethylene by the following reaction:



The catalyst used for this purpose by *Teijin* consists of thallic ions in solution in hydrochloric acid, while *Halcon* uses copper iodide and *Kuraray* employs palladium nitrate.

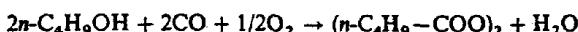
- The technique proposed by *Union Carbide*, employing synthesis gas and a catalyst consisting of complexes of rhodium carbonyl, yields glycol directly, as well as 1,2-propanediol and glycerin:



The process takes place at high pressure (140 to 340 . 106 Pa absolute) and between 125 and 130°C. The total molar yield is 65 per cent. Methyl formate, methanol and water

are formed as by-products. Other companies also claim the production of glycol from synthesis gas (*ARCO, Chevron, Du Pont, USI : US Industrial Chemicals Company, etc.*).

- The hydrogenation of *n*-butyl oxalate into ethylene glycol and *n*-butyl alcohol, jointly developed by *Union Carbide* and *Ube Industries*. Oxalate is obtained by oxidative carbonylation of *n*-butanol on the liquid phase, by using a palladium based catalyst and an accelerator (nitric acid, *n*-butyl nitrite, ...), at about 70°C and $6 \cdot 10^6$ Pa absolute:



Hydrogenation takes place in the presence of copper chromite, in the liquid phase, at 200°C and $3 \cdot 10^6$ Pa absolute:



7.3.3 Economic data

The economic data available on the production of ethylene glycol by the hydration of ethylene oxide are listed in Table 7.7.

TABLE 7.7
ETHYLENE GLYCOL PRODUCTION BY HYDRATION OF ETHYLENE OXIDE. ECONOMIC DATA
(France conditions, mid-1986)

Capacity (t/year)	100,000
Battery limits investments (10^6 US\$)	12
Consumption per ton of propylene glycol	
Raw materials	
Ethylene oxide (t)	0.81
By-products	
Diethylene glycol (kg)	100
Triethylene glycol (kg)	5
Utilities	
Steam (t)	5.3
Electricity (kWh)	30
Cooling water (m^3)	520
Process water (m^3)	5
Chemicals (US\$)	0.5
Labor (Operators per shift)	4

7.3.4 Uses and producers

The average commercial specifications of the main glycols produced from ethylene oxide are summarized in Table 7.8.

Uses for 1984 and figures for production, capacities and consumption of ethylene glycol in Western Europe, the United States and Japan are given in Table 7.9.

TABLE 7.8
AVERAGE COMMERCIAL SPECIFICATIONS OF MONO-, DI- AND TRIETHYLENE GLYCOLS

Glycol type	Monoethylene glycol	Diethylene glycol	Triethylene glycol
Grade	Chemical	Polymerization	-
$d_{20}^{20(1)}$	1.1151-1.1156	1.1151-1.1156	1.1170-1.2000
Distillation range (°C)	193-201.5	196-200	242-250
Diethylene glycol (ppm) max.	5,000	800	—
Acidity (ppm) max. (expressed as acetic acid)	50	50	50
Iron (ppm) max.	—	700	—
Water (ppm) max.	2,000	800	2,000
Non-volatile residue (ppm) max.	45	45	50
Color (Pt/Co) max.	10	5	15
100	—	1,000	25

(1) Specific gravity, 68.0/68.0.

TABLE 7.9
ETHYLENE GLYCOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Antifreeze	33	47	13
Polyethylene terephthalate resins	48	36	64
Unsaturated polyesters and alkyd resins	19	7	6
Miscellaneous ⁽¹⁾		10	17
Total	100	100	100
Production (10^3 t/year)	865	2,190	430
Capacity (10^3 t/year) ⁽²⁾	1,330	2,620	620
Consumption (10^3 t/year)	855	1,975	545

(1) Deicer, freezing-point depressant, precursor (glyoxal, esters, ethers...), solvent, stabilizer.

(2) In 1986 the worldwide production capacity of ethylene glycol was $7.2 \cdot 10^6$ t/year with the following distribution:

United States	2.6	Canada	0.5	Western Europe	1.3
Japan	0.6	Other	2.2		

7.4 PROPYLENE GLYCOL

Propylene glycol or 1,2-propanediol, $\text{CH}_3\text{—CHOH—CH}_2\text{OH}$ ($d_4^{20} = 1.036^{(5)}$, $\text{bp}_{1.013} = 187.3^\circ\text{C}$), is manufactured industrially by the hydration of propylene oxide, by a reaction similar to the hydration of ethylene oxide. However, while the production of ethylene glycol consumes 50 to 60 per cent of the ethylene oxide in various countries, the production of propylene glycol requires only about one-third of the propylene oxide produced. Processes for manufacturing propylene glycol directly from propylene are still awaiting industrial development.

7.4.1 Synthesis of propylene glycol by hydration of propylene oxide (Fig. 7.7)

As for the industrial production of ethylene glycol, propylene oxide must be diluted in a large excess of water to limit the formation of di- and tripropylene glycols. The dilute propylene oxide solution is introduced into the first of two agitated reactors mounted in series (water to oxide molar ratio 15/1). With a residence time of 30 min, and without catalyst, at 190°C and $2.1 \cdot 10^6 \text{ Pa absolute}$, propylene glycol is obtained with a molar selectivity of 85 per cent in relation to the oxide, together with dipropylene glycol (11 per cent), tripropylene glycol (1.5 per cent) and heavy products (2.5 per cent). After fractionation (5 trays) of the light products (unreacted oxide, acetone, propionaldehyde), the water is removed in a multistage evaporator and the last traces removed by vacuum distillation in a drying column (15 trays). Vacuum is necessary to limit the reboiling temperature and to prevent decomposition of the product.

Mono-, di- and tripropylene glycols are then isolated in the state of purity required by fractionation in a series of three columns, with about 30, 40 and 25 trays each. The heavier products are used as fuels.

7.4.2 Other processes for producing propylene glycol

Halcon has developed a process starting directly with propylene, but operating in two steps. In the first, the propylene, in the presence of acetic acid and oxygen, is converted to propylene glycol diacetate. In the second, the diacetate is hydrolysed to glycol.

The first conversion employs a catalyst based on tellurium oxide and lithium carbonate, and operates at 170°C . Glycol molar selectivity is 92 per cent for a propylene once-through conversion of 98.5 per cent. Acetaldehyde, carbon dioxide and diglycol diacetate are also formed. The second consists of hydrolysis at 90°C , under slight pressure ($0.5 \cdot 10^6 \text{ Pa absolute}$), and in the presence of an acidic catalyst (ion exchange resin). The molar yield of glycol in relation to propylene is about 88 per cent.

(5) Specific gravity, 68.0/39.2

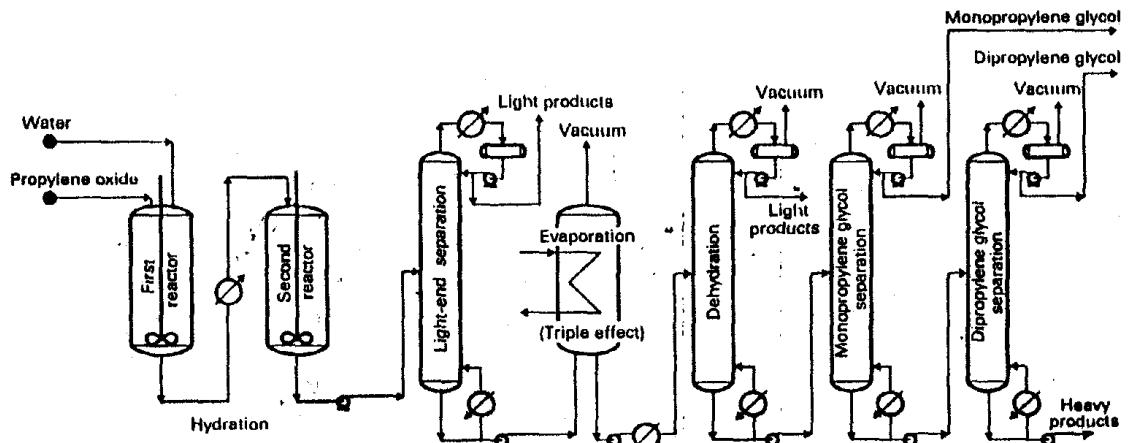


Fig. 7.7. Propylene glycol production by propylene oxide hydration.

7.4.3 Economic data

The main economic data concerning the process for manufacturing propylene glycol by hydration of propylene oxide are summarized in Table 7.10.

TABLE 7.10
PROPYLENE GLYCOL PRODUCTION BY HYDRATION OF PROPYLENE OXIDE. ECONOMIC DATA
(France conditions, mid-1986)

Capacity (t/year)	30,000
Battery limits investments (10^6 US\$)	7
Consumption per ton of propylene oxide	
Raw materials	
Propylene oxide (t)	0.80
By-products	
Dipropylene glycol (kg)	30
Utilities	
Steam (t)	2.2
Electricity (kWh)	100
Cooling water (m^3)	1,300
Process water (m^3)	1
Chemicals (US\$)	0.2
Labor (Operators per shift)	3

TABLE 7.11
AVERAGE COMMERCIAL SPECIFICATIONS OF MONOPROPYLENE GLYCOL

Characteristics	Values
$d_{40}^{20}(1)$	1.037-1.039
Distillation range ($^{\circ}\text{C}$)	186-189
Acidity expressed as	
acetic acid (ppm) max.	20
Iron (ppm) max.	0.5
Water (ppm) max.	1,000
Chlorides (expressed as chlorine) (ppm) max.	1
Non-volatile residue (ppm) max.	10
Color (Pt/Co) max.	5

(1) Specific gravity, 68.0/68.0.

7.4.4 Uses and producers

Table 7.11 gives the average commercial specifications of propylene glycol. Table 7.12 summarizes the uses of this product, as well as figures for production, capacities and consumption in 1984 for Western Europe, the United States and Japan.

TABLE 7.12
PROPYLENE GLYCOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Unsaturated polyester resins	90	45	44
Food additives.....		9	20
Pharmaceuticals and personal care		12	13
Tobacco humectant		8	
Cellophane	10	4	
Functional fluids		6	
Paints and coatings		6	19
Plasticizers		6	
Miscellaneous ⁽¹⁾		4	
Total	100	100	100
Production (10^3 t/year)	210	220	25
Capacity (10^3 t/year) ⁽²⁾	290	430	75
Consumption (10^3 t/year).....	170	210	35

(1) Intermediate and solvent.

(2) In 1986, as in 1984, the worldwide production capacity of propylene glycol was nearly $0.9 \cdot 10^6$ t/year with the following distribution:

United States	0.43	Western Europe	0.29	Middle East.....	—
Canada.....	0.01	Eastern Europe.....	n.a	Japan	0.08
Latin America	0.05	Africa	—	Asia and Far East ..	0.01

Chapter 8

ACETIC DERIVATIVES

8.1 ACETALDEHYDE

Acetaldehyde ($d_4^{20} = 0.7780^{(1)}$, bp_{1.013} = 20.8°C) is a petrochemical intermediate used primarily to manufacture acetic acid and acetic anhydride. The main manufacturing processes developed on the industrial scale are the following:

- (a) Dehydrogenation or partial oxidation of ethanol in the vapor phase.
- (b) Liquid phase hydration of acetylene.
- (c) Oxidation of saturated hydrocarbons at elevated temperature.
- (d) Liquid phase oxidation of ethylene (Wacker-Hoechst process) which represents the most widespread method for synthesizing acetaldehyde at the present time, and accounts for about 80 per cent of total world operating capacity.

8.1.1 Acetaldehyde synthesis by dehydrogenation or partial oxidation of ethanol in the vapor phase (Fig. 8.1)

Acetaldehyde is obtained from ethanol either by catalytic oxidation or by dehydrogenation. Oxidation was the most widespread industrial process up to 1968/1970.

8.1.1.1 Oxidation of ethanol

The overall reaction is as follows:



Ethanol is oxidized by the passage of preheated alcohol vapor and air over a silver base catalyst between 375 and 550°C. Copper catalysts are also employed. The reaction temperature, which varies along the catalyst bed, depends partly on the proportions of air, ethanol and steam, and also on the velocity of the gases over the catalyst. These

(1) Specific gravity, 68.0/39.2

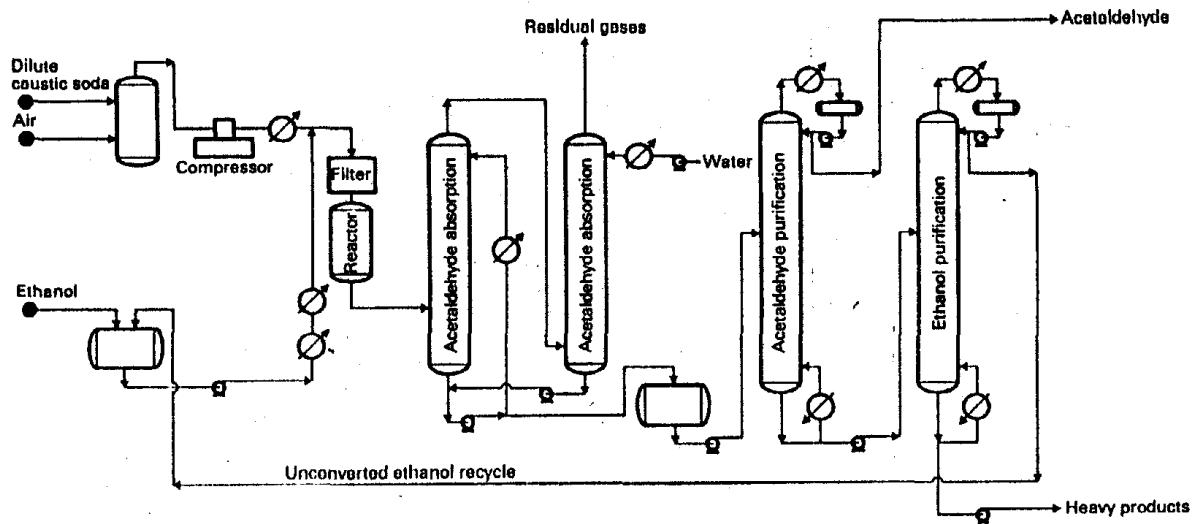


Fig. 8.1. Acetaldehyde production by dehydrogenation or partial oxidation of ethanol.

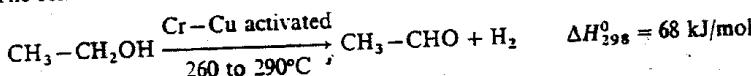
parameters can be optimized and a suitable technology employed to make the unit self-sufficient from the thermal standpoint.

Once-through conversion is 45 to 50 per cent and yields are 94 to 96 molar per cent. Unreacted ethanol and the acetaldehyde produced are extracted from the gases leaving the reactor by scrubbing with cold aqueous ethanol. The acetaldehyde and ethyl alcohol are separated by distillation, and the dilute ethanol is concentrated and recycled.

The main by-products are acetic acid, formic acid, ethyl acetate, methane and carbon monoxide.

8.1.1.2 Ethanol dehydrogenation

The reaction is as follows:



Ethyl alcohol is vaporized and sent over a chromium and activated copper catalyst, at atmospheric pressure and at a temperature between 260 and 290°C. Once-through conversion is 30 to 50 per cent depending on the velocity of the ethanol vapors and according to the reaction temperature. Yield is up to 85 to 90 molar per cent. The main by-products are acetic acid, ethyl acetate and 1-butanol.

After cooling and partial condensation of the reactor outlet stream, the residual gaseous fraction is scrubbed with water to extract the alcohol and acetic acid which it still contains. The condensate and the aqueous solution obtained are fractionated. Unconverted ethanol is recycled. The catalyst must be reactivated periodically, and it has a total life of several years.

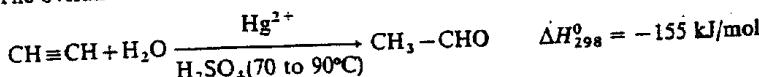
The hydrogen produced contains small amounts of methane and carbon monoxide. It can be employed for hydrogenation after the CO has been removed. The conversion and yield can be improved with copper base catalysts containing 5 per cent cobalt and 2 per cent chrome, and operating between 275 and 300°C.

Braunschweigische Maschinenbauanstalt has developed a thermally balanced process in the reaction section by combining oxidation and dehydrogenation. In this process, an air/ethanol/steam mixture is treated in the presence of a silver base catalyst, and the yield of the operation approaches 93 molar per cent.

8.1.2 Acetaldehyde synthesis by hydration of acetylene (Fig. 8.2)

This process has been industrialized since 1916. In the earliest installations, high purity acetylene (99.5 per cent), rid of impurities such as AsH_3 , PH_3 etc., is sent at low pressure (0.2 to $1 \cdot 10^6$ Pa absolute) to a vertical reactor containing the catalyst. The catalyst in this case is a mercuric complex obtained by attacking mercury with 18 to 25 per cent weight sulfuric acid. The temperature is between 70 and 90°C.

The overall reaction is as follows:



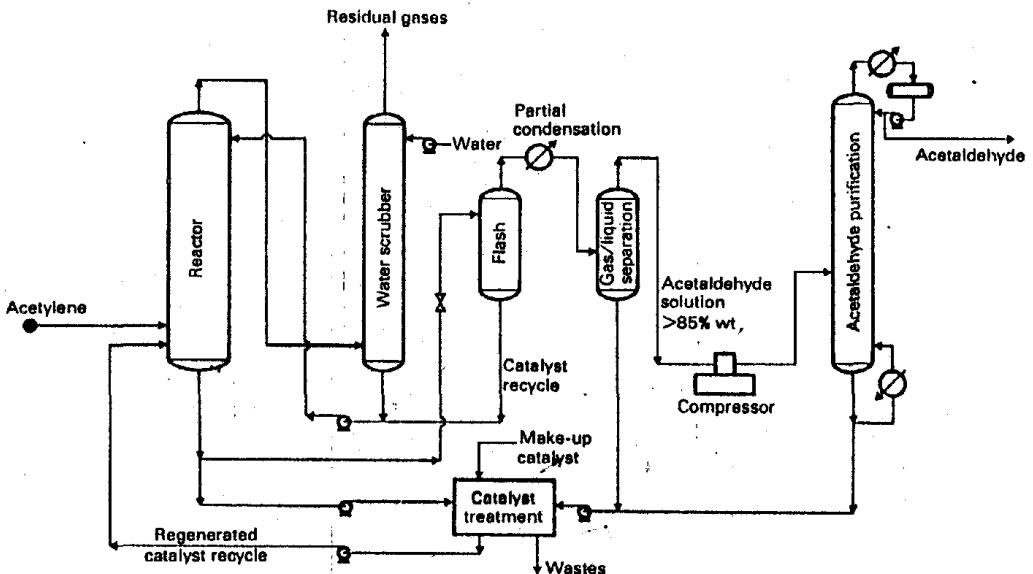


Fig. 8.2. Acetaldehyde production from acetylene. Chisso process.

• The excess acetylene entrains the acetaldehyde formed, which is then condensed by cooling, and then washed with water. The aldehyde is purified by distillation. Unreacted acetylene is recycled. During the operation, the catalytic ion Hg^{2+} is reduced partly to Hg^+ , and then to metallic mercury. This reduction can be prevented by adding Fe^{3+} ions to the catalyst solution (German process).

As a rule, techniques of this type achieve acetylene once-through conversions of 50 to 60 per cent, with molar yields above 95 per cent. Among the suggested variants to this initial scheme are:

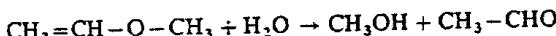
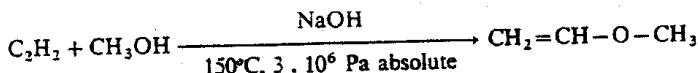
- (a) Total conversion of ethylene in a single pass.
- (b) Use of other catalyst systems: oxides, phosphates, silicates, tungstates etc, of zinc, copper, iron and cadmium etc.

The Chisso process, developed in Japan in the 1950s/1960s, represents one of the latest technologies for the hydration of acetylene. It operates at around $70^\circ C$ and $0.25 \cdot 10^6$ Pa absolute, in a vertical reactor. An aqueous solution of catalyst (mercury and iron salts) and sulfuric acid flows downward in countercurrent to the gaseous acetylene entering at the bottom. The heat liberated by the reaction is removed by vaporizing part of the medium. The acetaldehyde entrained in the off-gases is recovered by water scrubbing and returned to the reactor. It is contained in the liquid product stream at the rate of 2 per cent weight, with sulfuric acid (20 to 25 per cent weight) and mercury and iron salts. Most of the aldehyde (60 per cent) is separated by flash. By cooling and partial condensation of this stream, the acetaldehyde concentration in the remaining gaseous fraction is raised to over 85 per cent weight. This fraction is then recompressed at $0.25 \cdot 10^6$ Pa absolute and distilled. The 40 per cent of products which have not been separated by flash are found with the catalyst solution. It is recycled to the reactor after the catalyst system has been regenerated.

In this type of process, once-through conversion of acetylene is 60 per cent, and the molar yield nearly 90 per cent. The main by-products formed are acetic acid and croton-aldehyde.

Most of the installations employing this method have been closed, and only a few small plants are still operating in Western Europe.

Acetylene hydration can also be achieved by producing methyl vinyl ether as an intermediate, which is then hydrolysed to methanol and acetaldehyde. The following two reactions are involved:



The total acetaldehyde yield in relation to acetylene is 96 molar per cent.

8.1.3 Acetaldehyde synthesis by oxidation of saturated hydrocarbons

Acetaldehyde, together with many other oxygenated products, has been produced industrially by the vapor phase oxidation of paraffins such as butanes and propane/butane mixtures, or more generally from a light gasoline, according to a technology developed

by Celanese. A plant with a production capacity of 90.000 t/year, built in 1946 at Bishop, Texas, was shut down in 1972.

By this process, the hydrocarbon feed is mixed with compressed air and recycle gas containing unreacted paraffins. The recycle gas contains CO, CO₂ and N₂ in the volumetric ratio 1/2/7. The mixture is preheated to 370°C at 0.7 · 10⁶ Pa absolute, and oxidized at 450°C. After decomposition of the peroxides formed in a column containing a ceramic packing, the hot gases leaving the oxidation reactor are quenched with a cooled aqueous solution of formaldehyde containing 12 to 14 per cent weight, and then scrubbed with water to recover the oxygenated compounds. Unreacted hydrocarbons are separated and recycled. Fractionation and purification of the forty or so co-products produced by this conversion are highly complex, and involve simple, azeotropic and extractive distillations.

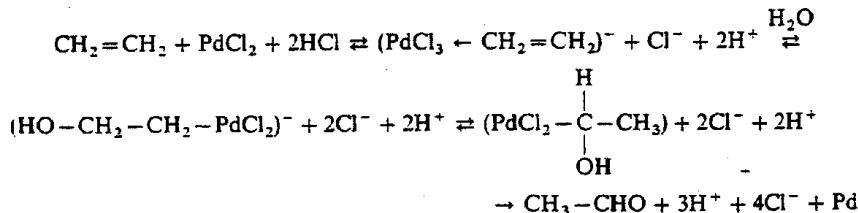
As a rule, the oxidation of 3 t of *n*-butane yields 1 t of acetaldehyde, 1 t of formaldehyde, 0.586 t of methanol, 0.352 t of miscellaneous oxygenated solvents, and 0.118 t of acetone.

8.1.4 Acetaldehyde synthesis by liquid phase oxidation of ethylene (Wacker-Hoechst processes)

This is currently the most widespread method for manufacturing acetaldehyde. Initial research and development conducted by the *Consortium für Electrochemische Industrie*, a *Wacker Chemie* affiliated organization, culminated in 1956 in the development of an industrial process with two variants. One of them, proposed by *Hoechst*, employs oxygen as the oxidant, and the second, examined by *Wacker*, employs air. The commercialization of these two alternatives by Aldehyd, a joint venture, led to the construction of the first industrial plant in 1960.

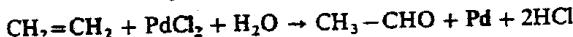
8.1.4.1 Principle

In theory, this transformation, in the presence of palladium chloride and in hydrochloric acid medium, gives rise, with ethylene, to the formation of a π complex which, through an intramolecular rearrangement with water, yields a hydroxyethyl palladium as an active intermediate, ultimately yielding acetaldehyde and palladium metal. The reaction mechanism is as follows:

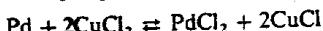


It is then necessary to re-oxidize the palladium, so that the significant reactions involved are the following:

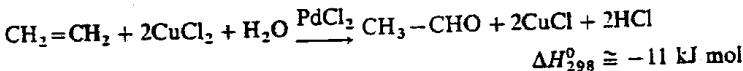
(a) Production of acetaldehyde:



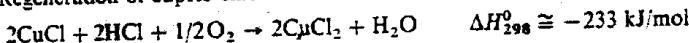
(b) Oxidation of palladium by cupric chloride:



The combination of these two reactions constitutes the first step of the process:



(c) Regeneration of cupric chloride with air or oxygen:



which represents the second step of the process.

The following overall exothermic reaction takes place:



From the kinetic standpoint, it can be shown that the rate of disappearance of ethylene (V), and hence of the production of acetaldehyde, assumes the form:

$$V = \frac{k(\text{PdCl}_4^{2-})(\text{C}_2\text{H}_4)}{(\text{H}^+)(\text{Cl}^-)^2}$$

Consequently, if the presence of palladium chloride proves favorable, that of H^+ and Cl^- ions exerts an inhibiting effect. Accordingly, a catalytic solution of cupric chloride containing chlorine below stoichiometry is more active than that corresponding to the theory, in other words exhibiting a Cl/Cu atomic ratio of 2/1. This encourages the formation of copper oxychloride, a basic salt which acts by neutralization to reduce the concentration of H^+ ions produced during the reaction.

Conversion generally takes place between 80 and 90°C, at between 0.2 and $5 \cdot 10^6 \text{ Pa}$ absolute, and regeneration of the catalyst system in similar conditions, so that both operations can be conducted jointly. The catalyst solution contains 50 to 500 times more copper atoms than palladium, and the Cl/Cu atomic ratio ranges from 1.4 to 1.8/1. Depending on the technology implemented, ethylene once-through conversion is between 20 and 50 per cent (single-step process) and up to 90 per cent (two-step process), which eliminates the need to recycle unconverted raw material.

In both cases, the molar yield of acetaldehyde is 95 per cent. The main by-products are acetic and oxalic acids, crotonaldehyde, and various chlorinated organic compounds (methyl and ethyl chlorides, chloroethanol, chloroacetaldehyde, chlorocrotonaldehyde, chloroacetic acid etc.).

To avoid the flammability range of the gas mixture (8 to 20 per cent volume of oxygen at low pressure, 8 to 14 per cent at higher pressure), the oxygen to ethylene ratio must be kept to a level below stoichiometry, in other words with an oxygen content less than 8 per cent volume.

8.1.4.2 Industrial manufacture

The process offers the following two variants:

- (a) Single step in the presence of oxygen, with recycle of unconverted reactants, according to the Hoechst scheme.
- (b) Two steps, in the presence of air, without recycle, according to the Wacker-Chemie scheme.

Both processes rely on the possibility as to whether or not acetaldehyde production and cupric chloride regeneration can be conducted simultaneously.

A. *Wacker-Hoechst single-step process* (Fig. 8.3)

In this version, high-purity ethylene (99.8 per cent volume) and oxygen (99.5 per cent volume), mixed with dilution steam, are introduced at different levels at the base of a titanium reactor more than 20 m high, containing 10 to 15 perforated trays and hold-up catalyst solution. Conversion takes place at 0.3 to $0.5 \cdot 10^6$ Pa absolute, at a temperature kept at around 120 to 130°C by the vaporization of a fraction of the reaction medium (especially water), which removes the heat liberated by the oxidation of ethylene.

The streams leaving the top of the reactor pass through a separator, where they are partly condensed. The liquid phase recovered is recycled. The remaining gases are sent to a quenching tower, where their temperature is lowered from 125 to 50°C, and then to a water scrub column to recover the small amounts of acetaldehyde entrained by the off-gases. These gases, rich in unconverted ethylene, are recompressed and returned to the reaction zone. A small part (1 per cent) is purged to prevent the accumulation of inert (especially nitrogen) in the recycle loop. The dilute acetaldehyde (8 to 10 per cent weight) obtained after quenching and water-scrubbing is concentrated and purified, first by stripping of light products in a column with about 25 trays, and then by the removal of heavy products and water in a second tower (20 trays). Acetaldehyde in a purity of 99.7 to 99.9 per cent weight is recovered at the top. A sidestream is drawn off to separate the crotonaldehyde by-product as well as many other organic compounds. The bottom consists chiefly of water, acetic acid and heavier products. A fraction of this is purged, but most of it is recycled to the scrubbing stage.

The catalyst solution deteriorates to some degree during oxidation, leading to the formation of copper oxalate. A regenerator operating on the liquid phase from the separator, around 170°C, in the presence of oxygen, serves to decompose the products thus formed and to restore the catalyst's activity. Make-up hydrochloric acid (30 per cent weight) is added in the reactor. For better acid corrosion resistance, the units are built of stainless steel, or even titanium, or provided with internal linings (titanium, elastomers etc.).

In this type of process, ethylene once-through conversion is about 25 to 30 per cent, and the total yield is about 94 molar per cent in relation to the fresh feed, and 90 molar per cent in relation to oxygen.

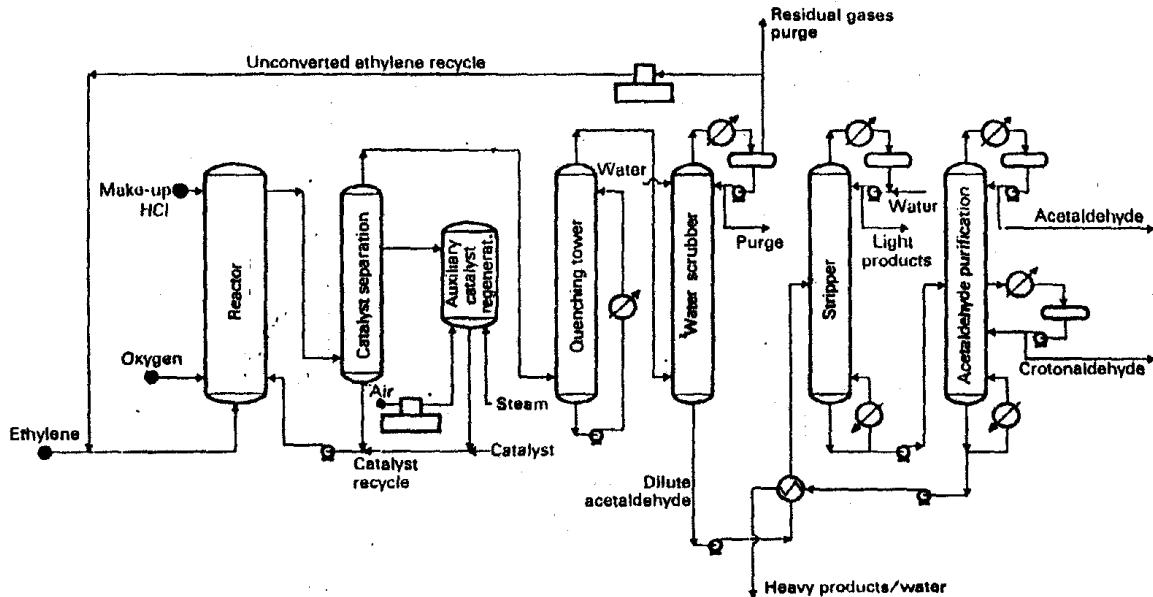


Fig. 8.3. Acetaldehyde production from ethylene. Wacker/Hoechst single-step process.

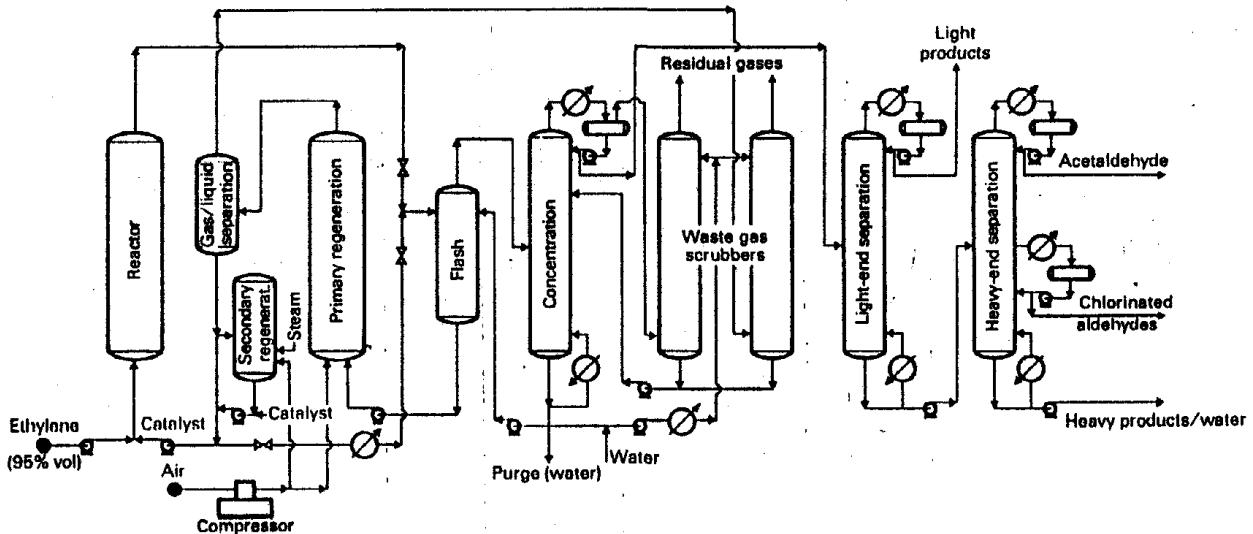


Fig. 8.4. Acetaldehyde production from ethylene. Wacker/Hoechst two-step process.

B. Wacker-Hoechst two-step process (Fig. 8.4)

This version offers the advantage of being able to operate with lower purity ethylene (95 per cent volume) and air as oxidant. However, it requires larger capital expenditure, although unconverted reactants are no longer recycled in this case.

The ethylene and catalyst solution are introduced simultaneously into a tubular titanium reactor operating at 110°C and between 0.8 and $0.9 \cdot 10^6$ Pa absolute. The effluent produced is flashed at atmospheric pressure. Owing to the heat released by the reaction, the acetaldehyde and water are contained in the vapor phase. The liquid phase, consisting essentially of catalyst, is pumped at $1 \cdot 10^6$ Pa absolute into the cupric chloride regenerator. This is also a tubular reactor, operating at 100°C, in which compressed air is also injected. After separation of the waste gases (mainly nitrogen) by flash, the bulk of the regenerated catalyst solution is returned to the first conversion stage. A small fraction is purged and heated to 160°C to destroy the degradation products formed (copper oxalate).

The gaseous mixture of acetaldehyde and steam obtained by flash is first concentrated to 60 to 90 per cent weight in a primary distillation column (10 trays). The light and heavy compounds (water, acetic acid etc) are removed in a series of two distillation columns containing about 25 and 20 trays respectively, and the second column is provided with a side stream consisting mainly of chlorinated aldehydes.

In the two-step variant, ethylene once-through conversion is between 97 and 98 per cent, and the molar yield between 94 and 95 per cent.

8.1.5 Other industrial methods for manufacturing acetaldehyde

Among the various other methods that have led or are capable shortly of leading to industrial development are the following:

- (a) Co-production of acetaldehyde in certain acrylonitrile manufacturing processes (see Section 9.4) or in the Shell technique for the simultaneous production of acetone and glycerin from propylene (see Section 10.2.2). The plant built by Shell at Norco, Louisiana, and shut down in 1980, had a production capacity of 5000 t/year of acetaldehyde.
- (b) Single-step synthesis of acetaldehyde from a 3/1 H₂/CO mixture, proposed in 1974/1975 by Union Carbide: conversion is carried out in the presence of a rhodium base catalyst (5 per cent weight) deposited on silica, around 300°C, at $2 \cdot 10^6$ Pa absolute. It yields various oxygenated products, including acetaldehyde (24 per cent weight), acetic acid (20) and ethanol (16).

8.1.6 Economic data

Table 3.1 gives economic data on the production of acetaldehyde by acetylene hydration and liquid phase oxidation of ethylene according to the Wacker-Hoechst (single-step and two-step) technologies.

TABLE 8.1
ACETALDEHYDE PRODUCTION: ECONOMIC DATA
(France conditions mid-86)
PRODUCTION CAPACITY 100,000 t/year

Process	Acetylene hydration	Ethylene oxidation	
Typical technology	Chisso	Wacker/Hoechst	
		Single-step	Two-step
Battery limits investments (10^6 US\$)	17.	19	30
Consumption per ton of acetaldehyde			
Raw materials			
Acetylene (t)	0.620	—	—
Ethylene (t)	—	0.675	0.675
Oxygen (Nm^3)	—	280	—
Utilities			
Steam (t)	2	1.2	1.2
Electricity (kWh)	350	100	500
Cooling water (m^3)	250	200	220
Water at 12°C (m^3)	—	—	15
Process water (m^3)	1	6	—
Treated water (m^3)	—	2	2
Chemicals and catalysts (US\$)	20	7	7
Hydrochloric acid (100% C) (kg)	—	10	50
Sulfuric acid (kg)	5	—	—
Labor (Operators per shift)	4	4	5

8.1.7 Uses and producers

Tables 8.2 lists the average commercial specifications of acetaldehyde.

Table 8.3 gives the main uses of acetaldehyde in 1984 for Western Europe, the United States and Japan, as well as the production, capacities and consumption for these three geographic areas.

TABLE 8.2
AVERAGE COMMERCIAL SPECIFICATIONS OF ACETALDEHYDE

Characteristics	Values
Purity (% Wt) min.	99.5
^{415.6} _{3.6}	0.78 to 0.79
Acidity (expressed as acetic acid) [% Wt] max.	0.1
Coloration (Pt/Co) (ppm) max.	10

(1) Specific gravity, 60.0/60.0.

TABLE 8.3
ACETALDEHYDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acetic acid - acetic anhydride	64	55	27
Peracetic acid		7	
Ethylacetate	18	8	45
Pentaerythritol	5	8	4
Synthetic pyridines	8	9	
Glyoxal	3	—	
Crotonaldehyde	1	3	24
1,3-butyleneglycol	—	3	
Miscellaneous ⁽¹⁾	1	15	
Total	100	100	100
Sources (% product)			
Acetylene	14	—	—
Ethanol	8	—	—
Ethylene	78	100	100
Total	100	100	100
Production (10^3 t/year)	540	290	295
Capacity (10^3 t/year) ⁽²⁾	1,030	330	675
Consumption (10^3 t/year)	550	255	265

(1) Chloral (trichloroacetaldehyde), lactic acid, isobutylacetate.

(2) The worldwide production capacity of acetaldehyde was nearly $3.1 \cdot 10^6$ t/year in 1984 and 1986 with the following distribution:

United States	0.35	Western Europe	1.05	Japan	0.75
Mexico	0.15	Eastern Europe	0.75	Asia and Far East	0.25

8.2 ACETIC ACID

Apart from the production of vinegar for food uses, the manufacture of dilute acetic acid by ethanol fermentation for industrial applications has practically disappeared and has been superseded chiefly by synthesis from hydrocarbons. In addition to the distillation of wood, which was originally widespread in the United States and is still practiced in certain European countries, three main methods are available for manufacturing concentrated acetic acid ($d_4^{20} = 1.0492$ ⁽²⁾, mp = 16.6°C, bp_{1.013} = 118.5°C):

- (a) Liquid phase oxidation of acetaldehyde.
- (b) Direct or indirect oxidation of hydrocarbons in the liquid phase.
- (c) Methanol carbonylation, a process developed early, but capable in its latest commercial version of supplanting the other technologies: this already accounts for more than one-third of worldwide installed capacity.

(1) Specific gravity, 68.0:39.2

8.2.1 Acetic acid synthesis by liquid phase oxidation of acetaldehyde

The catalytic oxidation of acetaldehyde in the liquid phase to acetic acid by air or oxygen is still widely applied, and accounts for about 40 per cent of installed worldwide production capacity.

8.2.1.1. Principle

This conversion employs the following exothermic reaction:



It is generally conducted in the liquid phase, in the presence of manganese, cobalt or copper salts (acetates), by a chain free radical mechanism involving the intermediate formation of peracetic acid. This may either decompose to form acetaldehyde and oxygen, or react with the components of the reaction medium to yield a mixed metallic complex of the acetaldehyde and the peracid.

Whereas the cobalt and manganese salts actually catalyze the oxidation, the effect of copper acetate essentially involves the decomposition of this complex to acetic acid. The reaction takes place in slightly different conditions, depending on the type of oxidant employed. They can be summarized as follows:

Oxidant.....	air	oxygen
Temperature (°C).....	55 to 65	70 to 80
Pressure $10^6 \text{ Pa absolute}^{(3)}$	0.2 to 1	0.15 to 0.3
Once-through conversion (%)	91 to 92	96 to 98
Yield (molar %).....	93 to 94	95 to 96

The main by-products are formaldehyde, formic acid, methyl and ethyl acetates, acetone, carbon dioxide etc, and ethylene oxide and ethylene glycol diacetate, if the acetaldehyde used derives from the conversion of ethylene.

Oxidation can also take place in the vapor phase, in the presence of water and a palladium base catalyst system, around 200 to 250°C , and between 0.2 and $1 \cdot 10^6 \text{ Pa absolute}$, with an acetaldehyde once-through conversion greater than 45 per cent and an acid molar yield of 92 per cent.

8.2.1.2 Industrial manufacture (Fig. 8.5)

Only liquid phase oxidation has hitherto been industrialized, particularly by *Hoechst*, who employs oxygen as the oxidizing agent. Make-up acetaldehyde in a purity of 99 to 99.8 per cent weight, as well as recycle aldehyde and acetic acid containing metallic salts used as catalysts in solution, are introduced at the top of a reactor with countercurrent flow of air, previously compressed and scrubbed with acetic acid. The heat liberated by the reaction is removed by forced circulation of a fraction of the reaction medium through an external heat exchanger. The operating conditions are designed to establish a steady state acetaldehyde concentration of about 5 per cent weight.

(3) A pressure of $0.12 \cdot 10^6 \text{ Pa absolute}$ is sufficient to maintain the acetaldehyde in the liquid phase at 50°C .

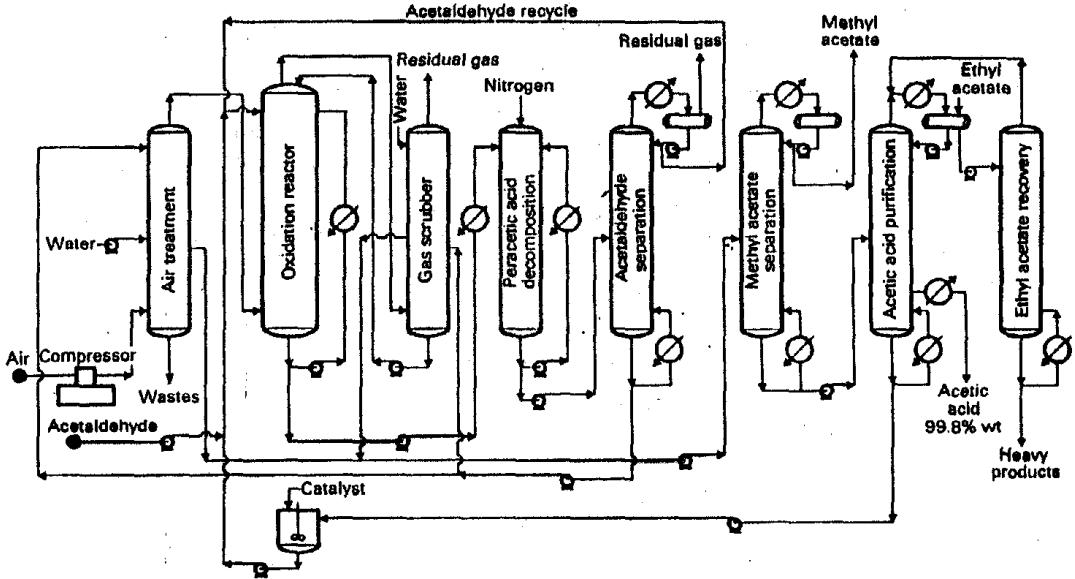


Fig. 8.5. Acetic acid production by acetaldehyde oxidation.

The off-gases, which entrain small amounts of products and reactants, are scrubbed with water and crude acetic acid, and then discharged to the atmosphere. The recovered condensates are recycled. The liquid stream drawn off from the reactor is first rid of most of the peracetic acid it contains by heating in an inert atmosphere around 85 to 90°C, followed by distillation.

This fractionation operation is performed in a series of four columns to achieve the following:

- (a) Separation of unconverted acetaldehyde in the distillate, which is then recycled to the reaction section, and an acetic acid rich fraction at the bottom, used to scrub the air and off-gases.
- (b) Removal of by-product methyl acetate at the top, in a distillation column supplied with the effluent from air pre-scrubbing and yielding crude acetic acid at the bottom.
- (c) Purification of the acetic acid obtained, by separation of water in the distillate, in the form of a heteroazeotrope with ethyl acetate ($\text{bp}_{1,013} = 70.4^\circ\text{C}$, water content, per cent weight, 8.5). Two layers are formed by cooling and settling; the upper organic fraction, containing 97 per cent weight acetate, is used as a reflux, and the lower aqueous fraction, containing 93 per cent water, is sent to the final column. A sidestream supplies glacial acetic acid in a purity of 99.8 per cent weight. The bottom, consisting chiefly of metallic acetates, is recycled to the reactor. This purification is carried out in the presence of potassium permanganate or sodium bichromate, to remove traces of contaminants liable to color the final product.
- (d) Recovery of the ethyl acetate contained in the aqueous phase by azeotropic distillation.

Given the high risk of corrosion, most of the equipment is built of stainless steel, or with an aluminum lining.

8.2.2 Acetic acid manufacture by oxidation of hydrocarbons

As a rule, this method can be applied to the oxidation of any paraffinic or olefinic hydrocarbon, pure or in a mixture, using air, sometimes enriched with oxygen. Industrial plants mainly process paraffins (propane, *n*-butane and light gasoline). However, considerable development work has been conducted on the conversion of olefins, and more precisely *n*-butenes, by direct oxidation or indirect oxidation (intermediate formation of acetates). These developments have culminated in plant construction in Western Europe only.

8.2.2.1 Oxidation of paraffinic hydrocarbons

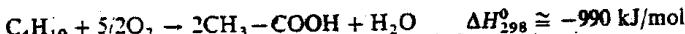
This operation is normally conducted in the liquid phase, by a chain free radical reaction mechanism, whose basic step is the formation of hydroperoxides, which then react and split to produce a wide variety of oxygenated compounds. The more complex the feed employed, the wider the variety of products obtained.

As in all conversions of this type, which are autocatalytic, the induction period is relatively long. Catalysts are used to shorten it. These catalysts are soluble salts of cobalt, chromium, vanadium or manganese, usually acetates. The oxidation rate rises with the number of carbon atoms in the hydrocarbon and with the extent to which the chain is linear. Thus, if it is 1 for ethane, it is as high as 100 for propane, 500 for *n*-butane and 1000 for *n*-pentane.

The oxidation temperature normally ranges from 130 to 200°C, preferably between 160 and 180°C. The pressure must be sufficient to maintain the medium in the liquid phase, or between 4.5 and 5.5 · 10⁶ Pa absolute in the case of *n*-butane, and between 2 and 4 · 10⁶ Pa absolute in the case of naphtha.

A. *n*-butane oxidation

n-butane is converted to acetic acid by the following overall reaction:



Many by-products are also obtained. These can be classified in two main categories:

- (a) Those with a boiling point lower than that of water: ethyl acetate, methyl ethyl ketone, methyl vinylketone etc.
- (b) Those with a boiling point higher than that of water: formic, propionic, acrylic, butyric and succinic acids, dimethyl glyoxal, acetyl acetone, acetonyl acetone, butyrolactone etc.

Formic acid displays an unusual behavior, however, significantly complicating the scheme for the separation of the different products formed and for the purification of the acetic acid. Formic acid, which boils at a temperature approaching that of water (bp_{1.013} = 100.7°C), forms an azeotrope with water, with a boiling point higher than those of the pure components (E_{1.013} = 107.2°C, water content, per cent weight, 22.6). Hence its separation requires azeotropic or extractive distillation.

This also applies to dimethyl glyoxal, which, even in very small amounts, colors the acetic acid yellow and makes it unsuitable for certain applications. This impurity can only be removed by specific treatment with hydroxylamine.

As a first approximation, the yields of these different products, expressed as a percentage of carbon, are as follows:

Formic and propionic acids, etc.....	4
Carbon dioxide and monoxide.....	17
Esters and ketones	22
Acetic acid	57
Total	100

Since the variety of the compounds formed increases only with the complexity of the feed, great similarity exists between the schemes for the treatment of effluents derived from the oxidation of *n*-butane and the oxidation of a light gasoline (see Fig. 8.6).

The main promoters of this technology are Celanese, whose first plant at Pampa, Texas (230,000 t/year) dates from 1952, and Hüls, whose Marl plant (40,000 t/year) is now shut down. The Celanese process involves oxidation in the presence of cobalt or manganese salts, and in the Hüls process conversion takes place without catalyst. Other process licensors include Distillers, Union Carbide, etc.

B. Oxidation of light gasolines (Fig. 8.6)

This process, developed by *Distillers*, and industrialized by *BP Chemicals* in the United Kingdom at Saltend (190,000 t/year), and in the Soviet Union at Yerevan (35,000 t/year), by *Rhône-Poulenc* in France at Pont de Claix (35,000 t/year) and by *Dainippon Chemical* in Japan in a plant that is currently shut down (15,000 t/year), operates on a light gasoline (naphtha) whose upper cut point is generally 95°C. Oxidation takes place by air in reactors in the form of towers, designed to achieve an effective mixture of the gas and liquid phases, and to ensure good temperature control, since the reaction is highly exothermic: $\Delta H \approx -420 \text{ kJ/mol}$ of oxygen converted.

The average operating conditions are as follows:

Temperature	180 to 185°C
Pressure	4.5 to 5. 10^6 Pa absolute
The oxygen to feed weight ratio must be at least 0.5 at the reactor inlet.	

The heat of reaction is used to produce low-pressure steam.

In addition to acetic acid, formic, propionic, butyric and succinic acids are mainly formed, together with carbon dioxide, carbon monoxide, water and a number of heavy oxygenated compounds. The remaining by-products (oxalic, glutaric and adipic acids, etc.) are recycled to the reactors. The use of a cobalt base catalyst serves to increase the acetic acid yield, at the expense in particular of formic acid and also of the total amount of upgraded acids. By altering the operating conditions, the respective output of the different acids can also be adjusted. Hence, in the *Rhône-Poulenc* plant, production is limited in practice to formic, acetic and propionic acids.

As a rule, the reactor streams are treated as follows:

- (a) The gaseous products are cooled to ambient temperature to condense most of the less volatile components, and then below 0°C to recover unconverted hydrocarbons. A suitable heat exchange system, combined with expansion turbines operating on the gas stream, helps to avoid the use of a refrigeration machine.
- (b) The liquid products are treated in a complex series of distillation columns (about 13). Light and heavy ends are first taken off. Most of the water is removed by azeotropic distillation in the presence of isopropyl ether. A new operation of this type, using toluene, then serves to isolate the formic acid, which is purified. Pure acetic and propionic acids are separated and purified by simple distillation. However, hydrogenation treatment of the propionic acid before its final purification is necessary to remove all traces of unsaturated compounds. Depending on each specific case, the succinic acid can be isolated from the residual products by crystallization.

To resist corrosion by organic acids, the reaction section of the installation is built of a stainless steel stabilized with titanium or niobium (Cr = 18 per cent, Ni = 14.5 per cent, Mo = 2.5 to 3 per cent, Ti = 0.3 to 0.5 per cent or Nb = 0.6 to 0.8 per cent) and a large part of the separation section is built of copper.

8.2.2.2 Oxidation of olefinic hydrocarbons

Acetic acid can be obtained by the direct oxidation of ethylene, but this represents a single-step version of industrial schemes for the manufacture and intermediate purification of acetaldehyde, which offer a better total yield for the time being.

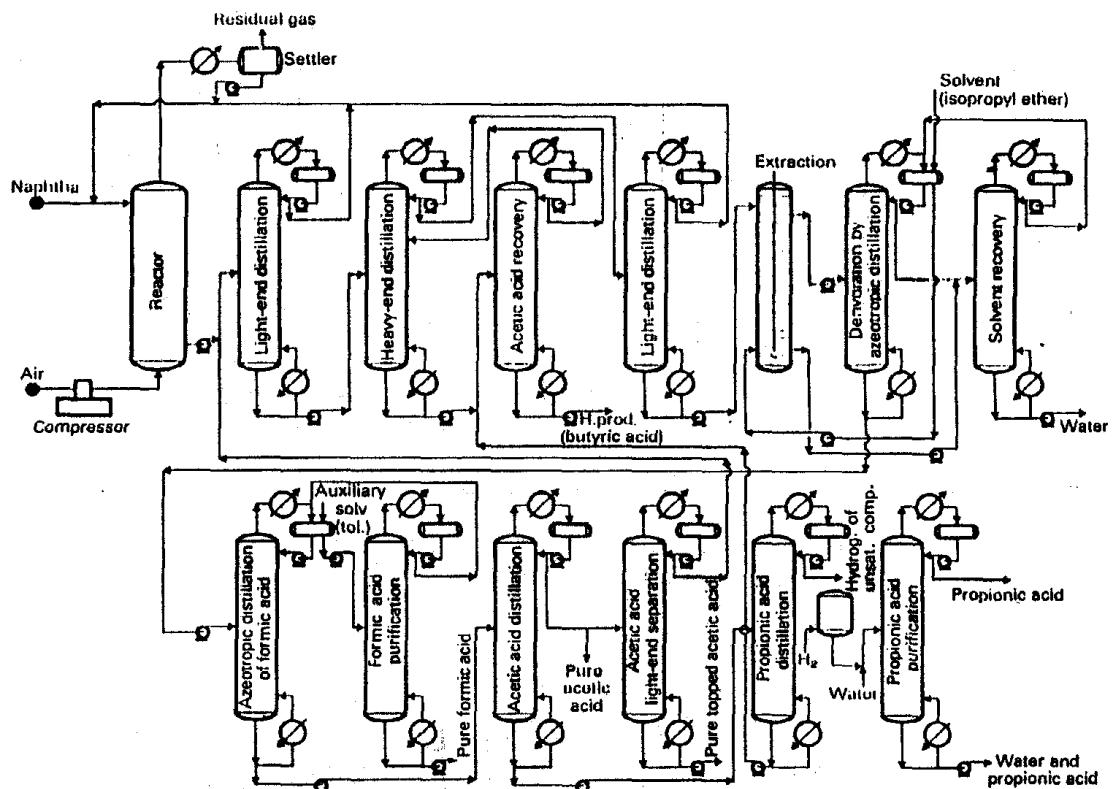


Fig. 8.6. Acetic acid production by naphtha oxidation. Distillers process.

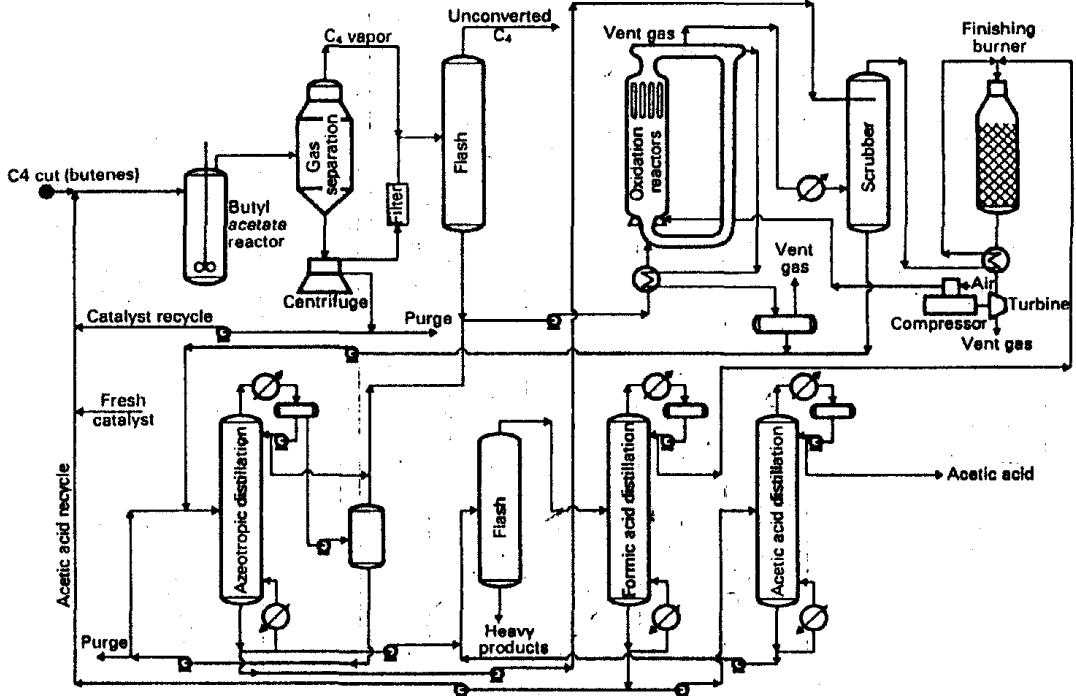


Fig. 8.7. Acetic acid production by oxidation of *n*-butenes. Bayer process.

Development work has also been undertaken to manufacture acetic acid from propylene, operating in the gas phase, in the presence of metallic oxide base catalysts (U, W, Mo, Ti, etc.) and steam, between 250 and 400°C, at atmospheric pressure, with molar yields not exceeding 50 to 70 per cent.

However, the ideal olefin for the synthesis of acetic acid remains the *n*-butenes, despite the few industrial achievements in this area. Conversion is carried out directly in the vapor or liquid phase, or indirectly with the intermediate formation of acetates.

*A. Direct oxidation of *n*-butenes*

The overall reaction is as follows:



This can be achieved on a mixture of isomers, considering the thermodynamic equilibrium existing between 1-butene and 2-butenes which can replenish the system permanently with the more rapidly converted substance. It appears that acetaldehyde and acetone are the ideal intermediates for the oxidation of *n*-butenes.

This is preferably conducted in the gas phase, in the presence of excess oxygen (oxygen to *n*-butenes molar ratio of 10 to 25) to achieve maximum once-through conversion (60 to 90 per cent) while maintaining high selectivity (50 to 70 molar per cent). The steam and oxygen exert complementary influences in this case. Conversion takes place between 250 and 300°C, at between 1.5 and $3 \cdot 10^6$ Pa absolute, in the presence of vanadium oxide base catalysts promoted by various other metals (Ti, Zn, Al, etc.). Many by-products are formed, including acids (formic, maleic, propionic, acrylic, etc.), aldehydes (formaldehyde, acetaldehyde, etc.), alcohols (isopropanol, butanol etc.), ketones (acetone, methyl ethyl-ketone, etc.), esters, carbon monoxide, carbon dioxide etc.

As a rule, the scheme of an industrial installation comprises two main sections:

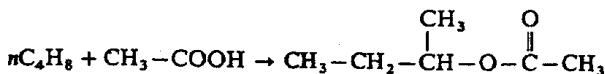
- The first features the introduction of the preheated *n*-butenes feed into an air oxidation reactor, operating under pressure in fixed or fluidized catalyst beds, and designed to ensure the removal of the heat liberated during the conversion by the production of steam.
- The second involves the removal of vent residual gases by flash followed by the separation of the different components of the reactor effluent in a relatively complex sequence of simple and azeotropic distillations, which may include solvent extraction stages.

This type of process has been developed in particular by *Chemische Werke Hüls* etc., but the lack of selectivity of the operation, which is even greater than in the oxidation of *n*-butane, has compromised its attainment of the industrial stage.

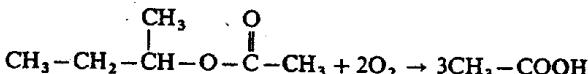
*B. Indirect oxidation of *n*-butenes (Fig. 8.7)*

To overcome the drawbacks of the direct conversion of *n*-butenes, *Bayer* has developed an indirect oxidation process that helps to improve the overall selectivity of the operation, and which consists in passing through the intermediate formation of secondary butyl acetate. Acetic acid is manufactured in two steps according to the following reaction mechanism:

(a) Esterification:



(b) Cracking:



In practice, the Bayer process (Fig. 8.7), which has not yet been industrialized, starts with a steam-cracked C₄ cut, for example, from which the butadiene and isobutene are extracted, and which therefore consists of about 20 per cent weight butanes and 80 per cent weight *n*-butenes. The butanes behave as a diluent. The unit has three sections:

- Catalytic esterification of *n*-butenes. This is carried out in stirred tank reactors, at 110°C and between 1.5 and 2 . 10⁶ Pa absolute. The depleted C₄ cut is introduced, together with acetic acid acid and a 20 per cent weight suspension of the catalyst system (ion exchange resin) in butyl acetate. The reactor effluent is flashed at 105°C and 0.7 . 10⁶ Pa absolute to separate the butanes and unconverted butenes. The catalyst is removed from the butyl acetate by centrifuging and recycled. One-through conversion of *n*-butenes is about 50 to 80 per cent. The complete conversion of *n*-butenes, by recycling, can only be achieved if extractive distillation is carried out on the residual C₄ cut after flash, in order to separate the butanes.

- Oxidizing cracking of butyl acetate. Cracking takes place in the liquid phase in the presence of air or oxygen, at 195°C, and 6 . 10⁶ Pa absolute, without catalyst, in a vertical reactor featuring appropriate stream flows to guarantee good recovery of the heat released by the reaction (500 kJ/mol of acetic acid formed). Once-through conversion is 30 to 50 per cent and the molar yield is about 80 per cent. The gases leaving the reactor are scrubbed with acetic acid, and then pass through a catalytic burner (490°C, 6 . 10⁶ Pa absolute) whose off-gas drives the turbine of the air compressor.

- Acetic acid separation and purification. Azeotropic distillation serves to separate and recycle the unconverted butyl acetate and the other intermediate products of the reaction. The formic and acetic acids are then isolated. The first is sent to the burner, and the second purified and partly recycled to esterification.

The entire installation must be built of stainless steel. The total yield of the operation is about 45 to 55 molar per cent. The presence of isobutene results in the formation of tertiary butyl acetate, which is much more stable than secondary butyl acetate, and is therefore liable to build up in the unconverted fraction recycle.

8.2.3 Acetic acid synthesis by methanol carbonylation

Acetic acid has been produced by the carbonylation of methanol for a very long time, with the earliest industrial development dating back to 1925 (*British Celanese, BASF : Badische Anilin und Soda Fabrik*), and is based on the use of catalysts containing phosphoric acid and copper phosphate. The development of cobalt/iodine systems led to

the construction of commercial plants, with a BASF technology unit built at Ludwigshafen (3600 t/year in 1960, raised to 12,000 t/year in 1964), and another at Geismar, Louisiana, for *Borden Chemical* (30,000 t/year in 1966, raised to 45,000 t/year in 1968).

The last generation of catalysts, based on rhodium complexes with iodine, developed by *Monsanto* and industrialized in 1970 in Texas City, Texas (135,000 t/year), has now supplanted all other methods for synthesizing acetic acid.

8.2.3.1 Principle

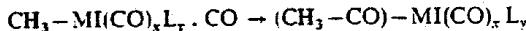
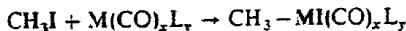
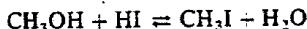
The process requires the following exothermic conversion:



It can be shown experimentally that this reaction is favored by development in the liquid phase, at a temperature between 220 and 250°C. The reaction rate is too low below 180°C, while the excessive formation of by-products occurs above 260°C. The pressure must also be kept above $30 \cdot 10^6$ Pa absolute. The presence of water (> 30 per cent volume) and the use of catalysts help to reduce the severity of the operating conditions, particularly the pressure, which is reduced to about $3 \text{ to } 7 \cdot 10^6$ Pa absolute in the latest systems, while the temperature ranges from 150 to 200°C.

The catalyst system employed generally has three main components: an active phase (oxides, organometallic compounds, coordination compounds or salts of precious metals such as rhodium-chlorocarbonyl-bis triphenylphosphine: $\text{Rh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$, or an identical complex of iridium), a promoter (halogen or halogenated compound, such as methyl iodide), and a solvent (a mixture of acetic acid and water, for example) in which the active phase and the initiator exist in a concentration of 10^{-3} mol. l⁻¹ and 1 mol. l⁻¹ respectively.

The interpretation of the reaction mechanism is related to the type of catalyst employed. In the case of cobalt and rhodium, however, the catalysts appear to act in the form of complexes as follows:



where

$\text{M} = \text{CO}^{II}$ or Rh^I

L = ligand other than CO, for example triphenylphosphine.

Whereas the cobalt catalyst systems developed by *BASF* in particular guarantee a methanol once-through conversion of 70 per cent and molar yields in relation to alcohol and carbon monoxide better than 85 and 60 per cent, those developed by *Monsanto*, based on rhodium, offer better performance. Methanol once-through conversion may exceed 90 per cent, and molar yields in relation to alcohol and carbon monoxide are between 98 and 99 per cent and 90 per cent respectively.

The main by-products formed are carbon dioxide, alcohols (ethanol, butanol, etc.), aldehydes (propionaldehyde, *n*- and isobutyraldehydes), acids (formic, propionic etc.), esters (methyl formate and acetate), and ethers (dimethyl ether, etc.). Some of them, obtained in large quantities (methyl acetate and dimethyl ether), can be recycled.

8.2.3.2 Industrial manufacture

Two technologies dominate this method for producing acetic acid by the carbonylation of methanol. They were developed by *BASF* and *Monsanto*.

A. *BASF* process

This process operates in the aqueous phase at 250°C, and $65 \cdot 10^6$ Pa absolute, in the presence of cobalt iodide as catalyst. The high-pressure reactor lined with hastelloy C for corrosion resistance features internal agitation of the liquid obtained by gas injection ("air lift" type). It is continuously supplied with a stream of methanol, dimethyl ether, carbon monoxide if required, and water preheated to between 40 and 80°C. The amount of water added is one-third of that of methanol by weight. The acid mixture and the unreacted gases are collected at the top of the reaction tower, cooled, and brought to $1 \cdot 10^6$ Pa absolute in a flash drum. The methyl iodide and heavier components in the flashed gases are recovered by scrubbing with methanol feed.

The liquid effluent from the flash drum is first degassed. The vapors consisting of methyl iodide and formate, acetaldehyde and methyl acetate, are dissolved in the azeotrope produced by the subsequent acetic acid dehydration column. The degassed acid mixture is then distilled to remove the light components and the cobalt iodide, which is recycled to the reactor in the form of an aqueous slurry. This mixture is then dehydrated and purified by azeotropic distillation. The third compound employed is one of the reaction products (methyl acetate, $\text{bp}_{1.013} = 70.4^\circ\text{C}$, water content 8.5 per cent weight). The column has about 60 trays.

Anhydrous acetic acid not containing formic acid is collected at the base of the dehydrator. This stream is then rid of the heavy compounds (propionic acid) and concentrated to 99.8 per cent weight by distillation (about 30 trays). Corrosion is limited by building some parts of the installation of copper, titanium or zirconium.

B. *Monsanto* process (Fig. 8.8)

In theory, the Monsanto scheme is closely related to that of the *BASF* technology. The main difference lies in the pressure, which is only about $3.5 \cdot 10^6$ Pa absolute with a temperature of around 200°C.

The unit has three main sections:

- › **Catalyst preparation.** In the first section, the catalyst system is prepared from fresh rhodium iodide and the catalyst recycle recovered by subsequent treatment. This recovery solution is first rid of the metallic ions it contains by ion exchange resins. It is then partially decomposed by heating to recover the rhodium-bearing components by cooling and precipitation. These compounds, with make-up iodide added, are then dissolved in hot acetic acid under carbon monoxide pressure.

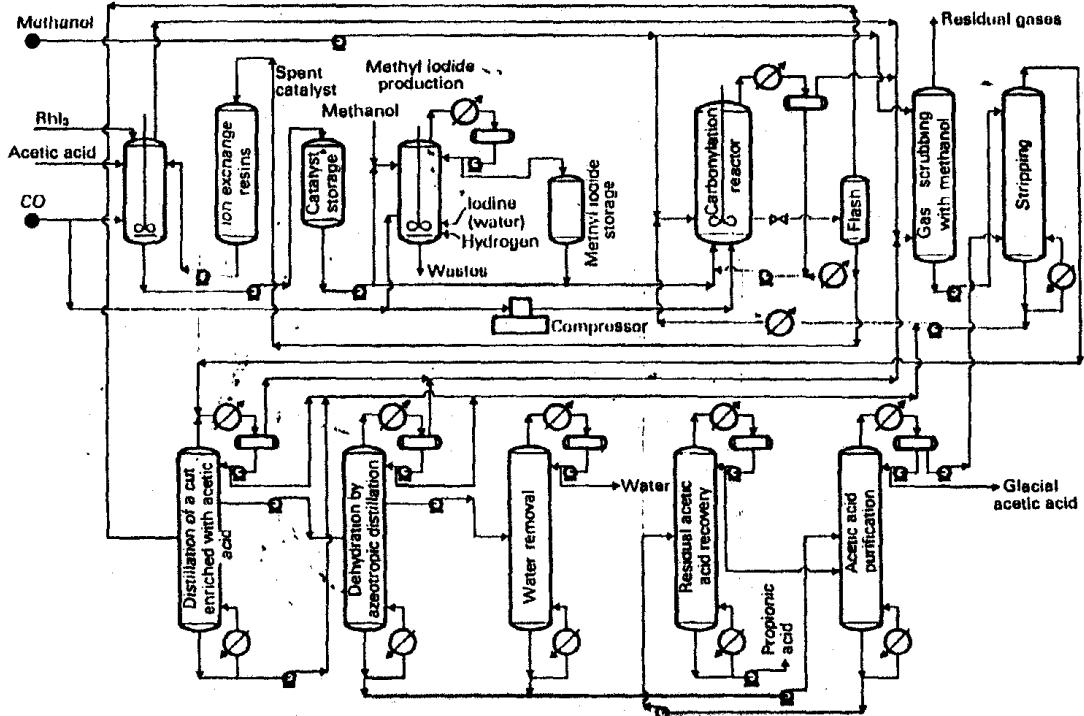


Fig. 8.8. Acetic acid production from methanol. Monsanto process.

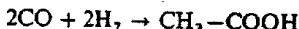
- **Carbonylation.** The methanol is carbonylated in the liquid phase in a stirred tank reactor. The temperature of the reaction medium is kept constant by the vaporization of a fraction of the reactants and products, thus removing the heat generated by the reaction. This gas phase, consisting chiefly of carbon monoxide, nitrogen, carbon dioxide, methanol and methyl iodide, is cooled and then scrubbed with methanol to recover most of the stripped raw materials.

The liquid effluent leaving the reactor is flashed. The gases containing acetic acid, moisture, methyl iodide, and formic and propionic acids, etc. are sent to the purification section. The liquid fraction, chiefly formed of the catalyst complex, methyl acetate and acetic acid, is cooled and sent to the reaction zone.

- **Product separation and purification:** the first distillation column is designed to produce a cut enriched with acetic acid by the removal of the lighter and heavier components (methyl iodide, methyl acetate, etc.). This cut is then dehydrated by heteroazeotropic distillation. The aqueous fraction recovered at the top is refluxed to remove excess water. The heavy stream is treated in a finishing column which produces glacial acetic acid in the distillate, while the residual acetic acid at the bottom is also recovered in a complementary fractionation that separates the heavy products such as propionic acid. These high-alloy steel columns each have between 35 and 45 actual trays.

8.2.4 Other industrial methods for manufacturing acetic acid

Among the developing technologies likely to reach the commercial stage is the direct production of acetic acid from a synthesis gas $\text{H}_2/\text{CO} = 1.1$ by the following reaction:



The conversion, developed in particular by *Union Carbide*, takes place with a yield of about 70 molar per cent, in the presence of a supported rhodium base catalyst, at a temperature between 250 and 350°C, and $10 \text{ to } 30 \cdot 10^6 \text{ Pa}$ absolute, with a carbon monoxide once-through conversion close to 20 per cent.

It should be pointed out that the carbonization of wood between 100 and 150°C leads to the formation of four large varieties of products: charcoal, an acid liquor, tars and incondensable gases. The second, after supplementary fractionation and purification, is used to produce various chemical compounds, particularly acetic acid.

8.2.5 Economic data

Table 8.4 gives the main economic data currently available on the leading industrial for synthesizing acetic acid.

8.2.6 Uses and producers

Table 8.5 gives the average commercial specifications of acetic acid. Table 8.6 lists the main uses in per cent in 1984 for Western Europe, the United States and Japan, as well as the production, capacities and consumption for these three geographic areas.

TABLE 8.4
ACETIC ACID PRODUCTION. ECONOMIC DATA
(France conditions mid-86)
PRODUCTION CAPACITY 80,000 t/year

Process	Acetaldehyde oxidation	n-butane oxidation	Naphtha oxidation	Methanol carboxylation	
Typical technology	Hoechst	Celanese	Distillers	BASF	Monsanto
Battery limits investments (10 ⁶ US\$)	17	35	56	53	28
Consumption per ton of acetic acid					
Raw materials					
Acetaldehyde (t)	0.77	—	—	—	—
n-butane (t)	—	1.08	—	—	—
Naphtha (t)	—	—	0.95	—	—
Methanol (t)	—	—	—	0.61	0.54
Carbon monoxide (t)	—	—	—	0.80	0.51
By-products					
Methyl acetate (kg)	35	—	—	—	—
Formic acid (kg)	—	50	290	—	—
Propionic acid (kg)	—	—	35	—	10
Butyric acid (kg)	—	—	7	—	—
Succinic acid (kg)	—	—	15	—	—
Acetone/methyl acetate (kg)	—	270	—	—	—
Methyl ethyl ketone/ethyl acetate (kg)	—	460	—	—	—
Utilities					
Steam (t)	3.6	8.0	5.5	3.0	2.0
Electricity (kWh)	290	1,550	1,530	350	180
Cooling water (m ³)	260	450	490	185	140
Process water (m ³)	5	25	20	—	—
Chemicals and catalysts (USS) ..	5	3.5	8	7	11
Labor (Operators per shift)	3	5	5	4	3

TABLE 8.5
AVERAGE COMMERCIAL SPECIFICATIONS OF ACETIC ACID

Characteristics	Values	
purity (% Wt) min.....	99.8	99.85
Crystallization temperature (°C)	16.2	16.35
<i>d</i> _{40/15} ¹⁾	—	1.0505-1.0520
Distillation range (°C)	—	1 about 118
Color (Pt/Co) max.....	15	10
Water (ppm) max.....	2,000	1,500
Formic acid (ppm) max.....	1,500	500
Acetaldehyde (ppm) max.....	300	500
Iron (ppm) max.....	5	1
Heavy metals (ppm) max.....	10	0.5
Chlorides (ppm) max.....	4	1
Sulfates (ppm) max.....	6	1
Sulfuric acid (ppm) max.....	—	1

(1) Specific gravity, 68.0/68.0.

TABLE 8.6
ACETIC ACID PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acetic anhydride	8	6	4
Cellulose acetate	12	10	18
Esters ⁽¹⁾	16	12	9
Monochloroacetic acid	9	2	5
Terephthalic acid, dimethylterephthalate	6	10	11
Vinyl acetate	37	52	27
Textiles		3	
Miscellaneous ⁽²⁾	12	5	26
Total	100	100	100
Sources (% product)			
Acetaldehyde	45	20	52
Butane and naphtha	16	17	6
Ethanol	5	—	—
Methanol	34	62	42
Miscellaneous ⁽³⁾	ε	1	—
Total	100	100	100
Production (10 ³ t/year)	955	1,200	330
Capacity (10 ³ t/year) ⁽⁴⁾	1,245	1,450	540
Consumption (10 ³ t/year)	960	1,175	330

(1) Amyl, benzyl, butyl, ethyl, 2-ethylhexyl, methyl and propyl acetates, glyceryl triacetate.

(2) Explosives, grain fumigants, herbicides, metallic salts, pharmaceuticals, photographic and rubber chemicals.

(3) By-products, spent acetic anhydride, terephthalic acid coproduct.

(4) The worldwide production capacity of acetic acid was $4.4 \cdot 10^6$ t/year in 1984 and $4.6 \cdot 10^6$ t/year in 1986.

8.3 ACETIC ANHYDRIDE

Acetic anhydride ($d_4^{20} = 1.082^{(4)}$, $bp_{1.013} = 138.6^\circ\text{C}$) is used chiefly to manufacture cellulose acetate. Since the turn of the century, several methods have been developed to produce it. Three leading methods exist today in the industrial stage, differing mainly in the type of raw material employed, acetic acid, acetone or acetaldehyde, and the first two are based on the intermediate formation of ketene.

(4) Specific gravity, 68.0 39.2

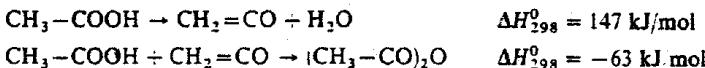
8.3.1 Production of acetic anhydride from acetic acid only

This operation comprises two steps:

- (a) Pyrolysis of acetic acid to ketene,
- (b) The action of the ketene obtained on the acetic acid.

8.3.1.1 Principle

The following reactions are involved:



The first conversion, which is highly endothermic, must take place in the vapor phase at high temperature (700 to 800°C), and at reduced pressure (10 to 20 kPa). Very short residence times, in the neighborhood of 1 s, and the presence of catalysts, serve to limit the formation of the by-products resulting in particular from the cracking of acetic acid and ketene: carbon dioxide, carbon monoxide, methane, coke deposits, hydrogen, ethylene, etc. The catalyst systems employed for dehydration are usually organic phosphates (triethyl, tricresyl, dimethylammonium, pyridinium phosphates, etc.) added continuously directly into the gas feed stream, at the rate of 0.2 to 0.5 per cent weight.

The addition of water in small concentrations (10 per cent weight) to the acetic acid offers similar advantages to those procured in steam cracking. In particular, it slows down the formation of coke. The addition of small amounts of ammonia (< 1000 ppm) exerts an indirect inhibiting effect on the polymerization of ketene. If these precautions are observed, once-through conversion is 85 to 90 per cent and the molar yield 90 to 95 per cent.

The second conversion, which is exothermic, can be carried out in the absence of catalyst, by absorption in acetic acid, between 30 and 40°C, at reduced pressure (7 to 20 kPa). Higher temperatures and pressures facilitate the dimerization of ketene to diketene, whose major drawback is to have a boiling point ($\text{bp}_{1.013} = 127.4^\circ\text{C}$) fairly close to that of the anhydride. Less than 2 per cent weight is usually formed, so that the yield of the operation, with respect to both the acid and ketene, is higher than 95 to 98 molar per cent.

8.3.1.2 Industrial manufacture (Fig. 8.9)

An industrial facility has four main sections:

- (a) Acetic acid pyrolysis.
- (b) Ketene absorption.
- (c) Acetic anhydride purification.
- (d) Recovery of unconverted acetic acid.

- The pyrolysis of about 53 per cent of the feed acetic acid, preheated to about 110°C and containing continuous additions of triethyl phosphate for example, is achieved by passage through a tubular furnace. Rather than standard high-alloy steels, which contain

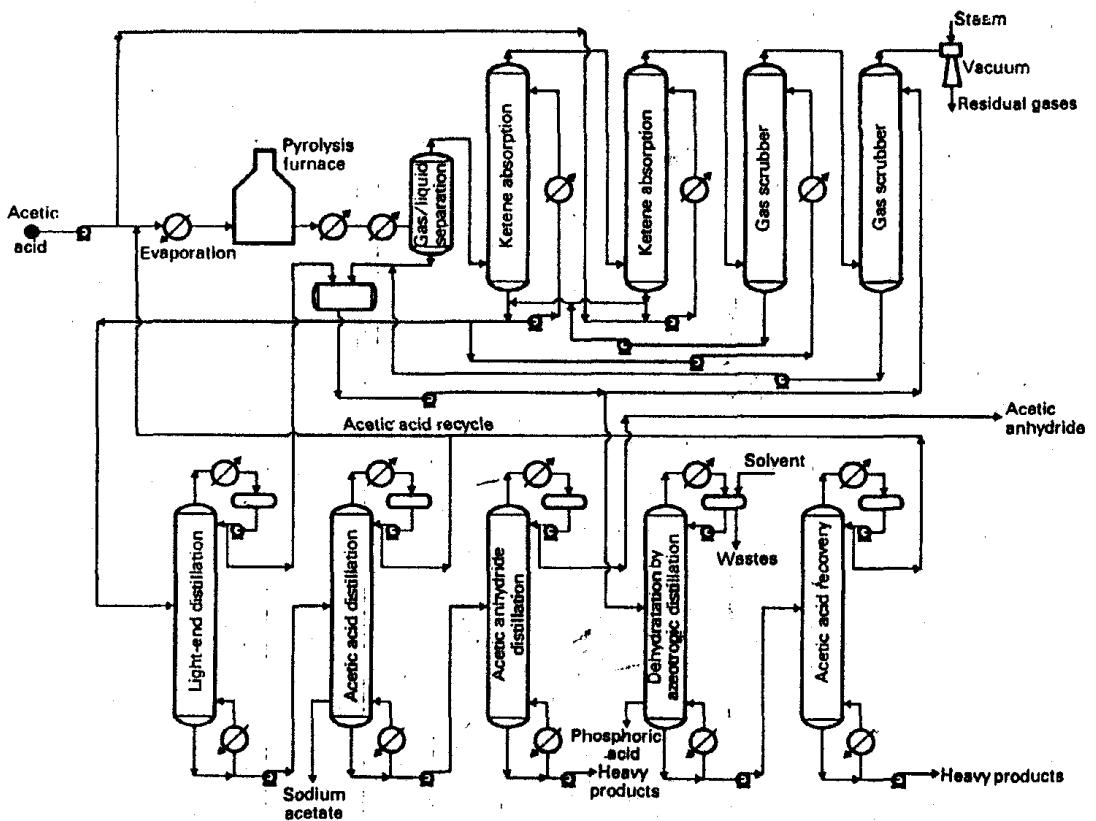


Fig. 8.9. Acetic anhydride production from acetic acid.

nickel and facilitate the complete cracking of the reactants and products, as well as the formation of coke, it is preferable to use high-chromium steels as the tube material, or alloys of chromium (23 per cent), aluminum (1.5 per cent) and silicon (1.5 per cent). If not, the coking process can also be slowed down by the addition of carbon disulfide to the feed. The reactor effluents, available at about 700°C, first receive an in-line injection of ammonia to neutralize the catalyst. They are then cooled rapidly to 0°C in a series of heat exchangers. The liquid obtained by condensation and containing about 35 per cent weight acetic acid is sent to the recovery section.

- Ketene absorption takes place on the off-gases, with a countercurrent of acetic acid, in two absorbers in series, the first collecting 80 per cent of the available ketene. A series of two scrubbers using cold acetic anhydride and acid then serves to recover the acetic acid entrained by these gases. These units operate at around 0°C and between 15 and 5 kPa absolute. The liquid leaving the absorption stage contains more than 90 per cent weight acetic anhydride. It is sent to the purification section.

- Purification takes place by distillation in a series of three columns, separating the following products in succession at the top: crude acid (\approx 70 trays), sent to the recovery stage, glacial acetic acid (\approx 100 trays), recycled to pyrolysis and absorption, and acetic anhydride in a purity of over 99 per cent (\approx 10 trays). The heavier components are collected at the bottom of the final fractionation.

- The recovered acetic acid (unconverted acetic acid) is reconcentrated in two columns (45 and 55 trays). The first removes excess water at the top in the form of a heteroazeotrope with *p*-xylene, for example. The organic phase obtained by condensation and settling serves as a reflux, and the aqueous phase is partly purged. The second column removes the polymerization products at the bottom and produces glacial acetic acid at the top, which is recycled.

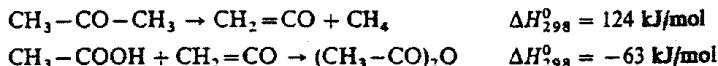
8.3.2 Acetic anhydride manufacture from acetone and acetic acid

This operation is rather similar to that conducted on acetic acid. It takes place in two steps:

- (a) Pyrolysis of acetone to ketene.
- (b) Absorption of ketene in acetic acid.

8.3.2.1 Principle

The main reactions involved are as follows:



The first conversion takes place around 700 to 800°C, at atmospheric pressure, in the vapor phase, usually in the absence of catalyst. Side reactions lead chiefly to the formation of coke, favored by the presence of a nickel base material. At 760°C, once-through

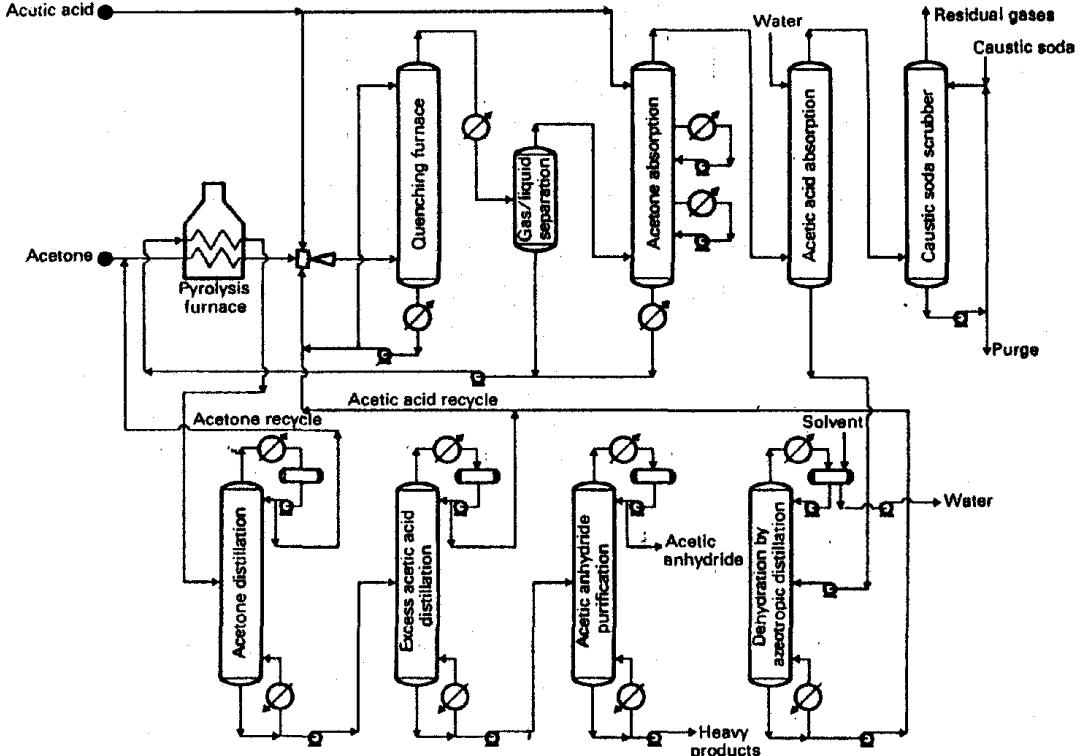


Fig. 8.10. Acetic anhydride production from acetone and acetic acid.

conversion is close to 25 per cent and the molar yield is greater than 70 per cent. The second transformation is similar to the one discussed in Section 8.3.1.1.

8.3.2.2 Industrial manufacture (Fig. 8.10)

Industrial manufacture comprises four main steps:

- The first is the pyrolysis of acetone in a tubular reactor. As for the cracking of acetic acid, it is preferable to use chromium steel (25 per cent) tubes. The use of conventional alloys may be feasible after passivation of the inner walls by a mixture of H_2 and CO , or by prior treatment with steam, or by the injection of small amounts of sulfur compounds (H_2S , CS_2 etc.). The effluents leaving the furnace are quenched in two stages:
 - (a) By in-line injection of a mixture consisting of fresh and recycled acid and acetic anhydride, which lowers the temperature from 760 to 550°C.
 - (b) By scrubbing in a packed tower, using the same mixture, lowering the temperature to about 150°C.
- The second stage, the production of acetic anhydride, takes place in two steps:
 - (a) 90 per cent of the potential anhydride is obtained by supplementary cooling to 70°C and partial condensation of the gases leaving the quenching stage, consisting chiefly of ketene, acetic acid, acetone and acetic anhydride.
 - (b) An additional 9 per cent is formed during the recovery of unconverted acetone entrained in the gases, by absorption in a packed tower featuring countercurrent flow of acetic acid.
- This is followed by recovery of the unconverted acid entrained in the off-gases, by scrubbing with water and reconcentration of the solution obtained by heteroazeotropic distillation (65 trays).
- Separation and purification. In the final step, the components of the liquid phase leaving with the quenching stage are separated and purified at 70°C in a series of three columns which yield the following products in succession at the top: unconverted acetone (20 trays), excess acetic acid (80 trays) and acetic anhydride of more than 99 per cent purity (10 trays). The effluents from the first two distillations are recycled. The second operates only on two-thirds of the stream drawn off from the first, with the remainder used as a quenching fluid.

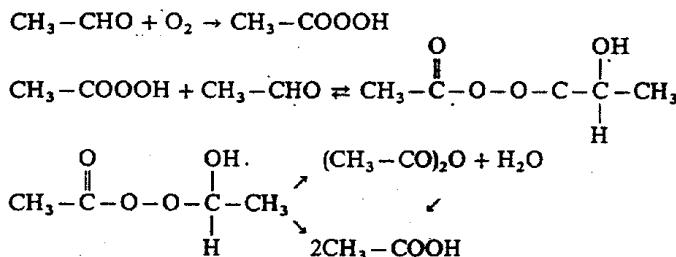
8.3.3 Acetic anhydride manufacture by the oxidation of acetaldehyde

This type of reaction, already implemented for the production of acetic acid, can be controlled to limit the conversion to the preferential production of acetic anhydride. A version of this type has been industrialized since 1930.

8.3.3.1 Principle

It appears to be accepted today that the general reaction mechanism of the formation of acetic anhydride and acid from acetaldehyde involves the production of intermediate

chemical compounds, such as peracetic acid and acetaldehyde monoperacetate, according to the following reactions:



Certain side reactions also occur:

- (a) Hydrolysis of acetic anhydride to the acid.
- (b) Oxidation of acetic anhydride by peracetic acid to yield diacetyl peroxide $(\text{CH}_3\text{CO})_2\text{O}_2$ and acetic acid.
- (c) Decomposition of this peroxide by water to produce peracetic and acetic acids.

Acetaldehyde monoperacetate normally decomposes to yield 97 per cent anhydride and water and 3 per cent acid. However, the hydrolysis takes place rapidly, so that acetic anhydride is merely the forerunner of the acid in the oxidation of acetaldehyde. The difficulty of the operation, which takes place in the liquid phase with oxygen or air, at moderate temperature (45 to 60°C) and low pressure (0.1 to 0.4 . 10⁶ Pa absolute), thus consists in preventing the hydrolysis of acetic anhydride from developing.

Independant of certain technical arrangements, this can be achieved in the presence of diluents and catalysts. The diluents are intended to reduce the hydrolysis rate and also lower the acetaldehyde concentration to limit the risks of explosion. The most widely used diluents are acetic acid and ethyl acetate, but aromatics (benzene), chlorinated compounds (carbon tetrachloride, chlorobenzene, etc.) and ketone compounds (cyclohexanone) can also be used. The catalyst systems are all based on the synergy effect existing between copper and cobalt acetates, introduced in a weight ratio of 3 to 4, with less than 2 per cent weight for the first and 0.5 per cent weight for the second.

Depending on the technology employed, once-through conversion varies from 30 to 80 per cent and molar yields from 50 to 80 per cent for acetic anhydride, and 15 to 45 per cent for the acid. The main by-products are carbon dioxide, methyl acetate, acetone, ethylidene diacetate and various heavy components, whose recycling serves to improve the anhydride selectivity.

8.3.3.2 Industrial manufacture

Two types of processes can be distinguished from the technological standpoint:

- (a) The previous ones draw off the reaction products in the liquid phase. They operate in the presence of oxygen, with acetaldehyde contents of 30 to 40 per cent weight in the reaction medium. Once-through conversion is 70 to 80 per cent, and molar yields are 50 to 75 per cent for acetic anhydride and 20 to 45 per cent for the acid.

These processes were developed in particular by *Celanese, Distillers, and Knap-sack* etc.

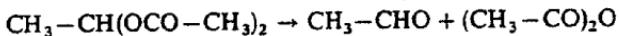
- (b) The most recent processes, developed in particular by *Usines de Melle, Eastman Kodak* etc., are based on the recovery of the reaction products in the vapor phase. They operate in the presence of air, with acetaldehyde concentrations in the reaction medium less than 6 per cent weight, to allow the entrainment of acetic anhydride and water in the off-gases as soon as these products are formed. Maintenance of a liquid phase is facilitated by recycling the heavier products. In these conditions, once-through conversion of the aldehyde is 30 to 50 per cent, and molar yields are 70 to 80 per cent for acetic anhydride, and 15 to 25 per cent for acetic acid.

In the industrial plants of the second type (Fig. 8.11), make-up and recycle acetaldehyde are introduced at the base of a vertical reactor, into which fresh air is blown together with the recirculation of off-gases depleted of oxygen. The heat liberated by the reaction is removed by vaporization as well as by passage through an external heat exchanger of part of the reaction medium, consisting mainly of acetic anhydride and the catalyst system. The vapors leaving the reactor are cooled and partly condensed. The remaining gaseous fraction is essentially recompressed and recycled. The purge is scrubbed with water to absorb entrained acetaldehyde and return it to the reaction zone, after having separated it by distillation ($\cong 30$ trays) from the liquid effluent obtained.

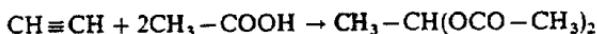
The condensed phase is first dehydrated by azeotropic fractionation ($\cong 50$ trays) in the presence of ethyl acetate existing in the medium and some make-up. The lighter organic compounds are recovered at the top, including acetaldehyde, which must be purified by distillation ($\cong 20$ trays) before recycling. A side stream supplies an aqueous solution, from which the organic components are separated by stripping. They are recycled to the azeotropic fractionation column. By two successive distillations on the withdrawal stream, glacial acetic acid ($\cong 50$ trays) and acetic anhydride ($\cong 35$ trays) are isolated from the heavier products obtained at the bottom of the last column.

8.3.4 Other industrial methods for manufacturing acetic anhydride

Acetic anhydride was formerly produced by the thermal decomposition of ethylidene diacetate by the following reaction:



The ethylidene diacetate was obtained by bubbling acetylene in glacial acetic acid at 60 to 85°C, in the presence of mercuric acetate and sulfate as catalyst, by the following reaction transformation:



Decomposition takes place either by distillation at between 300 and 400°C, and atmospheric pressure, or at 150°C under vacuum, in the presence of 1 to 3 per cent sodium pyrophosphate or zinc chloride.

TABLE 8.7
ACETIC ANHYDRIDE PRODUCTION, ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 80,000 t/year

Process.....	Ketene from acetic acid	Ketene from acetone	Acetaldehyde oxidation
Typical technology.....	Celanese	Courtaulds	Usines de Melle
Battery limits investments (10 ³ US\$)	15	19	23
Consumption per ton of acetic anhydride			
Raw materials			
Acetic acid (t)	1.30	0.65	-
Acetone (t)	-	0.85	-
Acetaldehyde (t)	-	-	1.10
By-products			
Acetic acid (t)	-	-	0.20
Light products (t)	-	-	0.03
Utilities			
Steam (t)	4.0	4.5	2.0
Electricity (kWh)	390	50	1,000
Fuel (10 ³ kJ)	7.0	30.0	-
Cooling water (m ³)	240	350	300
Process water (m ³)	1	1	2
Chemicals and catalysis (US\$).....	8	11	12
Labor (Operators per shift).....	5	5	5

TABLE 8.8
AVERAGE COMMERCIAL SPECIFICATIONS OF ACETIC ANHYDRIDE

Characteristics	Values
Purity (% Wt) min.....	99.0
d_{20}^{20} ⁽¹⁾	1.080 to 1.085
Color (Pt Co) max.....	10
Aluminum (ppm) max.....	1
Iron (ppm) max.....	1
Chlorides (ppm) max.....	1
Phosphates (ppm) max.....	1
Sulfates (ppm) max.....	1
Heavy metals.....	Nil
Nitrates.....	Nil
Permanganate test.....	Reduction of 0.1 cm ³ max. of 0.1 N KMnO ₄ in 5 min for a 2 cm ³ sample.

(1) Specific gravity, 68.6-68.0.

TABLE 8.9
ACETIC ANHYDRIDE PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan
Use (% product)			
Cellulose acetate.....	88	83	93
Cellulose fibers and tow	73	68	79
Plastics and films	15	15	14
Pharmaceuticals and miscellaneous ⁽²⁾	12	17	7
Total	100	100	100
Production (10 ³ t/year)	290	735	160
Capacity (10 ³ t/year) ⁽³⁾	460	820	210
Consumption (10 ³ t/year)	280	710	140

(1) Estimated.

(2) Acetanilide, acetylsalicylic acid, trimesic...

Among the latest developments are the carbonylation of methyl acetate to acetic anhydride in the presence of cobalt iodide or bromide (*BASF*) or of rhodium and methyl iodide base complexes (*Eastman Kodak/Halcon, Showa Denko, etc.*).

8.3.5 Economic data

Table 8.7 lists economic data concerning the manufacture of acetic anhydride.

8.3.6 Uses and producers

Table 8.8 gives the average commercial specifications of acetic anhydride.

Table 8.9 lists the uses in per cent of acetic anhydride in Western Europe, the United States and Japan, as well as the production, capacities and consumption for these three geographic areas.

Chapter 9

ALCOHOLS

9.1 ETHANOL

Processes for the manufacture of ethanol ($d_4^{20} = 0.789^{(1)}$, bp_{1.013} = 78.32°C) are divided into two groups:

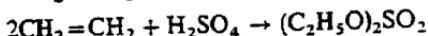
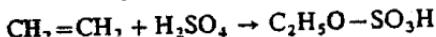
- (a) Techniques for the fermentation of carbohydrates using directly fermentable raw materials (cane sugar or molasses) or made fermentable by hydrolysis (starch, cellulosic materials). These processes will not be discussed here, although the oil crisis has made them serious competitors of petrochemical methods.
- (b) Synthesis from ethylene requiring:
 - . Indirect hydration by the addition of sulfuric acid, followed by hydrolysis of the esters formed.
 - . Direct catalytic hydration.

A new method, not yet industrialized, has been developed to manufacture ethanol from synthesis gas.

9.1.1 Ethanol synthesis by indirect hydration of ethylene (Fig. 9.1)

This technique, also called esterification/hydrolysis, comprises the following main steps:

- (a) Formation of ethyl acid sulfate and diethyl sulfate by the absorption of ethylene in concentrated sulfuric acid, by the following overall reaction mechanism:



(1) Specific gravity, 68.0 39.2

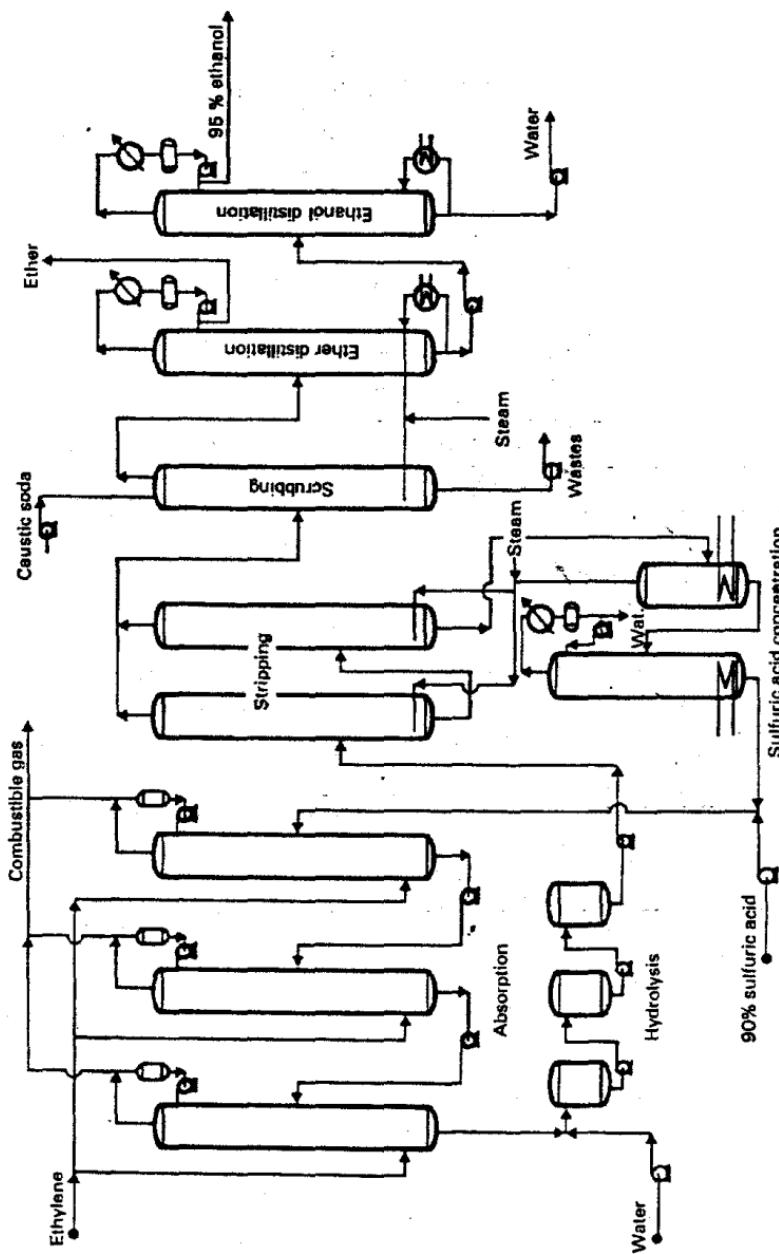
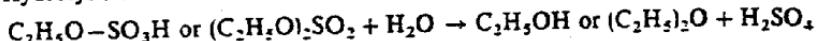


Fig. 9.1. Ethanol manufacture from ethylene by esterification and hydrolysis.

(b) Hydrolysis of sulfuric esters to ethanol:



The by-product formed is diethyl ether which results from the action of ethanol on diethyl sulfate.

(c) Reconcentration of the by-product sulfuric acid.

According to the operating principle of an industrial facility implementing these reactions, dilute ethylene is sent in countercurrent flow into an absorber containing 94 to 98 per cent weight sulfuric acid at 80°C and a pressure between 1.3 and $1.5 \cdot 10^6$ Pa absolute. The unabsorbed gases consist essentially of ethane, an impurity in the ethylene feed. The exothermicity of the reaction requires severe temperature control, which is achieved by external cooling and by an accurate determination of the volumes of reactants introduced. The absorbate, containing sulfuric esters and diethyl ether, is then hydrolysed by a quantity of water which lowers the acid concentration to about 50 per cent weight. The hydrolysis products are stripped into a column at the base of which the dilute sulfuric acid is recovered. The volatile effluents collected at the top are scrubbed with water or dilute caustic soda, and then fractionated to remove the diethyl ether formed. The dilute sulfuric acid is concentrated under vacuum in evaporators.

This process is much less widely used than direct catalytic hydration. Its main drawbacks are connected with corrosion problems created by the use of sulfuric acid, and the high cost of reconcentrating the acid, which accounts for most of the capital expenditure.

9.1.2 Ethanol synthesis by direct hydration of ethylene (Fig. 9.2)

This is the catalytic reaction of the addition of the elements of water to the ethylene double bond:



The most widely used catalyst is phosphoric acid deposited on a silica support. The high exothermicity of this reaction, which is accompanied by a decrease in the number of molecules, would justify operation at low temperature and under pressure. In practice, however, temperatures in the neighborhood of 300°C and pressures of about $7 \cdot 10^6$ Pa absolute are required to reach acceptable reaction rates. These elevated temperatures are unfavorable to the equilibrium of the reaction, so that the ethylene conversion rate is limited to 4 per cent. This raises the need to recycle very large amounts of ethylene, which must therefore be very pure to prevent the accumulation of inert gases. In particular, it must be free of acetylene, which could be hydrated to acetaldehyde. With respect to pressure, an excessively high pressure favors the formation of ethylene polymers. The partial pressure of steam must not be too high, at the risk of causing rapid deactivation of the catalyst by acid loss. The operation is conducted with an $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ molar ratio of 0.6/1 and very short residence times (Gas Hourly Space Velocity: GHSV about 50 h^{-1}).

The vapors leaving the reactor are partly condensed by heat exchange with the feed, and scrubbed by a dilute caustic solution to neutralize all traces of phosphoric acid. The gaseous effluent is again cooled in a second heat exchanger, and a water/alcohol fraction

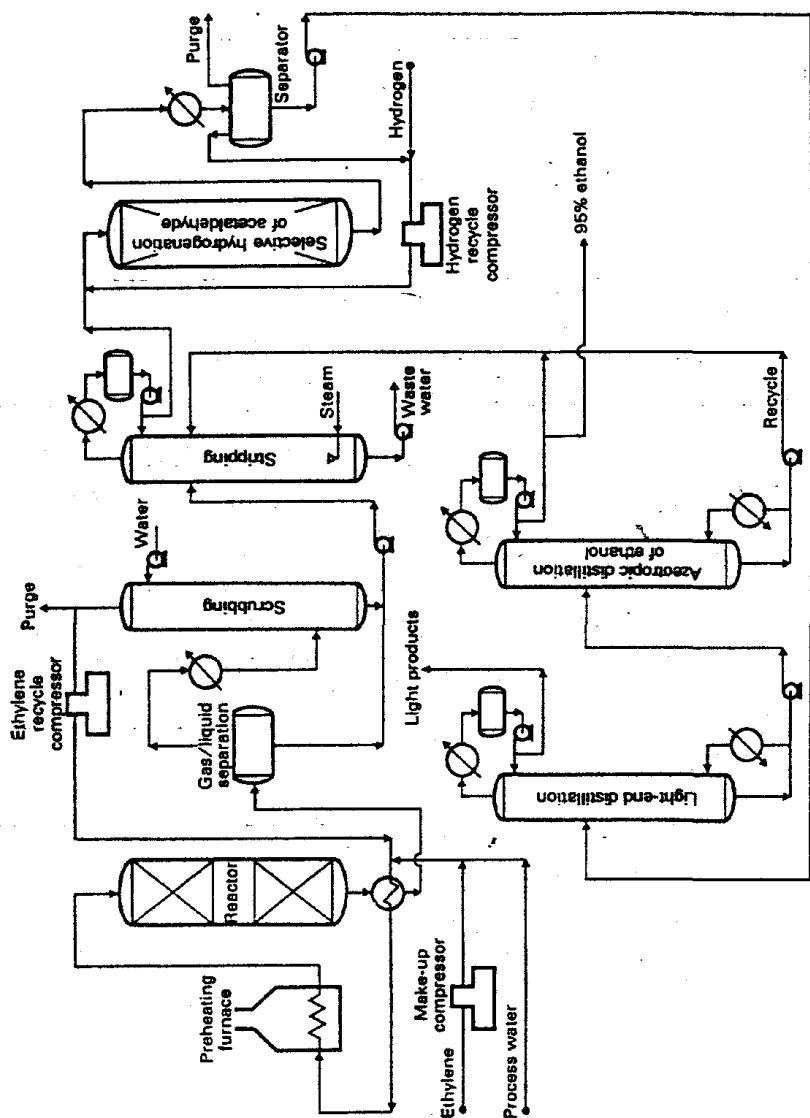


Fig. 9.2. Ethanol manufacture from ethylene by direct hydration. Shell process.

is thus condensed. After scrubbing with water and purge, the off-gases are compressed and recycled.

The water/ethanol mixture is sent to a first distillation column to remove light compounds (ethers), and then to a second where the water/95 per cent alcohol azeotrope is distilled. Catalytic hydrogenation on nickel converts any acetaldehyde formed to alcohol. Ethanol selectivity in relation to the ethylene used is 98.5 molar per cent.

9.1.3 Production of anhydrous ethanol

The older method to raise the azeotrope containing 95 per cent weight to 99.9 per cent ethanol consists in absorbing the water on lime (CaO). This costly process has been abandoned. Azeotropic distillation in the presence of benzene is employed today. In principle, simple low pressure distillation should allow the separation of alcohol and water, because the azeotrope disappears below 12 kPa. For ethanol concentrations between 95 and 100 per cent, however, the liquid and vapor phase compositions are substantially the same, implying extremely high reflux rates and a large number of trays.

As illustrated by Figure 9.3, the installation has two columns operating practically at atmospheric pressure:

- (a) The first (55 to 65 trays depending on the constructor) produces anhydrous alcohol at the bottom and the ternary azeotrope ($\text{bp}_{1.013} \cong 65^\circ\text{C}$) at the top, with the following per cent weight composition: water 7.4, ethanol 18.5, benzene 74.1.

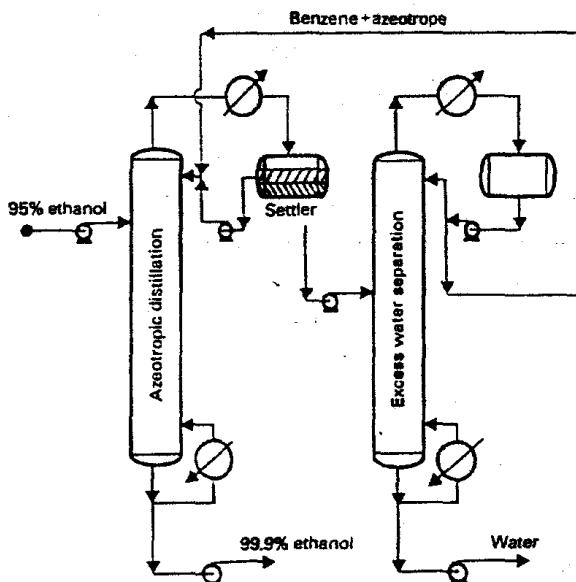


Fig. 9.3. Production of 99.9% ethanol by azeotropic distillation.

Two phases are formed by cooling and settling: a benzene-rich organic phase is used as reflux, and the second, aqueous phase, representing 15 per cent volume of the total, also consists of alcohol and benzene.

- (b) The second column operates on the aqueous phase, from which it separates the ternary azeotrope at the top by stripping, which is then condensed and recycled with the reflux from the first column, and excess water is produced at the bottom.

The considerable energy expenditure in the dehydration of ethanol, chiefly when it is produced by fermentation in concentrations often less than 10 per cent weight, encourages research into new processes for the separation of the water/alcohol mixture. Among those currently being investigated are the extraction of ethanol by CO₂ in the supercritical state, solvent extraction, vacuum distillation, distillation with vapor recompression, adsorption on molecular sieves, low-temperature phase separation of mixtures with hydrocarbons, and reverse osmosis.

9.1.4 Economic data

Since the indirect hydration process has gradually been superseded by direct hydration, the economic data listed in Table 9.1 concern only the latter process.

TABLE 9.1
ETHANOL PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Process	Ethylene hydration	Purification
Production capacity (t/year).....	200,000	40,000
Ethanol purity (% Wt)	96	99.9
Battery limits investments (10 ⁶ US\$)	55	1.5 ⁽¹⁾ -2.0 ⁽²⁾
Consumption per ton of product		
Raw materials		
Ethylene (t)	0.60	—
95% ethanol (t)	—	1.06
Utilities		
Steam (t)	5.4	1.3 ⁽¹⁾ -0.3 ⁽²⁾
Electricity (kWh)	100	15 ⁽¹⁾ -145 ⁽²⁾
Fuel (10 ⁶ kJ)	2.8	—
Cooling water (m ³)	140	40
Process water (m ³)	3	—
Chemicals and catalysts (US\$)	5	0.5
Labor (Operators per shift)	5	0.5

(1) With double-effect trays.

(2) With mechanical recompression of vapors from the first column.

TABLE 9.2
AVERAGE COMMERCIAL SPECIFICATIONS OF ETHANOL

Characteristics	Values	
Minimum purity (% vol.)	95	99.9
Acidity (as CH ₃ COOH) (ppm) max.	20	20
Non-volatile matter (g/100 ml)	0.001	0.001
Miscibility with water	Total	Total
KMnO ₄ test (min.) min.	50	30
Maximum water (ppm) max.	—	1.000

TABLE 9.3
ETHANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Chemicals	23.8	10.9	17.8
Acetaldehyde	5.1	—	—
Ethylic acetate	2.9	1.0	—
Ethyl acrylate	2.2	2.6	1.0
Ethylamines	1.8	2.0	—
Glycol ethers	4.5	1.8	—
Vinegar	2.2	2.3	9.2
Miscellaneous ⁽¹⁾	5.1	1.2	7.6
Fuel	8	74.0	8
Solvent	76.2	14.0	36.8
Miscellaneous ⁽²⁾		1.1	45.4
Total	100.0	100.0	100.0
Source (% product)			
Ethylene	31	22	45
Fermentation	65	77	55
Sulfite liquor	4	1	—
Total	100	100	100
Production (10 ³ t/year) ⁽³⁾	1,465	2,070	135
Capacity (10 ³ t/year) ⁽³⁾⁽⁴⁾	1,780	3,750	160
Consumption (10 ³ t/year)	1,405	2,470	145

(1) Chloral, dyes, organo-silicone products, pharmaceuticals, sodium ethylate, xanthates.

(2) Antifreeze, heating fuels, laboratory reagents, refrigerant.

(3) Of which synthetic ethanol:

	Western Europe	United States	Japan
Production (10 ³ t/year)	450	455	60
Capacity (10 ³ t/year)	600	630	80

(4) In 1984 and 1986 the worldwide production capacity of synthetic ethanol was about $2.2 \cdot 10^6$ t/year. In 1986 the distribution was the following:

United States	0.37	Western Europe	0.60	Middle East	0.22
Canada	0.06	Eastern Europe	0.73	Japan	0.08
Latin America ⁽⁵⁾	—	Africa	—	Asia and Far East	0.18

(a) Brazil is the major producer of ethanol in the world with a fermentation capacity higher than $9.0 \cdot 10^6$ t/year.

9.1.5 Uses and producers

Table 9.2 gives the average commercial specifications of ethanol at a 95 and 99 per cent weight level.

The synthesis of acetaldehyde, essentially intended for conversion to acetic acid, was the main outlet for ethanol until a few years ago. The industrial development of methanol carbonylation to acetic acid has relegated this application to the background. Ethanol is chiefly used today as a solvent and for the preparation of esters (ethyl acetate, ethyl chloride). It is also employed in cosmetics and pharmaceuticals.

A significant increase in its consumption is connected with its use as a fuel and, in certain developing countries, for the production of ethylene, but these uses concern fermentation ethanol. Table 9.3 gives the percentage breakdown of ethanol markets and the production and consumption in Western Europe, the United States and Japan in 1984.

9.2 ISOPROPANOL

Isopropanol or 2-propanol ($d_4^{20} = 0.785^{(2)}$, $bp_{1.013} = 82.3^\circ\text{C}$) is manufactured industrially by techniques similar to those used to produce ethanol:

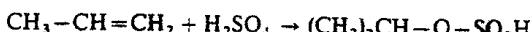
- (a) Esterification by sulfuric acid and hydrolysis.
- (b) Direct catalytic hydration.

Isopropanol is not produced by fermentation.

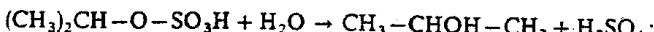
9.2.1 Isopropanol synthesis by esterification of propylene and hydrolysis

The operation takes place in two steps:

- (a) In the first, isopropyl acid sulfate is produced by the addition of sulfuric acid to propylene, according to the following reaction:



- (b) In the second step, this ester is hydrolysed by reducing the acid concentration by the addition of water or steam:



The dilute acid is then reconcentrated by one of the three following methods: passage through multistage evaporators operating under vacuum, entrainment of the water in the form of steam by hot gases issuing from a furnace, or by gases produced by submerged combustion. In this operation, the heavy organics are burnt.

(2) Specific gravity, 68.0/39.2

The conversion can be carried out in two separate reactors or in a single one in the gas phase. In the most widely used processes, a liquid C₃ cut (propylene content above 65 per cent weight) is treated with 70 to 75 per cent weight sulfuric acid between 2 and 3 . 10⁶ Pa absolute at ambient temperature. Isopropanol selectivity ranges from 90 to 95 molar per cent, depending on the propylene concentration in the feed.

The advantage of this process, which is still exploited by *BP (British Petroleum), Shell and Texaco*, is to enable the use of a feed with a low propylene content (up to 50 per cent weight). However, it incurs corrosion processes associated with the presence of the acid, whose wastes raise environmental problems. These drawbacks have favored the development of catalytic hydration processes.

9.2.2 Isopropanol synthesis by catalytic hydration of propylene

The overall reaction involved is the following:



Since it is exothermic and occurs with a reduction in the number of molecules, it is favored by low temperature and high pressure. However, for reasons associated with the kinetics, it is necessary to operate at relatively elevated temperatures, depending on the catalyst employed.

Several processes exist operating in the vapor or liquid phase, or in a mixed phase by trickling. In the vapor phase, the ICI (*Imperial Chemical Industries*) process uses a tungsten base catalyst on silica (WO₃/SiO₂) and operates at 250°C and 25 . 10⁶ Pa absolute. The Veba process employs phosphoric acid on silica and operates at 180°C and 4 . 10⁶ Pa absolute. In these technologies, the propylene conversion rate is very low (5 per cent), requiring considerable recycling and the use of pure propylene (99 per cent). Isopropanol selectivity is 97 molar per cent. In the liquid phase, the Tokuyama process uses a silico-tungstate as catalyst and operates between 270 and 280°C and at 20 . 10⁶ Pa absolute. Selectivity is better (about 99 molar per cent) and the propylene conversion rate is much higher (60 to 70 per cent).

In the mixed phase, the Deutsche Texaco process uses an acidic ion exchange resin and operates between 130 and 150°C and 6 and 10 . 10⁶ Pa absolute (Fig. 9.4). The liquid feed and recovery propylene is added to a first preheated fraction of recycled deionized water, of which the proportion must be very high (water/propane molar ratio 12.5 to 15), to prevent the development of polymerization side reactions. The mixture thus obtained is introduced in the supercritical state at the top of a reactor with fixed catalyst beds, between which the remaining deionized water is injected at a lower temperature, in order to absorb the heat liberated by the conversion and to control the temperature.

The reaction effluent is flashed in two stages, with intermediate cooling, to recover unconverted propylene in the gaseous state, which is recycled after compression and rid eventually of any propane that it contains. The liquid phase is neutralized and then fractionated in a series of four distillation columns. The first separates the light components at the top, from which diisopropyl ether can be extracted if necessary. The second produces a sidestream containing most of the water, which is recycled after having been deionized on ion exchange resins. The water/propanol azeotrope (bp_{1.013} = 80.3°C, water

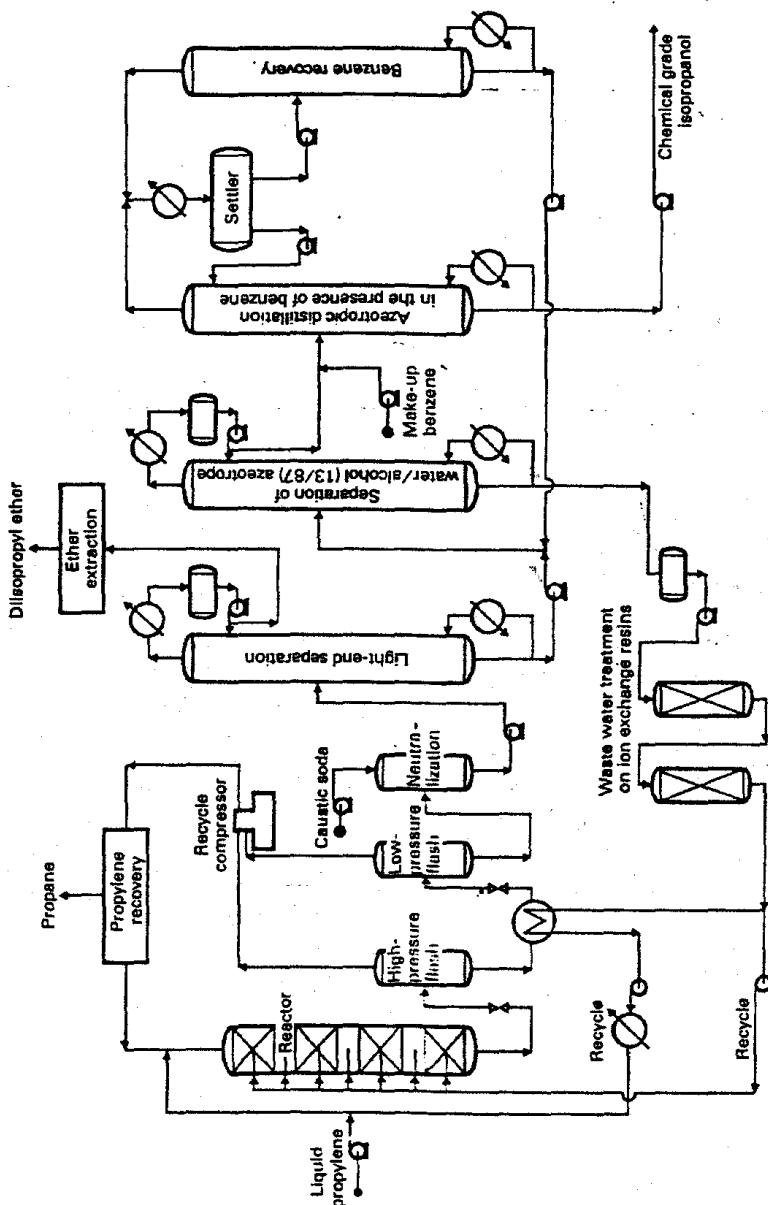


Fig. 9.4. Isopropanol manufacture by direct hydration of propylene, Deutsche Texaco process.

content, per cent weight, 12.6) is isolated in the distillate, and dehydrated in the presence of benzene in the third column. In this column, isopropanol (chemical grade) is separated at the bottom, with the water benzene heteroazeotrope at the top. The latter is cooled and condensed to form two phases: the upper organic layer is used as reflux, and the lower aqueous fraction is sent to the final distillation stage to recover entrained benzene.

Once-through conversion is 75 per cent. Since the recycle rate is low, propylene in a purity of 95 per cent weight can be used. Very few by-products are formed (diisopropyl ether, acetone and oligomers of propylene).

9.2.3 Economic data

Table 9.4 gives economic data concerning the production of isopropanol by the indirect and direct hydration processes.

TABLE 9.4
ISOPROPANOL PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 150,000 t/year

Process	Indirect hydration	Direct hydration ⁽¹⁾	
Raw material grade	Refining	Chemical	Refining
Typical technology		Deutsche Texaco	Tokuyama Soda
Battery limits investments (10 ⁶ US\$)	26	28	35
Consumption per ton of isopropanol			
Raw material: propylene (100%) (t)	0.78	0.74	0.80
Utilities			
Steam (t)	2.1	4.6	6.6
Electricity (kWh)	25	90	95
Fuel (10 ⁶ kJ)	5.2	—	(—)20
Cooling water (m ³)	130	190	280
Process water (m ³)	3	1	1
Nitrogen (Nm ³)	—	25	25
Chemicals and catalysts (USS)	—	1.8	2.1
Sulfuric acid (98%) (t)	0.1	—	—
Caustic soda (100%) (kg)	6	—	—
Labor (Operators per shift)	5	3	3

(1) 50% anhydrous and 50% to 91% vol.

9.2.4 Uses and producers

Nearly half of all the isopropanol produced worldwide is used to synthesize acetone. The remainder is put to various uses (chemicals, solvents, cosmetics, pharmaceuticals, etc.).

Table 9.5 summarizes the average commercial specifications of isopropyl alcohols of different grades. Table 9.6 lists the uses and production of isopropanol in Western Europe, the United States and Japan.

TABLE 9.5
AVERAGE COMMERCIAL SPECIFICATIONS OF ISOPROPANOL

Characteristics	Values		
Minimum purity (% vol.)	91	95	99.85 (anhydrous)
$d_{20}^{20(1)}$ min.	0.8169	0.8035	0.7861
$d_{20}^{20(1)}$ max.	0.8193	0.8055	0.7866
Acidity (as CH_3COOH) (ppm) max.	24	2	2
Acidity (mg KOH/g)	0.023		0.019
Distillation range ($^{\circ}\text{C}$)			
Initial temperature	79.9	80.0	82.05
Final temperature	80.9	83.0	82.55
Water (ppm) max.	—	—	1.000
Non-volatile matter (g/100 ml) max.	0.002	—	0.001
Solubility in water	Total	Total	Total

(1) Specific gravity, 68.0/68.0.

TABLE 9.6
ISOPROPANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acetone	38	10	0
Cosmetics, pharmaceuticals		20	
Solvents	62	55	
Other chemicals ⁽¹⁾		15	100
Total	100	100	100
Production (10^3 t/year)	540	520	90
Capacity (10^3 t/year)	860	1.110	130
Consumption (10^3 t/year)	485	500	80

(1) Aluminum isopropoxide, isopropyl acetate, isopropylamines, isopropyl myristate, isopropyl xanthates, ...
(2) In 1984 and 1986 the worldwide production capacity of isopropanol was about $2.45 \cdot 10^6$ t/year. In 1986 the distribution was the following:

United States	1.11	Western Europe	0.83	Middle East	—
Canada	0.09	Eastern Europe	0.20	Japan	0.13
Latin America	0.05	Africa	—	Asia and Far East	0.04

9.3 BUTANOLS

9.3.1 1-Butanol (normal butanol)

1-butanol ($d_4^{20} = 0.8098^{(3)}$, bp_{1.013} = 117.7°C) can be produced industrially by the following techniques:

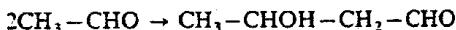
- (a) Condensation of acetaldehyde.
- (b) Hydroformylation of propylene.
- (c) Oxidation of butane (see Section 8.2.2.1).

Another industrial source of 1-butanol is the acetone-butanol fermentation of sugars or polysaccharides.

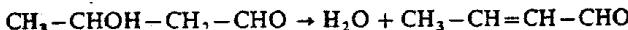
9.3.1.1 1-butanol synthesis by the condensation of acetaldehyde

The following reactions are involved:

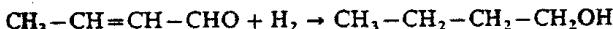
(a) Aldolization:



(b) Dehydration:



(c) Hydrogenation:



Aldolization takes place between 5 and 25°C in a 1.25 per cent weight caustic solution used in the weight ratio of 2/1 in relation to acetaldehyde. Residence time is such as to achieve 50 per cent conversion to aldol. The heat liberated by the reaction is removed by the vaporization of part of the acetaldehyde. The product is distilled after acidification by phosphoric or acetic acid. Unconverted acetaldehyde is recycled, and the crotonaldehyde resulting from the dehydration is recovered. Hydrogenation then takes place on a nickel/chromium catalyst around 180°C at $0.2 \cdot 10^6$ Pa absolute. The 1-butanol yield in relation to acetaldehyde is 85 molar per cent.

9.3.1.2 1-butanol synthesis by hydroformylation applied to propylene (Table 9.7)

A. General characteristics of the reaction

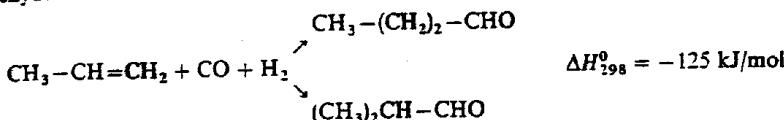
The hydroformylation reaction, still called the Oxo synthesis, was discovered in 1938 by Rohlen (*Ruhrchemie*). It consists in adding hydrogen and the formyl (—CHO) group to the double bond of an olefin, by treating the olefin with a mixture of CO and H₂ in the presence of a cobalt catalyst. For non-symmetrical olefins, this reaction leads to the

(3) Specific gravity, 68.0/39.2.

TABLE 9.7
MAIN PROCESSES FOR OXO SYNTHESIS ON PROPYLENE

Catalyst	Cobalt	Modified cobalt		Rhodium	Modified rhodium	
Catalyst system	HCo(CO) ₄ or HCo(CO) ₃	HCo(CO) ₃ Tributyl-phosphine	HCo(CO) ₃ Zinc acetonylacetate	Rh carbonyls formed in situ Polar solvent	II Rh(CO) ₂ Triphenylphosphine Aldehydes	II Rh(CO) Triphenylphosphine Toluene or dibutylphthalate
Company	Ruhrchemie BASF, Kuhlmann, ICI	Shell	Exxon	Mitsubishi	Union Carbide, Davey Power Gas, Johnson Matthey	Mitsubishi, BASF
Temperature (°C)	110-180	180-200	180	70-120	80-120	100
Pressure (10 ⁶ Pa absolute)	20-35	5	20	20-30	1.5-2	2-3
n/iso ratio	3 to 5	7 to 8	9	≈ 1	> 10	≈ 4
Remarks		Simultaneous hydrogenation of aldehydes	Simultaneous oxo synthesis and aldolization	—	—	BASF uses dibutylphthalate

production of two aldehydes. In the case of propylene, butyraldehyde and isobutyraldehyde are obtained, which can then be hydrogenated to the corresponding alcohols:



Hydroformylation is a homogeneous catalysis reaction which employs a coordination complex of cobalt with the olefin. The catalyst precursor is a cobalt salt which is converted *in situ*, in the presence of CO and H₂, to cobalt tetracarbonyl hydride in equilibrium with cobalt tricarbonyl hydride. The latter, which displays a vacant coordination position, forms a complex with the olefin. The olefin undergoes chemical conversions leading to the production of two isomeric aldehydes, and the normal aldehyde is favored in relation to the iso-compound in the ratio of 4/1.

B. Industrial manufacture

Oxo synthesis takes place in the following conditions: temperature between 110 and 180°C, pressure between 20 and 35 . 10⁶ Pa absolute, CO/H₂ molar ratio between 1/1 and 1/1.2, residence time 1 to 5 min, catalyst 0.2 to 1 per cent weight in relation to propylene. The cobalt catalyst is still the most widely used for Oxo synthesis of propylene (BASF, ICI, PCUK and Ruhrchemie). Since the normal aldehyde enjoys a much larger market than the iso-isomer, it is preferable to increase the *n*/iso ratio. This can be achieved partly by lowering the temperature and increasing the CO pressure. However, the catalyst can be modified for the same purpose.

Shell employs a cobalt hydrocarbonyl substituted by a phosphine (HCo(CO)₃P(*n*C₄H₉)₃), which yields an *n*/iso ratio of up to 9/1. It operates between 180 and 200°C and at pressures between 5 and 10 . 10⁶ Pa absolute. However, the activity of such a system is lower and it tends to favor hydrogenation side reactions of the olefin and the aldehyde more than the conventional catalyst. It also helps to synthesize butanol in a single step.

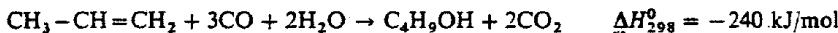
Cobalt can also be replaced by rhodium, whose catalytic activity is 100 to 10,000 times greater, but whose total recycle, which is necessitated by its high price, raises problems that are difficult to solve. Moreover, the *n*/iso ratio is less favorable, and decreases from 4/1 for unmodified cobalt to 1/1. However, by modifying carbonyl rhodium by triphenylphosphine, Union Carbide succeeded in developing a catalyst system yielding a highly favorable *n*/iso ratio of 10/1 in very moderate conditions (temperature between 60 and 120°C, pressure between 0.1 and 5 . 10⁶ Pa absolute). Table 9.7 enables a comparison of the main industrial processes employed today.

In the Ruhrchemie process, the propylene, recycled catalyst and make-up catalyst are introduced at the same time as the synthesis gas (H₂ + CO) into the reactor. This unit, of the multilayer type with an internal lining of high-alloy steel for the shell, provides effective agitation and serves to remove the heat liberated by the reaction ($\Delta H_{298}^0 = -125 \text{ kJ/mol}$) with the production of low-pressure steam. The effluent is then sent to the decobalting unit, where the cobalt precipitates by flashing and stripping. The metal is separated by centrifuging and the catalyst system regenerated and then recycled. The catalyst-free effluent contains 80 to 85 per cent weight of the *n* and iso aldehydes in the ratio 4/1, the corresponding alcohols, butyl formate and various com-

pounds resulting from aldolization, acetalization, hydrogenation side reactions etc. It is subjected to a first series of distillations to separate the heavier components. The mixture of *n* and iso aldehydes is then hydrogenated to the corresponding alcohols. Operations are conducted between 5 and $10 \cdot 10^6$ Pa absolute and between 150 and 200°C in the presence of a copper or nickel base catalyst. The hydrogenated product then goes to a second series of distillations to separate the light effluents and the two butanols. Special hydrogenating cracking treatment of the heavy products may be used to enhance the alcohol yields (Fig. 9.5).

Despite the improvement in the *n*/iso ratio, the co-production of isobutyraldehyde, which has few applications, raises economic problems. Accordingly, *Ruhrchemie* has proposed a process which consists in catalytically cracking the isobutyraldehyde and recycling the cracked products (propylene, CO and H₂).

If hydrogen is replaced by steam, a mixture of primary butanols can be obtained directly. This is the BASF process (Reppé synthesis) with one unit operating in Japan. It produces an effluent containing 88 per cent *n*-butanol and 12 per cent isobutanol. The main reaction involved is the following:



The system operates at 100°C and $1.5 \cdot 10^6$ Pa absolute, in the presence of pentacarbonyl iron, butylpyrrolidone and water.

9.3.1.3 Production of 1-butanol by acetone-butanol fermentation

This process, which was developed in the United Kingdom by Chaim Weizmann between 1911 and 1913 to manufacture butadiene from butanol, was continued during the First World War to manufacture the acetone required to produce gun cotton. Plants were subsequently built in the United States and Western Europe, but were forced to shut down due to competition from petrochemicals. Interest in this process has been revived since the increase in the price of crude oil. It operates in anaerobiosis in the presence of a bacteria, *Clostridium acetobutylicum*, at a temperature of about 34°C and a pH ranging between 6.5 and 5. The substrate may consist of C₆ sugars (glucose, fructose), C₅ sugars (xylose), disaccharides (sucrose, lactose) or polysaccharides (starch). Use can also be made of all the sugars resulting from the enzymatic hydrolysis of certain lignocellulosic substrates. Ethanol and isopropanol are also produced in addition to acetone and *n*-butanol (per cent weight):

	(%) Wt)
<i>n</i> -butanol	57 to 75
Acetone	20 to 35
Ethanol	1 to 10
Isopropanol	0 to 2

9.3.1.4 Economic data

Table 9.8 gives economic data about Oxo synthesis on propylene for processes using cobalt tetracarbonyl hydride phosphine-modified cobalt and phosphine-modified rhodium catalysts.

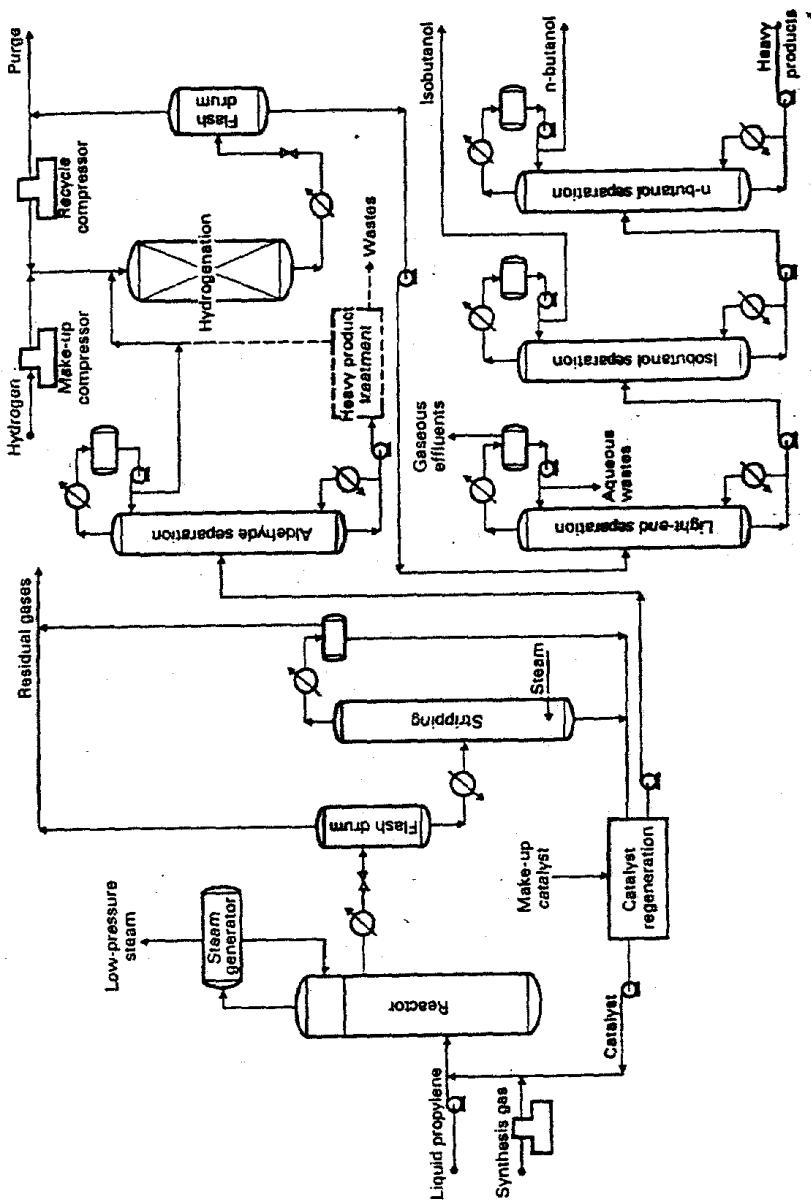


Fig. 9.5. Manufacture of butanols by Oxo synthesis. Rhône-Poulenc process.

TABLE 9.8
n-BUTANOL PRODUCTION. ECONOMIC DATA
 (France conditions, mid-1986)

Process	Oxo synthesis		
Catalyst	HCo(CO) ₄	HCo(CO) ₃ PR ₃	Rh
Typical technology	Ruhrchemie	Shell	Celanese
Production capacity (t/year)	70,000	70,000	70,000
Battery limits investments (10 ⁶ US\$)	46	24	30
Consumption per ton of alcohol			
Raw materials			
Propylene (t)	0.85	0.78	0.72
Synthesis gas (1/l) (Nm ³)	1,100	1,350	780
Hydrogen (100%) (kg)	35	—	30
By-products: isobutanol (t)	0.30	0.11	0.08
Utilities			
Steam (t)	5.0	2.2	2.5
Electricity (kWh)	350	200	150
Fuel (10 ⁶ kJ)	(-)9.5	(-)12	(-)9
Cooling water (m ³)	120	150	110
Process water (m ³)	1	—	1
Nitrogen (Nm ³)	4	—	9
Chemicals and catalysts (US\$)	12	55 ⁽¹⁾	15
Labor (Operators per shift)	5	5	5

(1) Including 30 US\$ for catalyst.

TABLE 9.9
 AVERAGE COMMERCIAL SPECIFICATIONS OF *n*-BUTANOL AND ISOBUTANOL

Characteristics	<i>n</i> -butanol	Isobutanol
Minimum purity (% Wt)	99.0	99.3
<i>d</i> ₂₀ ²⁰⁽¹⁾	0.810-0.812	0.800-0.805
Distillation (°C)	117.3-118	107.3-108.2
Acidity (as CH ₃ COOH) (ppm) max.	50	100
Water (ppm) max.	500-1,000	700
Non-volatile matter (g/100 ml)	0.005	—
Matter in suspension	Nil	Nil

(1) Specific gravity, 68.0/68.0.

TABLE 9.10
n-BUTANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Butyl acetate	17	11	19
Butyl acrylate and methacrylate	18	34	28
Glycol ethers ⁽¹⁾	7	27	17
Plasticizers ⁽²⁾	12	5	12
Solvents	39	17	16
Amino resins	4	2	
Butylamines		2	
Miscellaneous ⁽³⁾	3	2	8
Total	100	100	100
Production (10^3 t/year)	360	415	95
Capacity (10^3 t/year)	395	705	120
Consumption (10^3 t/year)	340	400	100

(1) 2-butoxyethanol, diethyleneglycol monobutyl ether, triethyleneglycol monobutyl ether, -

(2) Butylbenzyl phthalate, butyl octyl phthalate, butyl stearate, dibutyl phthalate, -

(3) Butyl benzoate, n-butyl bromide, butyl ester of the herbicide 2,4-D, dibutyl maleate, tributyl phosphate, tertiary oil recovery, -

(4) The worldwide production capacity of n-butanol in 1985 was nearly $1.5 \cdot 10^6$ t/year.

TABLE 9.11
ISOBUTANOL PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Isobutyl acetate	18	19	23
Isobutyl acrylate and methacrylate	12	5	12
Lube oil additives	-	21	-
Octane booster	25	2	-
Solvent	32	28	53
Amino resins	3	8	-
Isobutylamines	10	11	
Miscellaneous ⁽²⁾		6	12
Total	100	100	100
Production (10^3 t/year)	185	70	35
Capacity (10^3 t/year) ⁽³⁾	200	125	55
Consumption (10^3 t/year)	205	65	35

(1) Estimated values.

(2) Agricultural grease additive, diisobutyl sodium sulfosuccinate, foundry resin binders, plasticizers (adipate, phthalate, sebacate, ...), tertiary oil recovery, textile chemicals, ...

(3) The worldwide production capacity of isobutanol in 1984 was about $0.8 \cdot 10^6$ t/year.

TABLE 9.12

PRODUCTION OF SECONDARY AND TERTIARY BUTANOLS BY HYDRATION OF *n*-BUTENES AND ISOBUTENE
 ECONOMIC DATA
 (France conditions, mid-1986)

Alcohol	Secondary butanol	Tertiary butanol
Catalyst	Sulfuric acid	Resins
Typical technology	Maruzen	BASF
Capacity (t/year)	40,000	50,000
Battery limits investments (10^6 US\$)	11	7
Consumption per ton of alcohol		
Raw material: C ₄ cut (t)	1.15 ⁽¹⁾	1.90 ⁽²⁾
By-products: C ₄ cut (t)	0.30	1.15
Utilities		
Steam (t)	11.0	1.9
Electricity (kWh)	140	35
Cooling water (m ³)	580	60
Process water (m ³)	15	1
Chemicals and catalysts (US\$)	—	9
Sulfuric acid (kg)	9	—
Caustic soda (kg)	22	—
Labor (Operators per shift)	3	3

(1) Composition (% Wt); *n*-butenes = 73.5; isobutene = 2; C₅+ = 2; butanes = 22.5.

(2) Isobutene content (% Wt) = 45.0.

TABLE 9.13

SEC-BUTANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Methylethylketone	96	95	90
Miscellaneous ⁽¹⁾	4	5	10
Total	100	100	100
Production (10^3 t/year)	275	275	120
Capacity (10^3 t/year) ⁽²⁾	365	370	135
Consumption (10^3 t/year)	290	260	120

(1) Chemical intermediates, coatings, lubricants, xanthates, ...

(2) The worldwide production capacity of sec-butanol was about $0.9 \cdot 10^6$ t/year in 1984 and more than $1.1 \cdot 10^6$ t/year in 1986.

9.3.1.5 Uses and producers

Table 9.9 lists the commercial specifications of butanols. Tables 9.10 and 9.11 give the uses and production of *n*-butanol and isobutanol for Western Europe, the United States and Japan in 1984.

9.3.2 Secondary butanol or 2-butanol

The value of 2-butanol ($d_4^{20} = 0.808^{(4)}$, $bp_{1.013} = 99.5^\circ\text{C}$) resides in the fact that 90 per cent of its total production is used for the synthesis of MEK (methyleneethylketone) by dehydrogenation. It is manufactured by the indirect hydration of *n*-butenes, of which the 1- and 2-isomers yield the same 2-butanol. They are absorbed in 80 per cent weight sulfuric acid, between 15 and 20°C, and $0.7 \cdot 10^6 \text{ Pa absolute}$. The sulfuric esters obtained are then hydrolysed between 25 and 35°C at $0.1 \cdot 10^6 \text{ Pa absolute}$, with 65 to 75 per cent weight sulfuric acid (Exxon, Maruzen and Shell processes). Despite considerable research work (*Deutsche Texaco, Mitsubishi, Mitsui, Petrotex and Shell*), the direct catalytic hydration of *n*-butenes has not yet reached the industrial stage.

Economic data concerning the manufacture of 2-butanol by the Maruzen technology are given in Table 9.12. Table 9.13 lists the uses and production of 2-butanol in Western Europe, the United States and Japan in 1984.

9.3.3 Tertiary butanol or tertiary butyl alcohol (TBA)

Tertiary butyl alcohol ($d_4^{20} = 0.7856^{(5)}$, $bp_{1.013} = 82.5^\circ\text{C}$) can be produced by the hydration of isobutene either by dilute sulfuric acid (50 to 65 per cent weight) or in the presence of acidic ion exchange resins. Apart from the Shell facility in the United States, which employs sulfuric hydration, no industrial plant of a significant size using this technique exists today.

The only industrial method for producing tertiary butyl alcohol is based on a variant of the Oxirane (*ARCO Chemical*) process for manufacturing propylene oxide, in which isobutane is used as a co-reactant and the alcohol is a co-product. The technological analysis of this scheme and the related economic data are given in Section 7.2.4, which discusses the manufacture of propylene oxide.

Economic information available on the direct hydration of isobutene on ion exchange resins are given in Table 9.12. The leading producer of tertiary butyl alcohol in Western Europe is *ARCO Chemical* at Rozenburg in the Netherlands, with a 1986 capacity of about 550,000 t/year and the construction of a 380,000 t/year unit at Fos-sur-Mer in France, expected to go on stream around 1988. In the United States, apart from the small Shell plant (5000 t/year), *ARCO Chemical* is also the largest manufacturer of terbutyl alcohol with a capacity of about $1.1 \cdot 10^6 \text{ t/year}$, installed at Bayport, Texas, most of which is presently converted into MTBE due to the decrease in gasoline prices. In both cases, the target market is essentially that of replacement fuels or preferably

(4) (5) Specific gravity, 68.0:39.2

octane promoters, with the marketing of GTBA (Gasoline Tertiary Butyl Alcohol) whose specifications are given in Table 9.14, and Oxinol, a mixture with the following per cent weight composition: tertiary butyl alcohol = 45 to 55; methanol = 45 to 55; butanes = 1.5 to 2; water = 0.5 to 0.8; other oxygenated compounds = 0.2 to 0.5. Some isobutene is also produced by dehydration.

TABLE 9.14
AVERAGE COMMERCIAL SPECIFICATIONS OF TERTIARY BUTYL ALCOHOL
(FUEL USE)

Characteristics	Values
Composition (% Wt)	
Tertiary butyl alcohol min.....	95
Butanes max.....	2.5
Acetone max.....	1.0
Water max.....	1.0
Other oxygenated components max.....	0.5
$d_{20}^{20(1)}$	0.785
Reid vapor pressure (psia).....	7
Distillation curve (°C)	
10%	80
90%	83
Final point	86
Crystallization temperature (°C)	13

(1) Specific gravity, 68.0/68.0.

In Japan, *Mitsui Petrochemical* and *Kuraray Isoprene Chemical* manufacture 52,000 and 13,000 t/year of tertiary butyl alcohol respectively, used for the manufacture of methyl methacrylate, employing the reverse operation to the above, namely the hydration of isobutene.

Remark. Pentanols or amyl alcohols, and more specifically 1-pentanol, 2-methyl 1-butanol, and 3-methyl 1-butanol, do not enjoy the industrial importance of the above alcohols. They are prepared by Oxo synthesis and hydrogenation from *n*-butenes and isobutene. They are used as solvents and their esters as perfumes.

9.4 HIGHER ALCOHOLS

This category includes the primary and secondary alcohols, linear and branched, with an even or odd number of carbon atoms between 6 and 18. Their two main markets are plasticizers for C_6 to C_{11} , and detergents for C_{12} to C_{18} . They can be produced by the following methods:

- (a) Oxidation of *n*-paraffins.
- (b) Oxo synthesis on olefins, followed by hydrogenation of the aldehydes formed or of their aldolization product.
- (c) Oligomerization of ethylene followed by oxidation (Alfol process).
- (d) Hydrogenolysis of methyl esters of fatty acids, resulting from the transesterification of animal fats and vegetable oils by methanol; this process, which lies beyond the framework of this book, will not be discussed here, although the increase in the price of crude oil has given it a certain importance.

9.4.1 Synthesis of higher alcohols by oxidation of paraffins

The direct oxidation of paraffins by atmospheric oxygen is a non-selective reaction which yields a complex mixture of alcohols, ketones, acids and esters. It was used in Germany during the Second World War to manufacture fatty acids. The orientation of this reaction towards the production of alcohols results from research by the Japanese Nobori and Kawai (1943) and the Russian Bashkirov (1956). Alcohol selectivity in relation to the other oxidation products derives from the use of boric acid which withdraws the secondary alkyl hydroperoxides from any subsequent oxidation by converting them to stable boric esters.

The paraffin is oxidized by air between 150 and 200°C in the presence of 0.1 per cent weight potassium permanganate and 5 per cent weight boric acid, limiting the conversion to 15 to 20 per cent. Unconverted paraffins are recovered by distillation and recycled, and the borates are hydrolysed. They are then neutralized with caustic soda to remove acidic compounds and the alcohols are separated by distillation. Boric acid in aqueous solution is recovered and recycled in turn.

The selectivities are 70 molar per cent for secondary alcohols, 20 per cent for ketones and 10 per cent for organic acids.

9.4.2 Synthesis of higher alcohols by hydroformylation of olefins

Hydroformylation or Oxo synthesis applied to propylene and butenes for the manufacture of light alcohols (see Section 9.3.1.2) also serves to produce the higher alcohols from heavier olefins. With longchain olefins, the isomerization of a double bond may lead to a larger number of isomeric aldehydes. Moreover, the presence of branches, chiefly groups fixed to the double bond, considerably decreases the hydroformylation rate. The aldehydes formed are hydrogenated to alcohols.

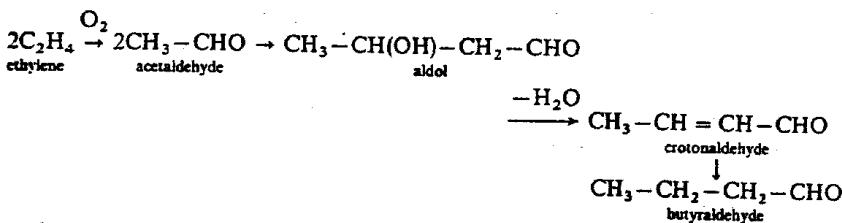
Apart from propylene, which can be used as a raw material for the production of 2-ethyl hexanol, the main olefins employed in the Oxo synthesis of higher alcohols result from:

- (a) Cracking of paraffin waxes (see Section 2.3.2).
- (b) Oligomerization of ethylene (see Section 2.3.3.1).
- (c) Dimerization of light olefins (IFP Dimersol process) (see Section 2.3.3.2).
- (d) Oligomerization of propylene and butenes in the presence of phosphoric acid (see Section 2.3.3.2).
- (e) Dehydrogenation of *n*-paraffins (see Section 2.3.4).

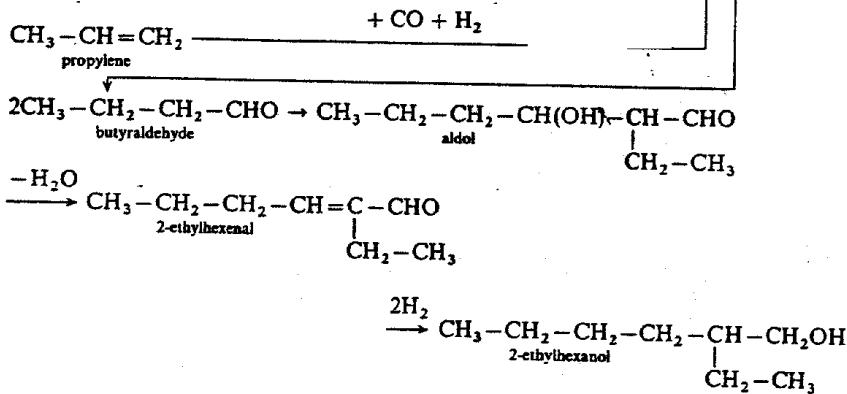
9.4.2.1 Synthesis of 2-ethyl hexanol

This consists in the aldolization of butyraldehyde, followed by the dehydration and hydrogenation of the aldon. The butyraldehyde can be obtained either by the aldolization of acetaldehyde, or by Oxo synthesis of propylene, which is the more widely used method. These different possibilities can be summarized as follows:

(a) Raw material: ethylene



(b) Raw material: propylene



The aldolic condensation of butyraldehyde occurs in the presence of caustic soda, which acts as a catalyst (Ruhrcemie process). The system operates in this case between 80 and 130°C and between 0.3 and $1 \cdot 10^6$ Pa absolute. The continuous removal of one molecule of water yields 2-ethylhexenal, which is hydrogenated in the presence of a nickel catalyst between 100 and 150°C and between 5 and $10 \cdot 10^6$ Pa absolute.

The Oxo synthesis on propylene was described in Section 9.3.1.2.

9.4.2.2 The Aldox process (Fig. 9.6)

One variant of the synthesis of 2-ethylhexanol consists in combining the hydroformylation of the olefin and the aldolization of the resulting aldehyde in a single step. This is the Aldox process used by Exxon in the United States and Japan, and by Shell in the United Kingdom and the United States. This process is theoretically applicable to the production of other high molecular weight and non-linear alcohols. For olefins higher

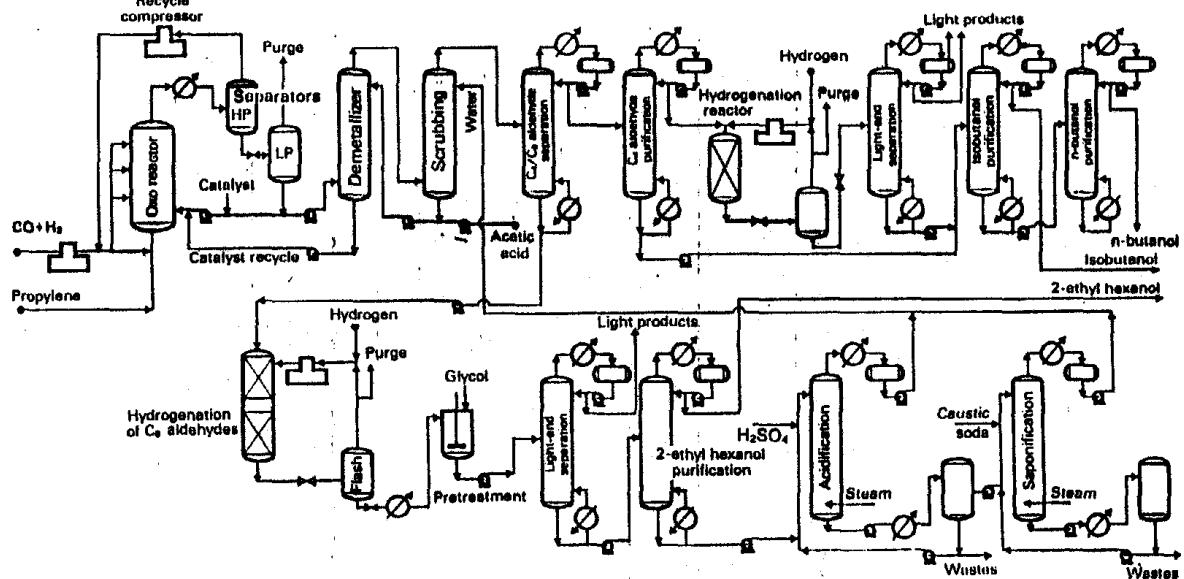
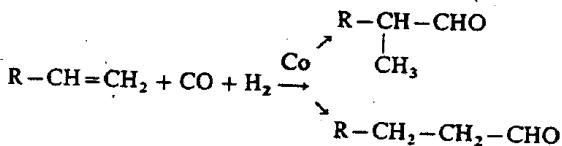


Fig. 9.6. 2-ethyl hexanol manufacture. Aldox process.

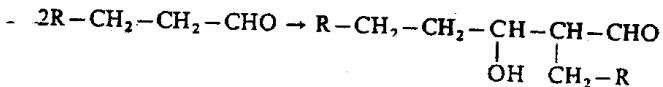
than propylene, however, the alcohol selectivity decreases owing to the large number of cross-aldozilations liable to occur between the different isomeric aldehydes.

The conversion obeys the following general mechanism:

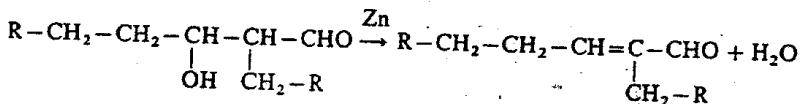
(a) Hydroformylation:



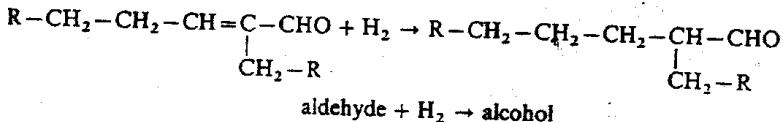
(b) Aldolization:



(c) Dehydration:



(d) Hydrogenation:



A co-catalyst is added to the hydroformylation catalyst to favor the aldolization reaction. This co-catalyst may be zinc acetylacetone or magnesium ethylate, for unmodified cobalt base systems. Shell employs potassium for cobalt/phosphine catalysts.

9.4.2.3 Oxo synthesis applied to heavy olefins

A. Oxo synthesis on heptenes and octenes

These olefins are present in light gasolines produced by catalytic cracking, steam cracking or resid coking, from which they can be extracted. However, they are usually produced by the dimerization or codimerization of propylene and butenes (see Section 2.3.3.2).

Oxo synthesis for C₇ compounds takes place between 170 and 185°C and a pressure between 18 and 25 . 10⁶ Pa absolute, and for C₈ compounds between 150 and 175°C and a pressure between 20 and 30 . 10⁶ Pa absolute.

A. Oxo synthesis on other higher olefins

Apart from the isoctanol and isononanol discussed above, isodecanol can be produced from the trimer of propylene and isotridecanol from its tetramer. Alcohols with 8

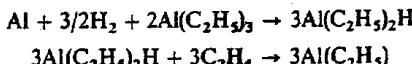
to 14 carbon atoms can also be produced by Oxo synthesis on olefins from the cracking of waxes and on olefins resulting from the oligomerization of ethylene or the dehydrogenation of paraffins.

9.4.3 Synthesis of higher alcohols by oligomerization of ethylene. The Alfol process

9.4.3.1 Principle

A derivative of the Ziegler ethylene polymerization process (Alfene process producing α -linear olefins), this technique is used to produce high molecular weight linear alcohols with an even number of carbon atoms (C_4 to C_{20}). It was developed by *Continental Oil Company*, and employs the growth reaction of polyethylene from triethylaluminum. The rupture of the chain is caused by oxidation of the product:

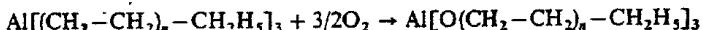
(a) Catalyst preparation:



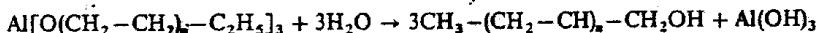
(b) Growth or addition reaction:



(c) Oxidation:



(d) Hydrolysis:



The temperature is generally kept below 130°C and the operation conducted under pressure to increase the ethylene combination rate. Polymerization is highly exothermic. It is essential to remain below 250°C, above which explosive decomposition of the reaction product occurs.

The highly exothermic oxidation is complete. It must take place in the absence of water to prevent the hydrolysis of unoxidized aluminum alkyls. The main by-products of the reaction are esters, ethers, acids and aldehydes. The alcohols obtained display a molecular weight distribution according to the Poisson law. Hence a maximum quantity of the desired product is accompanied by heavier and lighter alcohols with an even number of carbon atoms.

9.4.3.2 Industrial manufacture (Fig. 9.7)

Industrial manufacture takes place in several stages, beginning with the preparation of the catalyst. The aluminum powder, finely divided by grinding, is dispersed in a solvent. The activated sludge, to which recycle triethylaluminum is added, is then hydrogenated under pressure by dry 90 per cent hydrogen. By contact with pressurized ethylene, the diethylaluminum hydride obtained yields triethylaluminum, of which two molecules are recycled to the hydrogenation stage for each molecule sent to the polymerization stage.

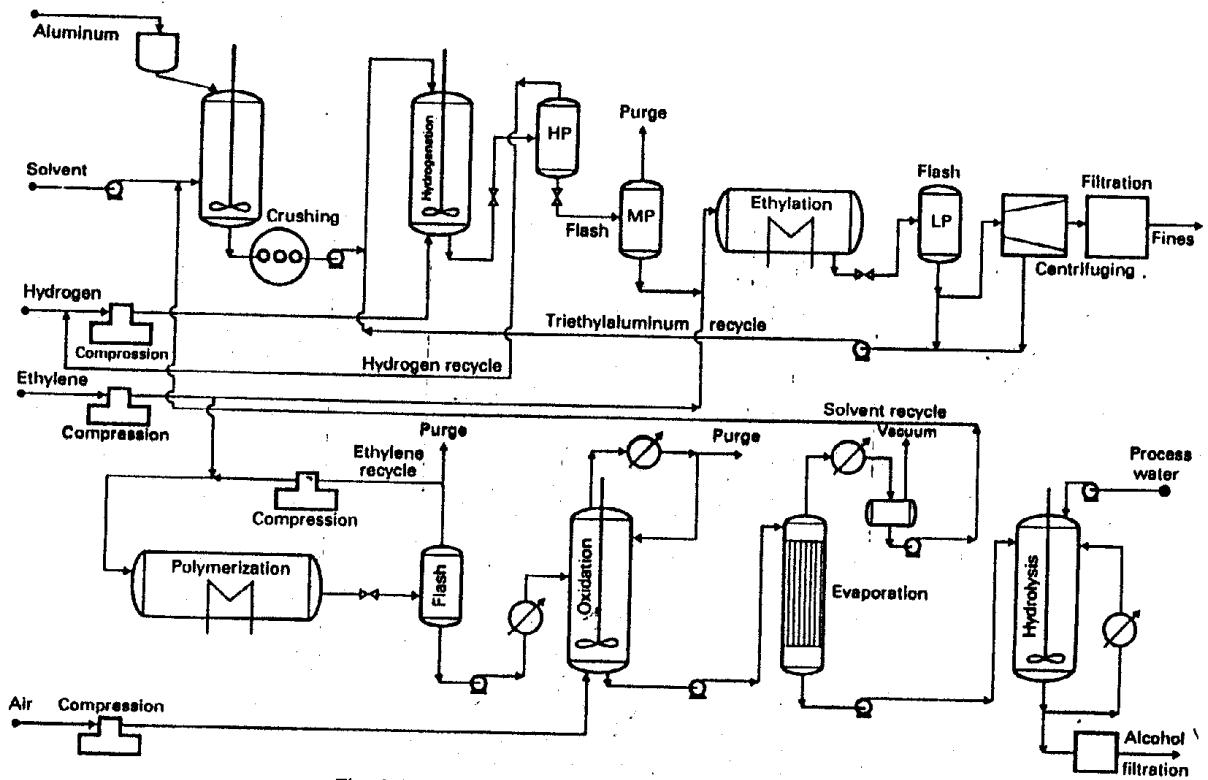


Fig. 9.7. Manufacture of higher alcohols. Alfol process.

The polymerization or growth reaction yields a product distribution according to the Poisson law. These compounds may range from C_2 to C_{22} . To provide an example, one of the distributions initially obtained was the following (per cent weight): $C_2 = 1.1$, $C_4 = 9.6$, $C_6 = 17.4$, $C_8 = 24.5$, $C_{10} = 20.9$, $C_{12} = 13.8$, $C_{14} = 7.2$, $C_{16} = 3.5$, $C_{18} = 1.3$, $C_{20} = 0.5$ and $C_{22} = 0.2$.

A large flow of excess olefins is sometimes used to increase the growth rate (Zosel technique). This makes the reaction 5 to 16 times faster at between 160 and 170°C. The removal of heat raises a particularly delicate technological problem. Owing to potential leaks in the cooling system, water cannot be used directly due to its affinity for aluminum alkyls. The double jacket system recommended uses an intermediate fluid (isopentane), which is itself cooled by water.

Oxidation is carried out with air. In the preparation of the catalyst, the residual nitrogen serves to maintain an inert atmosphere in the storage of the aluminum powder required to produce triethylaluminum. Heat can be removed by water.

Hydrolysis is carried out with 98 per cent sulfuric acid and yields very pure alumina as a by-product. *Conoco* employs a technique enabling it to prevent corrosion of the equipment. The residual sulfuric acid is neutralized by a dilute sodium hydroxide solution. The alcohols are then washed with water to remove sodium sulfate.

The final stage is fractionation. The raw alcohols are first rid of water by distillation, and then separated in pairs in a series of columns operating under vacuum to prevent any thermal decomposition.

Two processes have been commercialized on the basis of the oligomerization of ethylene, one by *Conoco Chemical* and the second by *Ethyl Corporation*. They differ in the distribution curve of the different alcohols formed. Whereas Conoco's "Alfol" alcohols range from C_2 to C_{22} with about 55 per cent C_{12} or above (Fig. 9.8), the alcohol distribution of the Ethyl process is narrower and comprises 85 per cent C_{12+} . This change in the distribution curve results from the insertion of an additional stage of transalkylation by triisobutylaluminum.

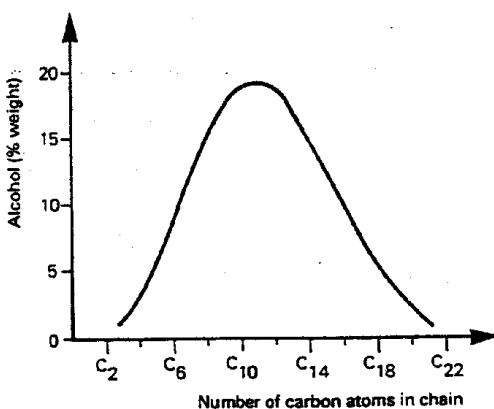


Fig. 9.8. Alcohol distribution curve in the Conoco process.

9.4.4 Economic data

Tables 9.15 and 9.16 summarize the main economic data available in the literature or recalculated, concerning the production of 2-ethyl hexanol, isoctanols in mixtures, or higher alcohols by different industrial processes.

TABLE 9.15
ISOCTANOL PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Alcohol	2-ethyl hexanol				Other isoctanols
Catalyst	HCo(CO) ₄	HCo(CO) ₃ PR ₃	Rh	HCo(CO) ₄ + Zn(Aldox)	HCo(CO) ₄
Typical technology	Ruhrchemie	Shell	Celanese	Exxon-Shell	Ruhrchemie
Production capacity (t/year)	50,000	50,000	50,000	30,000	40,000
Battery limits investments (10 US\$)	52	30	35	40	32
Consumption per ton of alcohol					
Raw materials					
Propylene (t)	1.10	0.90	0.85	1.4 ⁽¹⁾	—
Heptenes (t)	—	—	—	—	1.20
Synthesis gas (l/l) (Nm ³)	1,400	1,380	900	1,500	880
Hydrogen (100%) (kg)	45	—	35	35	40
By-products					
n-butanol (t)	(—)0.15	(—)0.10	—	(—)0.15	—
Isobutanol (t)	(—)0.35	—	—	(—)0.40	—
Isobutyraldehyde (t)	—	—	(—)0.10	—	—
Utilities					
Steam					
HP (t)	5.5	3.0	3.0	2.9	3.5
LP (t)	(—)1.2	—	(—)0.5	—	—
Electricity (kWh)	420	580	200	690	240
Fuel (10 ⁶ kJ)	(—)110	(—)16	(—)10	(—)123	(—)23
Cooling water (m ³)	180	240	200	220	180
Process water (m ³)	1	—	1	5	2
Boiler feedwater (m ³)	2	—	—	—	—
Nitrogen (Nm ³)	5	—	10	—	10
Chemicals and catalysts (USS)	14	60 ⁽²⁾	18	70 ⁽²⁾	16
Caustic soda (t)	—	—	—	0.35	—
Sulfuric acid (kg)	—	—	—	40	—
Labor (Operators per shift)	7	5	7	6	5

(1) 91% Wt propylene.

(2) Including 35 US\$ of catalyst.

TABLE 9.16
PRODUCTION OF HIGHER ALCOHOLS. ECONOMIC DATA
(France conditions, mid-1986)

Process	Hydroformylation of olefins		Oxidation of <i>n</i> -paraffins	Alfol	
Catalyst	$\text{HCo}(\text{CO})_4$; $\text{HCo}(\text{O})_3\text{PR}_3$; Boric acid		—	—	
Typical technology	Ruhrchemie	Shell	Russian	Conoco	Ethyl
Production capacity (t/year)	40,000	40,000	25,000	50,000	100,000
Battery limits investments (10^6 US\$)	40	32	24	60	120
Consumption per ton of alcohol	—	—	—	—	—
Raw materials	—	—	—	—	—
Ethylene (t)	—	—	—	1.1	1.4
Olefins ($\text{C}_{10}\text{-C}_{20}$) (t)	1.45	1.05	—	—	—
<i>n</i> -paraffins (t)	—	—	1.35	—	—
Synthesis gas (Nm^3)	500 ⁽¹⁾	520 ⁽²⁾	—	—	—
Hydrogen (kg)	20	—	—	10	15
By-products: alcohols (t)	—	—	—	—	(—)0.3
Utilities	—	—	—	—	—
Steam (t)	3.8	3.0	5.0	1.0	1.5
Electricity (kWh)	240	250	180	240	420
Fuel (10^6 kJ)	(—)25	(—)10	1.0	7.0	6.5
Cooling water (m^3)	180	120	200	100	120
Process water (m^3)	4	2	8	8	50
Boiler feedwater (m^3)	—	—	—	10	12
Nitrogen (Nm^3)	10	10	3	—	—
Chemicals and catalysts (US\$)	15	65 ⁽³⁾	—	4	5
Aluminum (kg)	—	—	—	65	20
Boric acid (kg)	—	—	15	—	—
Sulfuric acid (t)	—	—	—	0.35	0.10
Caustic soda (kg)	—	—	200	15	—
Ammonia (kg)	—	—	—	15	—
Labor (Operators per shift)	5 ⁽⁴⁾	5	4	6	10

(1) $\text{H}_2/\text{CO} \approx 1/1$.(2) $\text{H}_2/\text{CO} \approx 2/1$.

(3) Including 38 US\$ of catalyst.

9.4.5 Uses and producers

Table 9.17 gives the average commercial specifications of 2-ethyl hexanol and of various higher oxo alcohols.

Only one *n*-paraffin oxidation plant is currently in operation in Japan in Kawasaki (18,000 t/year) operated on behalf of *Nippon Shokubai*. Another one in the United States

TABLE 9.17

AVERAGE COMMERCIAL SPECIFICATIONS OF 2-ETHYL HEXANOL AND HIGHER OXO ALCOHOLS

Alcohol	2-ethyl hexanol	Isooctyl alcohol	Nonyl alcohol	Hexadecyl alcohol
Purity (% Wt) min.	—	99.6	—	—
$d_{20}^{20(1)}$	0.8325-0.8345	0.831-0.832	0.827	0.839
Distillation range (°C)	182-186	186-190	193-197.8	152-161 ⁽²⁾
Acidity (as acetic acid) (ppm) min.	100	10	10	—
Water (ppm) min.	100	500	500	1,000
Flash point (open cup) (°C)	76.7	74-82 ⁺	80	135

(1) Specific gravity, 68.0/68.0.

(2) At 1.3 . 10³ Pa.

TABLE 9.18

2-ETHYL HEXANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
2-ethylhexylacrylate	3	15	9
Plasticizers	93	63	
Diethyl phthalate	90	46	
Diethyl adipate	3	5	85
Miscellaneous ⁽¹⁾		12	
Surfactants			3
Diesel-fuel additive	4	6	
Lube oil additives		4	6
Miscellaneous ⁽²⁾		9	
Total	100	100	100
Production (10 ³ t/year)	660	245	245
Capacity (10 ³ t/year) ⁽³⁾	805	340	330
Consumption (10 ³ t/year)	420	235	230

(1) Azidate, sebacate, terephthalate, trioctyl trimellitate.

(2) Defoamer, herbicides (octyl ester of 2,4-D), polymerization inhibitor (di(2-ethylhexyl) peroxydicarbonate), stabilizers (2-ethylhexylmercaptoacetate), solvents, uranium extraction (di(2-ethylhexyl) phosphoric acid).

(3) The worldwide production capacity of 2-ethylhexanol was about $1.9 \cdot 10^6$ t/year in 1984 and more than $2.0 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.32	Western Europe	0.82	Middle East	—
Canada	0.06	Eastern Europe	>0.24	Japan	0.33
Latin America	0.12	Africa	—	Asia and Far East	>0.07

TABLE 9.19
OXO ALCOHOLS PRODUCTION IN 1984
(% Wt)

Geographic areas	Western Europe	United States	Japan
n-butanol	21	40	22
Isobutanol	15	7	7
Amyl alcohol	1	2	—
Hexyl alcohol	—	1	—
Heptyl alcohol	—	1	6
2-ethylhexyl alcohol	41	22	54
Nonyl alcohol	7	3	—
Decyl alcohol	6	7	4
C ₆ -C ₁₁ linear oxo	6	6	2
Alcohols	2	9	5
Tridecyl alcohol	1	2	—
Total	100	100	100

TABLE 9.20
PLASTICIZER ALCOHOLS (C₆-C₁₁) CONSUMPTION IN 1984
(% Wt)

Geographic areas	Western Europe	United States	Japan
n-butanol	20	38	22
Isobutanol	15	7	8
Amyl alcohol	1	2	—
Hexyl alcohol	—	1	—
Heptyl alcohol	—	1	3
2-ethylhexyl alcohol	40	19	51
Octyl alcohol	7	4	—
Nonyl alcohol	6	6	7
Decyl alcohol	6	7	2
C ₆ -C ₁₀ and C ₇ -C ₁₁ linear alcohols	4	13	7
Tridecyl alcohol	1	2	—
Total	100	100	100

in Texas City (23,000 t/year), belonging to *Union Carbide*, closed in 1977. Both plants process or processed paraffinic feeds consisting of molecules with 11 to 15 carbon atoms and produce the corresponding secondary alcohols, with a statistical distribution of the hydroxyl function.

The hydroformylation of olefins is much more widespread, both for the manufacture of 2-ethyl hexanol, for which Table 9.18 gives the distribution of applications in Western Europe, the United States and Japan, together with data concerning the production.

capacities and consumption for these three geographic areas, and for the manufacture of various other alcohols obtained by Oxo synthesis. From this standpoint, Tables 9.19 and 9.20 illustrate the relative economic importance of these products in the three major industrial regions mentioned, and their use in the main application for which they are employed, namely the manufacture of plasticizers.

Production capacities for detergent alcohols ($C \geq 12$) in the United States, in Western Europe and in Japan were 520,000, 380,000 and 120,000 t/year in 1984 respectively; of which 400,000, 200,000 and 80,000 t/year of synthetic alcohols.

The Alfol technology is commercialized in the United States by *Conoco* (110,000 t/year of C_6 to C_{22} alcohols at Lake Charles, Louisiana) and *Ethyl Corporation* (115,000 t/year of C_6 to C_{20} alcohols in Pasadena, Texas). In Western Europe, *Condea Chemie* has a 50,000 t/year capacity plant in Brunsbuettel (West Germany). These alcohols are essentially used to manufacture detergents.

Chapter 10

PHENOL, ACETONE AND METHYL ETHYL KETONE

10.1 PHENOL

Phenol ($d_4^{20} = 1.072^{(1)}$, mp = 41°C , bp₁₃ = 182°C) played a major role in the earliest developments of plastics (resins) and synthetic fibers (nylon). While it has been supplanted in these uses by new plastics, and as an intermediate by cyclohexane and its derivatives, it nevertheless remains one of the major products of the organic chemical industry.

Industrial processes for the manufacture of phenol include the following:

- (a) The two earliest processes, which have practically disappeared, the first operating by the sulfonation of benzene followed by alkaline fusion of the sulfonic acid formed, and the second by catalytic chlorination combined with the basic hydrolysis of the chlorobenzene obtained.
- (b) Two other processes, which are more recent, account for only a small part of world output today. The first employs the vapor phase oxychlorination of benzene, supplemented by hydrolysis (Hooken/Raschig process). The second converts toluene by catalytic oxidation in the liquid phase using a complex reaction mechanism (Dow process).
- (c) The liquid phase oxidation of cyclohexane, which is followed in a second stage by the catalytic dehydrogenation of the products obtained (Scientific Design process), has only led to the construction of a single plant, which is now shut down.
- (d) Despite the fact that it is relatively old, the most popular process (Table 10.1) remains the oxidation of cumene, obtained by the propylene alkylation of benzene. The hydroperoxide formed is then split into phenol and acetone.

(1) Specific gravity, 68.0.39.2

Various development projects, while they have not yet culminated in the construction of industrial plants, have contributed to the development of processes employing the following different methods:

- Hydroperoxidation of phenylcyclohexane, produced by the hydroalkylation of benzene, followed by the splitting of the hydroperoxide into phenol and cyclohexanone (Phillips process).
- Hydrolysis to phenol and acetic acid of phenyl acetate produced by the acetoxylation of benzene in the presence of air and acetic acid.
- Liquid phase oxychlorination of benzene, followed by hydrolysis of the chlorobenzene obtained to phenol (Gulf process).
- Vapor phase conversion of benzoic acid to phenol, using the acid produced by the liquid phase oxidation of toluene (Lummus process).

The latter two methods are variants of the Hooker/Raschig and Dow processes, which are already industrialized.

A small share of commercial phenol is produced by the distillation of coal tars (about 2 per cent of world output) or the conversion of cresols (MRI Dynaphen process, for example).

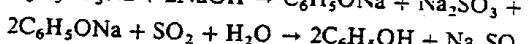
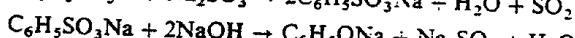
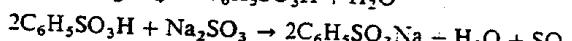
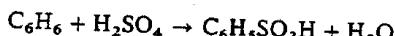
TABLE 10.1
RELATIVE IMPORTANCE OF DIFFERENT INDUSTRIAL METHODS
FOR SYNTHESIZING PHENOL WORLDWIDE IN 1986

Process	% Wt of capacity
Benzene sulfonation	0.1
Benzene chlorination	0.2
Benzene oxychlorination	0.2
Cumene method	92.0
Toluene oxidation	6.5
Carbochemistry	1.0
Total	100.0

10.1.1 Phenol synthesis by sulfonation of benzene

This process, which reached the commercial stage between 1914 and 1918, is now the earliest phenol manufacturing technique still used on the industrial scale (one plant in Japan). Its popularity is largely due to the quality of the phenol obtained, whose purity, which was difficult to obtain by the new processes until relatively recently, was highly desirable for the synthesis of dyes.

It involves the following reactions:



The different steps are as follows:

- (a) Sulfonation of benzene by oleum around 150°C in a cast iron reactor. To maintain the acid concentration, water is removed continuously in the form of an azeotrope with benzene added in excess.
- (b) Conversion of the benzene sulfonic acid obtained to its sodium salt by means of sodium sulfate. The sulfur dioxide formed is used for subsequent acidification of sodium phenate. Excess sulfuric acid is neutralized and the sodium sulfate formed is removed by filtration.
- (c) Alkaline fusion of sodium benzene sulfonate. This takes place at 300°C with 40 per cent weight caustic soda in a cast iron reactor, to produce sodium phenate. The water content is kept at a level such that the sodium sulfite precipitates and can be separated by centrifuging.
- (d) Treatment of sodium phenate by sulfur dioxide produced by the neutralization of benzene sulfonic acid, to liberate the phenol. The upper organic phase obtained by settling contains most of the phenol formed, and is accompanied by an aqueous phase containing the sulfite and the rest of the phenol, which is used directly to neutralize the benzene sulfonic acid.
- (e) Purification of the phenol by distillation in three successive columns.

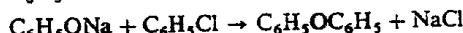
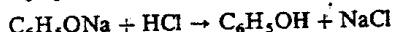
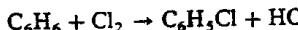
The total yield ranges between 85 and 92 molar per cent in relation to benzene.

This technique offers the advantage of requiring only moderate capital expenditure and yields a very pure product. However, continuous operation is unfeasible, and the consumption of energy and chemicals, as well as labor costs, are high. Moreover, the excess sodium sulfite produced must be sold, and one of the main outlets is the paper pulp industry.

Techniques for the intensive purification of phenol, which have witnessed new advances recently, have contributed to the virtually total disappearance of industrial plants employing the sulfonation of benzene.

10.1.2 The Dow process for phenol synthesis by the chlorination of benzene

This process, commercialized for the first time around 1920, is still used industrially in a few units, notably in India. It employs the following main reactions:



These reactions correspond to the following chemical operations:

- (a) Chlorination of benzene catalyzed in the liquid phase by ferric chloride. The composition of the mixtures obtained varies in the following proportions: chlorobenzene 30 to 50 per cent, polychlorobenzenes 3 to 12 per cent, unconverted benzene 30

to 50 per cent. The temperature is maintained at 35°C. The products are washed and neutralized by dilute sodium hydroxide.

- (b) Purification of chlorobenzene by distillation.
- (c) Hydrolysis of chlorobenzene by caustic soda to yield sodium phenate and sodium chloride. The reaction takes place between 25 and 30 . 10^6 Pa absolute. 2 to 2.5 mol of sodium hydroxide are used per mol of chlorobenzene. Phenyl ether is produced in this step, part of which is recycled.
- (d) Liberation of phenol by the action of hydrochloric acid on sodium phenate.
- (e) Purification of phenol by fractional distillation.

The total phenol yield is 75 to 80 molar per cent in relation to benzene. The main by-products formed (paradichlorobenzene, diphenyl ether, etc.) are easy to separate and can be sold.

This technique consumes a considerable amount of costly chlorine (about 1 t/t of phenol). It also presents the drawback of incurring corrosion of the installation and consequently high maintenance expenses, unless very expensive corrosion-resistant materials are employed.

10.1.3 Phenol synthesis by the oxychlorination of benzene

This operation was first carried out in the vapor phase by the Hooker/Raschig technique, in various industrial facilities, of which a limited number are still active, particularly in South America. Gulf has since proposed a liquid phase version designed to overcome a number of technological problems and to improve performance at higher temperature.

10.1.3.1 The Hooker/Raschig process

This process involves four main steps. The first, conducted at elevated temperature (230 to 270°C) concerns the action of benzene on a mixture of hydrochloric acid gas and air in the presence of an oxychlorination catalyst, consisting of copper and iron chlorides on an inert support. Once-through conversion is limited to between 10 and 15 per cent, to prevent the excessive formation of polychlorobenzenes (10 to 12 molar per cent). This conversion is as high as 98 per cent in relation to the hydrochloric acid. Since the reaction is exothermic, the catalyst is distributed in several beds, between which benzene injections at a lower temperature than those of the reaction streams serve to control the overall temperature.

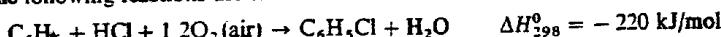
This step is followed by the purification of monochlorobenzene by distillation. In its initial version, this operation first involves the partial condensation of the oxychlorination products, followed by their introduction into a brick-lined column, with separation of the water/benzene azeotrope at the top, which is recycled to the reactor after settling. The 1/1 mixture of benzene and chlorobenzenes obtained at the bottom is neutralized with caustic soda, washed with water, and distilled in two columns to separate the dichlorobenzenes, monochlorobenzene and benzene.

This is followed by hydrolysis around 450 to 500°C of the monochlorobenzene by steam added at the rate of 1/1 by weight, in the presence of a tricalcium phosphate or silica gel base catalyst, which can be reactivated periodically to reduce carbon deposits.

This hydrochloric acid gas co-produced is recycled after absorption, extraction, and possible reconcentration in evaporators. Once-through conversion is about 10 to 15 per cent, and the hydrolysis yield is 85 to 95 molar per cent.

The final step is the purification of phenol by solvent extraction (water and benzene) and distillation.

The following reactions are involved:



The formation of dichlorobenzenes in the oxychlorination reaction and that of polyphenols during hydrolysis reduce the total yield.

Improvements made to the initial process scheme have dealt with the following aspects (Fig. 10.1):

- Handling of hydrochloric acid in all its forms. Above 130°C, there is practically no steel corrosion by HCl whether or not water is present. Below this temperature, the material employed is "karbate", a petroleum coke impregnated with synthetic resins.
- Removal of heat. The oxychlorination catalyst is concentrated in a single shell. The reactant vapors are cooled as they pass through the reactor by calculated injections of the same vapors, previously cooled.
- Benzene separation and recycle. The use of direct contact condensers facilitates and simplifies the recirculation of unconverted benzene to the reaction section. Through a suitable arrangement of the different separation columns, before the benzene is returned to the oxychlorination reactor, the different effluents which it contains (make-up, azeotrope with water, mixture with monochlorobenzene) can be used to facilitate the recovery of the phenol subsequently produced.
- Development of a hydrolysis catalyst which allows the conversion of dichlorobenzenes to phenol either directly or through intermediate chlorophenols. However, the activity of this type of catalyst is reduced by deposits of organic materials. Steam regeneration is periodically necessary, requiring the use of a double series of hydrolysers. The use of this catalyst system avoids the purification of chlorobenzene between the oxychlorination and hydrolysis stages.

The phenol is obtained in a purity of up to 97 per cent weight. The yield of the operation is relatively limited (80 to 90 molar per cent). This process offers the advantage over direct chlorination of using hydrochloric acid instead of chlorine. However, capital expenditure and energy consumption are high. Maintenance costs incurred by the handling of corrosive acidic substances have a direct effect on the economics of this technique.

10.1.3.2 The Gulf process

The oxychlorination of benzene by an aqueous solution of hydrochloric acid takes place in this case in the liquid phase, in an agitated reactor, around 135°C and between 1 and $1.2 \cdot 10^6$ Pa absolute, in the presence of oxygen and nitric acid. Benzene once-through conversion is better than 80 per cent, and monochlorobenzene selectivity is better than 90 molar per cent. The reactor output is settled to produce two phases:

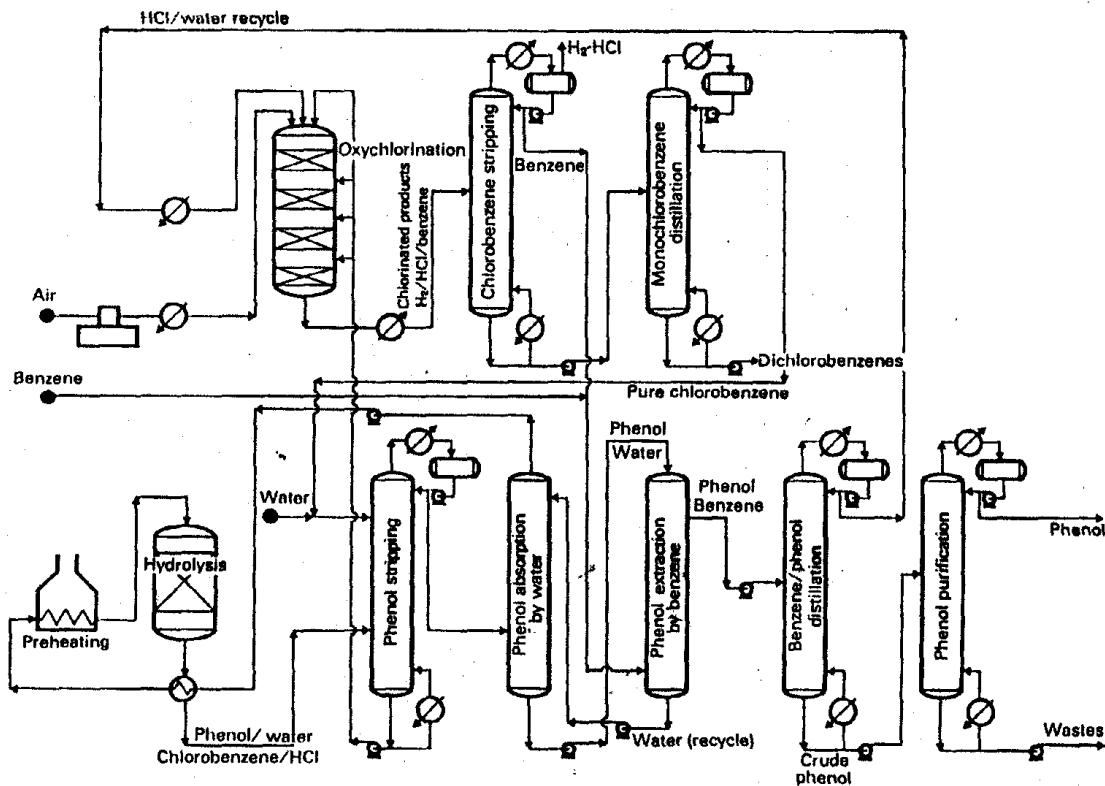


Fig. 10.1. Phenol manufacture by oxychlorination of benzene. Hooker/Raschig process.

an organic phase, consisting of benzene and its chlorinated derivatives, is neutralized with caustic soda and then fractionated. The aqueous phase is concentrated by evaporation to recover and recycle the hydrochloric acid contained.

Hydrolysis is conducted in the vapor phase, at atmospheric pressure, around 550°C, with a steam to chlorobenzene molar ratio of about 3/1. It is carried out directly on the fraction of chlorinated derivatives of benzene produced by the oxychlorination stage, previously vaporized by passage through a furnace, in the presence of a fixed catalyst bed of lanthanum phosphate promoted by copper, which enables once-through conversions approaching 40 per cent and a phenol selectivity greater than 90 molar per cent. The reactor output also leads to the formation of two phases by condensation and settling: the organic phase contains phenol and unconverted chlorobenzenes, and the aqueous phase consists chiefly of hydrochloric acid. They are treated separately to isolate the different components, purify them or concentrate them, and recycle them if necessary.

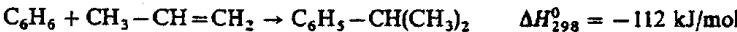
Despite its better performance than the vapor phase process, Gulf type oxychlorination remains subject to the use of highly corrosive reactants, resulting in high capital expenditures.

10.1.4 The cumene method

The method is based on the research of Hock and Lang (1944) concerning the splitting of cumyl hydroperoxide into phenol and acetone. Only in 1952, however, after experiencing a number of development problems, did the first industrial plant built by Hercules-Power produce phenol regularly. Despite the advent of new techniques on the market, which temporarily appeared to threaten the virtual monopoly of the cumene method, the industry continues to demonstrate considerable confidence in this method.

Two types of process are involved:

- Alkylation of benzene by propylene to cumene:

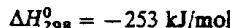


- Conversion of cumene to phenol and acetone in two main steps:

- (a) Oxidation of cumene to the hydroperoxide:



- (b) Splitting of the hydroperoxide:



A third advanced purification step must be added, due to the evolving requirements of users who demand increasingly pure phenol. The main process holders are *Allied Chemical*, *BP (British Petroleum) (Distillers)*, *Chevron, Power Gas, Hercules, Rhône-Poulenc, SIR (Societa Italiana Resine)* and *UOP (Universal Oil Products) (Cumox process)*.

10.1.4.1 Alkylation of benzene by propylene to isopropylbenzene (cumene) (Fig. 10.2)

A. Principle

The different industrial techniques available to perform this alkylation are in principle similar to those employed to synthesize ethylbenzene (see Section 6.4.1). They involve several types of catalyst:

- Aluminum chloride employed at a temperature between 10 and 95°C.
- Phosphoric acid, which may or may not be promoted, deposited on a solid support (solid phosphoric acid).
- Bentonites, activated by an acid allowing the reaction to take place between 70 and 105°C.
- A silico-aluminate, introduced in similar form to that of the cracking catalyst, at a temperature of about 200°C.

B. Industrial manufacture

On the industrial scale, phosphoric acid is mainly used to synthesize cumene. In the reactors of these plants, the reactants may circulate either in downflow, a method adopted in the older installations, or in upflow in more recent versions. In the former case, the propylene feed containing 92 per cent weight (chemical grade or ex-refinery), to which propane recycle is added to obtain a molar ratio of 1/1 at the reactor inlet, is mixed with make-up and recycle benzene. The benzene to propylene molar ratio in the feed is maintained at a high level, about 8 to 10/1, in order to minimize the formation of polyalkylbenzenes and polymers.

This preheated feed is introduced at the top of a reactor with superimposed catalyst beds, formed of phosphoric acid deposited on kieselguhr, which may be promoted by boron trifluoride (*UOP*), at a temperature between 190 and 200°C and a pressure between 3.5 and $4 \cdot 10^6$ Pa absolute. The LHSV (Liquid Hourly Space Velocity) in relation to benzene is about 1.5. Propane, containing a calculated amount of water (about 300 ppm in relation to the reactor feed) is injected between the catalyst beds to remove the heat liberated by the reaction, for better control of the temperature rise, which must not exceed 30 to 50°C in each of the beds, and to maintain the catalyst system in a suitable state of hydration. Performance is accordingly improved.

Furthermore, better irrigation by the reactants keeps the catalyst more active. This is achieved by maintaining a certain fraction of these reactants in the liquid phase, by adjusting the temperature and pressure at the reactor outlet. In principle, upflow circulation facilitates this wetting and serves to increase catalyst life.

After filtration of the reactor outstream, the propane is extracted in a depropanizer and partly recycled. Excess benzene and cumene, which is obtained in a purity of 99.9 per cent weight, are recovered by distillation in columns with about 30 trays each. The cumene contains about 1200 ppm of impurities, usually consisting of 0.02 per cent weight ethylbenzene, 0.05 per cent weight n-propylbenzene, and 0.05 per cent weight butylbenzene. The yield is 96 to 97 molar per cent in relation to benzene, and 91 to 92 per cent in relation to propylene. The fractionation section of the unit is of carbon steel. In some cases, part of the reactor and other equipment may be of stainless steel.

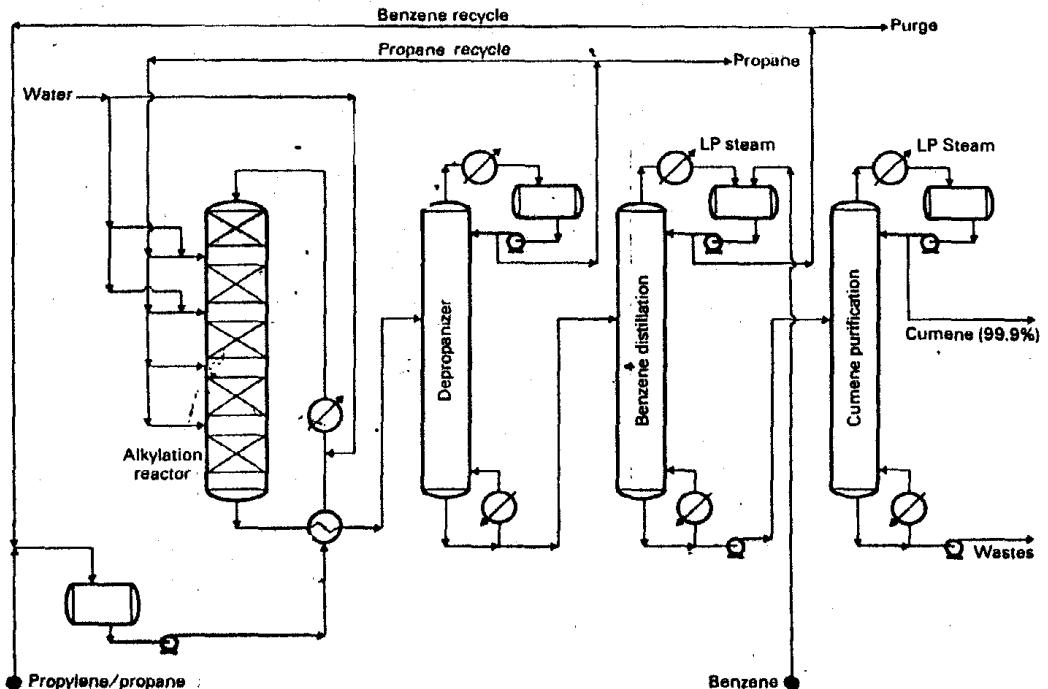


Fig. 10.2. Cumene manufacture. Alkylation of benzene by propylene. UOP process.

Benzene and cumene are condensed with the production of low-pressure steam. Make-up benzene can be introduced either in the depropanizer, or at the top of the recovery column, for better control of the moisture content in the recycle streams. A purge is sometimes provided to remove non-aromatic components and to prevent their buildup in the benzene recirculation loop.

C. Variant

This type of process does not provide for a separate reactor for the transalkylation of the polyalkylbenzenes formed, as in the case of the synthesis of ethylbenzene. So far, their formation has been limited preferably by using a large excess of benzene.

The Japanese company *Showa Denka* has, for several years already, proposed a catalyst capable of transalkylating diisopropylbenzene and benzene to two molecules of cumene. The operating conditions are as follows: temperature between 180 and 250°C, benzene/diisopropylbenzene molar ratio between 5 and 10, LHSV between 1 and 2, pressure about $2 \cdot 10^6$ Pa absolute. Diisopropylbenzene once-through conversion is 53 per cent, and the cumene yield is 93 molar per cent. This process thus enhances the total alkylation yield and reduces the amount of excess benzene required.

The Crest technology, developed by *Monsanto-Lummus* for producing ethylbenzene (see Section 6.4.1), has been licensed to three companies, whose plants are currently in operation in Texas, France and Finland, for making cumene. As in the ethylbenzene process, the alkylation is performed in the presence of an anhydrous organic aluminum chloride catalyst complex. Some polyisopropylbenzenes are formed, even though excess benzene is used. This is the reason why a transalkylation is added which is fed with alkylation outlet and di- and tri-isopropylbenzenes recovered from the purification section. As a result of this transalkylation step yields greater than 99.0% are achievable.

10.1.4.2 Conversion of cumene to phenol and acetone

A. Oxidation of cumene to the hydroperoxide (Fig. 10.3)

a. Principle

Given the risks and difficulties inherent in the manufacture of cumyl hydroperoxide, a number of precautions of a technological nature must be observed. Two alternatives are available industrially, the older operating with an emulsion, and the more recent in a homogeneous phase.

In the former, cumene is dispersed in a medium that is made alkaline (pH 8.5 to 10.5) by sodium carbonate and emulsified by a compound such as sodium stearate, ricinoleate or lauryl sulfate. This dispersion takes place in the liquid phase at a temperature between 80 and 120°C, with a water/cumene molar ratio between 2 and 5/1, in the presence of oxygen (pressure around $0.1 \cdot 10^6$ Pa absolute) or air (pressure about 0.5 to $0.7 \cdot 10^6$ Pa absolute), devoid of carbon dioxide and possibly enriched with oxygen.

In the latter case, the homogeneity of the reaction medium is achieved by adding concentrated sodium hydroxide solution. This enables operation at a slightly higher temperature, 115 to 130°C, in conditions that are otherwise more or less identical.

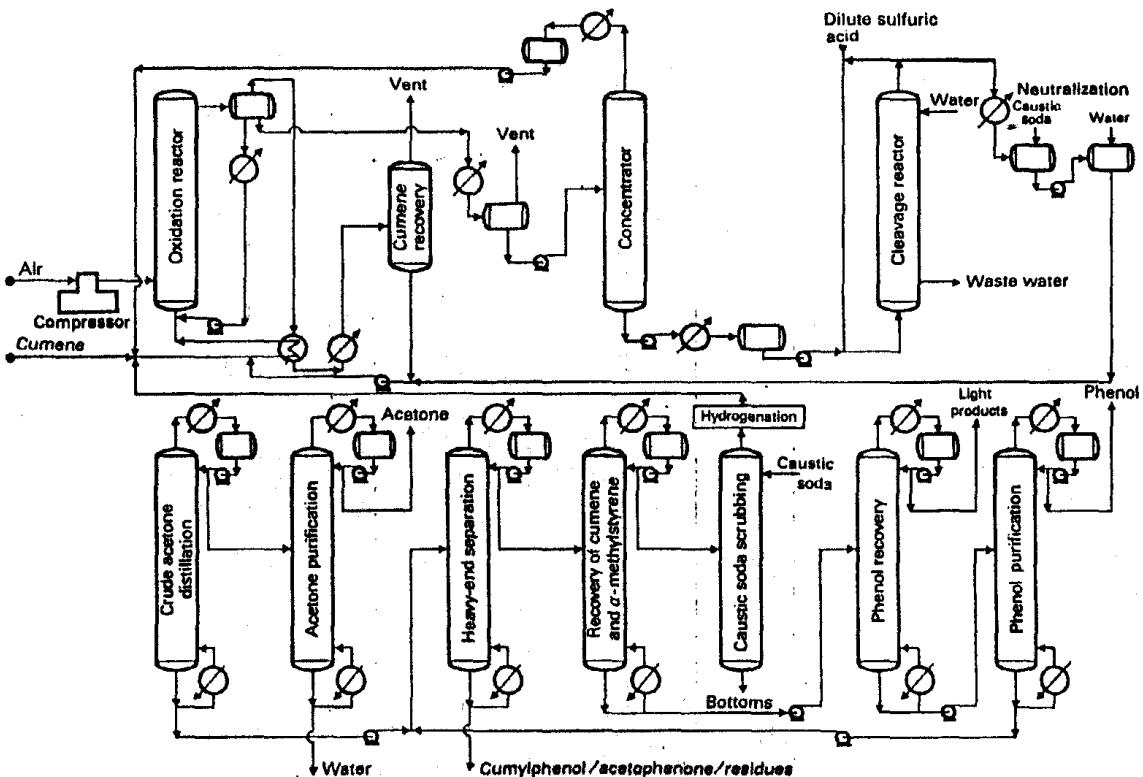


Fig. 10.3. Phenol manufacture. Cumene method.

The conversion takes place by a chain free radical mechanism which obeys the following general kinetic equation:

$$\frac{d(O_2)}{dt} = \sqrt{\frac{2k_i}{k_r}} k_p [ROOH]^{0.5} [RH]$$

where k_i , k_p and k_r represent the rate constants of the initiation, propagation and rupture reactions.

This auto-catalytic process is characterized by a rather long induction period, which can be shortened by initiating the conversion by the introduction of small amounts (0.05 to 0.5 per cent weight in relation to the feed) of cumyl hydroperoxide or of its sodium salt. Other initiators or oxidation catalysts are sometimes introduced: these may be soluble salts of heavy metals (Mn, Co, Cu) or alkaline and alkaline earth derivatives of lead, bismuth, tin and antimony.

The cumene feed must be free of oxidation propagation chain splitters, especially sulfur compounds, styrene, aniline and phenol. Since the reaction rate is extremely sensitive to these impurities, special care is taken to remove them. Phenol can be removed by treatment with caustic soda. However, its effect is less harmful than it appears, because it exerts an even more inhibitory action on side reactions, leading for instance to acetophenone or 2-phenyl 2-propanol, than on the main hydroperoxidation reaction, and because, in small amounts (10 to 1000 ppm), and combined with the sodium salt of cumyl hydroperoxide, its effect enhances the final yield of the operation.

Among the other by-products are light acids (formic and acetic acids) which promote the decomposition of the hydroperoxide. They are partly neutralized by the basicity of the reaction medium, and partly stripped in the gas phase by partial vaporization of the reactants, since the conversion is exothermic.

The liquid stream can be expected to contain cumyl hydroperoxide concentrations of 35 to 50 per cent weight; but its rate of decomposition to acetophenone and 2-phenyl 2-propanol then tends to increase. It is therefore preferable to limit once-through conversion to between 20 and 25 per cent so that selectivity remains above 90 to 92 molar per cent, and even reaches 95 to 97 molar per cent in present-day processes.

b. Industrial manufacture

Industrial conversion takes place in several series of multistage reactors, operating at decreasing temperature and also performing unit conversions that progressively decrease. They exist in the form of large empty stainless steel columns, into which air is blown by a compressor which ensures vigorous agitation. Residence time in each of them ranges from 1 to 2 h. The heat liberated by oxidation can be removed by one or a combination of the following technological alternatives: external circulation of the reaction medium in a device equipped with a pump and heat exchange, the use of a coolant fluid flowing in the double jacket forming the reactor wall, or in coils mounted inside, partial vaporization of the reactants with subsequent recondensation, the use of auxiliary heat exchangers between the different stages, etc.

This equipment may be supplemented upstream by the washing with cumene of the different liquid streams recovered (gas treatment, separation of solids), and downstream by the purification of the light ends, by cooling and condensation, and the removal of sodium carbonate and catalyst in the separators, particularly by washing with water.

The hydroperoxide in solution in cumene is concentrated by evaporation under vacuum (7 kPa) in a two-stage falling film unit, for example, or by stripping. The unconverted cumene recovered at the top is recycled. The heavy ends obtained contain 75 to 85 per cent weight cumyl hydroperoxide, 3 to 6 per cent acetophenone and 2-phenyl 2-propanol, 8 to 17 per cent cumene, α -methylstyrene and a number of other impurities (such as hydroxyacetone).

B. Splitting of cumyl hydroperoxide

The hydroperoxide is a relatively stable compound, and at 100°C the induction period of its auto-catalytic decomposition is 8 h. Since it yields many undesirable components (aromatic alcohols and ketones), it must take place in specific conditions.

To achieve good phenol selectivity (94 to 95 molar per cent), splitting must take place catalytically. This can be done by using strong acids, such as sulfonic acids, ion exchange resins, etc., which offer the advantage of not requiring subsequent neutralization, but present the drawback of excessively slow conversion rates. It is preferred to use concentrated sulfuric acid (98 per cent weight) used in a low concentration (0.2 to 1 per cent weight), to avoid introducing water which slows down the decomposition and prevents it from being complete, and to limit new side reactions which, based on the acetone produced, yield compounds such as mesityl oxide, hydroxyacetone, alcohol diacetone and isophorone.

To prevent the thermal decomposition of cumyl hydroperoxide, which gives rise chiefly to acetophenone, dissociation takes place at a relatively low temperature (between 70 and 80°C), at low pressure (0.1 to 0.2 . 10^6 Pa absolute), in an agitated reactor, suitably cooled to remove easily the heat generated by this decomposition. This is achieved either by allowing part of the reaction products (especially acetone) to be vaporized, and subsequently recondensed and recycled, or by means of an external circulation of the reaction medium, with pumping and heat exchange.

To minimize the risks of initiating undesirable chain reactions and explosions, the hydroperoxide must be totally converted at the reactor exit. This requirement can be met by maintaining a residence time of about 20 to 30 min. Hot spots and the accumulation of hydroperoxide in the splitting reactor are also avoided by homogenizing the medium by dilution with the main conversion products, acetone (Hercules process) and phenol (Rhône-Poulenc process).

To limit acid corrosion and avoid the use of high-alloy steels, the effluents must be neutralized upon leaving the reactor. The addition of caustic soda, sodium carbonate, lime etc., in the form of aqueous solutions or directly in solid form, presents many drawbacks (gelatinous or colloidal precipitates difficult to separate, handling of solids, slow reaction rates, etc.). It is preferable to use aqueous sodium phenate, which acts rapidly in stoichiometric quantities and yields sodium sulfate in solution, that is easy to remove. This phenate can also be obtained in the unit itself from the phenol produced.

C. Phenol purification

Several purification schemes are feasible. As a rule (Unisir version for example), the crude acetone is first separated at the top of a first distillation column (\approx 55 trays), followed by light ends separation (20 trays) of the light products (especially acetaldehyde)

and heavy ends separation (50 trays) of the heavy products (cumylphenol, acetophenone, polymeric residues, small amounts of water, cumene and α -methylstyrene) ultimately yielding acetone to commercial specifications. The withdrawal from the first distillation is itself retreated in a series of columns for the successive separation of the heavy products (20 trays), followed by hydrocarbons (more than 100 trays, for unconverted cumene and α -methylstyrene), and finally phenol, which is sent to final purification (60 trays). Given the closeness of the boiling points, it is preferable to avoid isolating the α -methylstyrene from the other components of the hydrocarbon cut, in favor of total selective hydrogenation in the liquid phase, around 90 to 95°C, in the presence of a nickel base catalyst. This operation generates additional amounts of cumene which are recycled to oxidation. It is exothermic and requires a division of the catalyst system into several beds, between which cold cumene is injected to control the temperature rise.

A variant (BP scheme) consists in first separating the crude phenol from the acetone/hydrocarbon combination, which is then treated separately. The phenol thus produced has a purity of about 99.8 per cent weight. The 2000 ppm of ketone impurities which it contains make it often unsuitable for use in sulfonation, chlorination and condensation with acetone (bisphenol), in line with the increasingly stringent quality requirements of commercial products.

This is why, in recent years, various processes were developed for additional purification, using distillation, crystallization, solvent extraction, etc. They can operate either on purified phenol (to 99.8 per cent), or directly on the crude product (at 92 per cent weight for example), to yield a product with a purity of 99.99 per cent. In the latter eventuality, the general scheme of the unit can be rearranged to include the production of the sodium phenate required for neutralization. Separation of the hydrocarbons by distillation and final phenol purification are then designed to yield a product meeting the desired specifications, at the cost of large losses of phenol at the top of the first column and the bottom of the second. While the withdrawal is recycled to heavy product separation, the hydrocarbon distillate is treated by a 10 per cent weight sodium hydroxide solution. The phenol is thus extracted in the form of sodium phenate, soluble in the aqueous phase subsequently obtained by settling. A fraction of this stream is sent to neutralization. The excess is treated with sulfuric acid to regenerate the phenol, which is then sent to heavy product separation to include it in the previous purification scheme. The organic phase is subjected to the hydrogenation of the α -methylstyrene which it contains.

The chief advantage of the cumene method is the technical simplicity of the operation, the high phenol yield in relation to cumene (92 molar per cent) and the outstanding control demonstrated by the process licensors in the handling of cumyl hydroperoxide. In some cases, however, the co-production of acetone may constitute an economic handicap. Various alternatives have been proposed to solve the problem of commercializing this product, consisting in particular of obtaining a different co-product, or of developing acetone-consuming industries, such as the manufacture of methyl methacrylate, etc. Procedures for obtaining a different co-product involve:

- (a) The simultaneous production of phenol and acetaldehyde by splitting ethylbenzene hydroperoxide, starting with benzene and ethylene.
- (b) Substitution of methyl ethyl ketone for the acetone by splitting of the 2-phenyl butane hydroperoxide (secondary butylbenzene), starting with benzene and 1- and 2-*n*-butenes.

- (c) Splitting of cyclohexylbenzene hydroperoxide into phenol and cyclohexanone, with the initial step of the hydroalkylation of benzene on itself.

10.1.5 Phenol synthesis by the oxidation of toluene

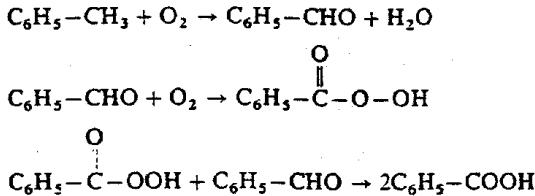
The production of phenol from toluene comprises two main steps:

- (a) Oxidation of toluene to benzoic acid, by a classical liquid phase technique developed in particular by *Amoco*, *Dow* and *S.N.I.A Viscosa (Societa Nazionale Industria Applicazioni)*.
- (b) Catalytic conversion of benzoic acid to phenol, by two methods:
 - . In the liquid phase, a technology industrialized by *Dow/DSM (Nederlandse Staats Mijnen)*.
 - . In the vapor phase, a process proposed in particular by *Lummus*.

10.1.5.1 Oxidation of toluene to benzoic acid

A. Principle

This conversion takes place in the liquid phase by a chain free radical mechanism, in which the initiation step is based on the prior formation of benzaldehyde and the propagation step on the production of perbenzoic acid as follows:



on the whole amounting to:



Various side reactions also occur. In particular, they yield benzyl alcohol and benzyl benzoate, which may play the role of intermediates, or a number of by-products such as diphenyl, methyldiphenyl, carbon dioxide, formic and acetic acids etc.

The oxidation of benzaldehyde is catalyzed by certain metallic ions, including those of the transition metals (Co, Fe, Ni, Cr, Cu, V, etc.) usually introduced in the form of naphthenates, benzoates, stearates etc, at the rate of 500 to 1000 ppm in relation to toluene. Certain initiators, such as bromine compounds, increase the reaction rate obtained with metallic salts by a factor of 10 to 30.

The influence of temperature is decisive, and the temperature routinely ranges between 140 and 180°C. The effect of pressure is much less pronounced: the pressure must be sufficient to maintain the reaction medium in the liquid phase, or between 0.2 and $1 \cdot 10^6$ Pa absolute, depending on whether the oxidant employed is oxygen or air. To achieve

sufficiently high selectivity (91 to 93 molar per cent), toluene once-through conversion is limited to between 20 and 40 per cent.

B. Industrial manufacture (Fig. 10.4)

In practice, industrial plants operate in the presence of excess air and a soluble cobalt salt, at a temperature of about 170°C and between 0.8 and $1 \cdot 10^6$ Pa absolute, and with a total residence time of around 2 h. in reactors mounted in series. These units are designed to achieve effective agitation and to allow the removal of the heat generated by the reaction. To do this, recourse is had either to empty columns, into which air is blown to agitate the reactants and where vaporization of a fraction of the reaction medium (water, toluene) maintains the temperature, or to mechanically agitated reactors, with a double shell, internal coils, and also partial vaporization of reactants and products.

A large part of the vapors stripped by the residual air is cooled and condensed. Traces of toluene remaining in the incondensables are retained on activated charcoal, while part of the remaining vent gases may be recycled, after recompression, to increase the content of inerts in the gas holdup present in the reactors and thus reduce the explosion hazard.

The condensate is separated into two phases by settling:

- An organic phase, consisting chiefly of toluene and also benzyl alcohols and benzaldehyde; this is recycled to the reaction zone.
- An aqueous phase, mainly containing formic and acetic acids; this is sent to the waste treatment section of the installation.

The heat liberated by the reaction can be recovered to produce low-pressure steam during recondensation of the vaporized effluents, or directly by means of a boiler feed-water circulating through the reaction zone.

A liquid stream withdrawn from the oxidation stage is fractionated and purified by distillation. In a first column (15 to 20 trays), it is first rid of the light components, consisting of unconverted toluene, benzaldehyde, benzyl alcohol, formic and acetic acids, water, etc. An organic phase and an aqueous phase are then obtained by cooling and settling. The former is recycled to the reactors, and the latter is sent to waste treatment. The benzoic acid recovered at the bottom is purified to 99 per cent weight in a second column (≥ 20 trays) operating under vacuum (185°C, 13 kPa at the top). The withdrawal consisting of benzyl benzoate, cobalt salt and heavy products is partly returned to the reaction section, and partly purged of organic derivatives by water extraction of the catalyst, which, being soluble, is then recycled.

In view of its properties ($bp_{1.013} = 249^\circ\text{C}$, $mp = 122^\circ\text{C}$. sublimation at 100°C), the storage and handling of benzoic acid require special precautions (heated tank, steam-traced lines, etc.).

10.1.5.2. Catalytic conversion of benzoic acid to phenol

A. Principle

The conversion of benzoic acid to phenol in the presence of cupric benzoate has formed the subject of various interpretations. The most widespread assumes the formation

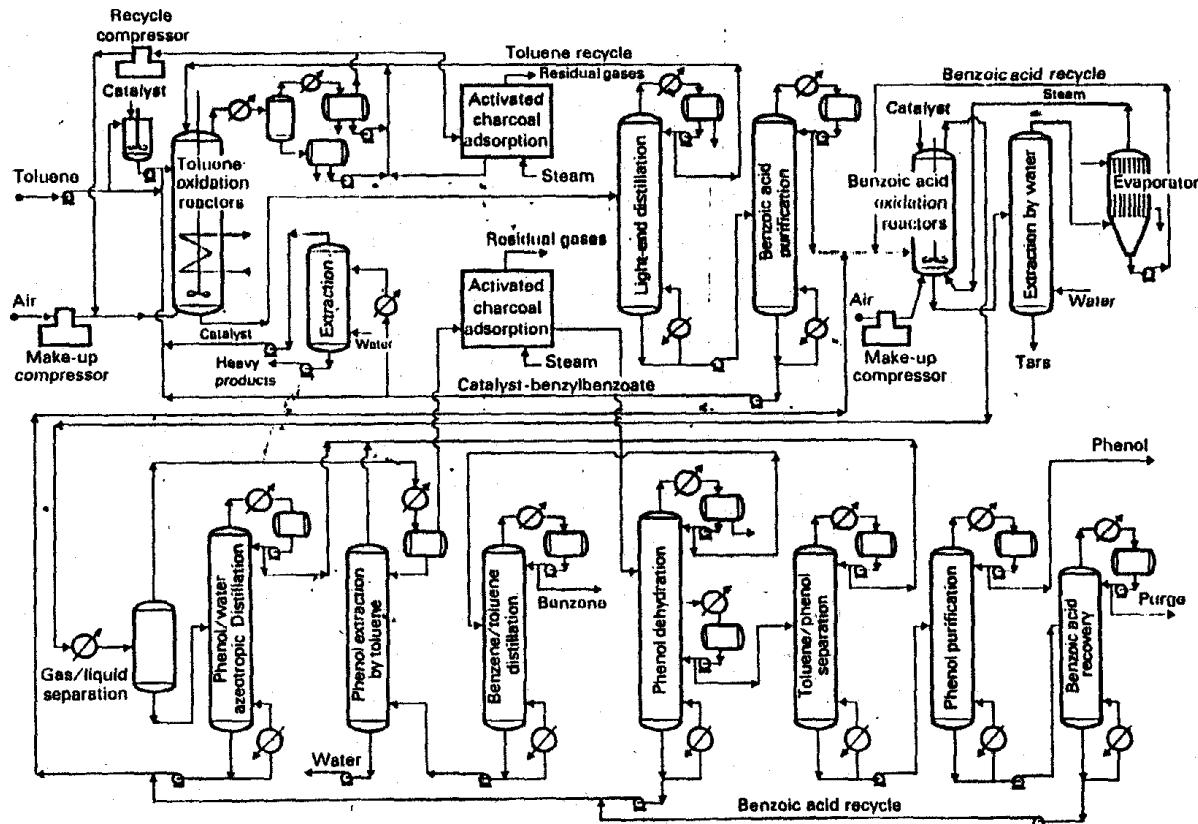
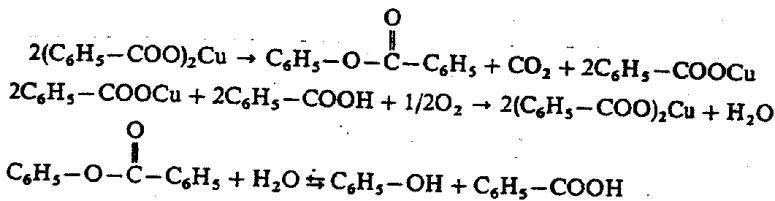


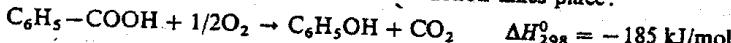
Fig. 10.4. Phenol manufacture from toluene. Dow/DSM process.

of phenyl benzoate as an intermediate. The general reaction mechanism in this case is as follows:



Cupric benzoate decarboxylates thermally with the production of cuprous benzoate and phenyl benzoate. It is regenerated by the action of oxygen and benzoic acid. Phenol is obtained by the steam hydrolysis of phenyl benzoate.

The following overall exothermic oxidation reaction takes place:



In this mechanism, the copper acts as a redox catalyst. Various initiators are combined with it to catalyze the hydrolysis, including magnesium benzoate, or salts of different metals (Li, Na, K, Ba, Co, etc.). The main side reactions are the decarboxylation of benzoic acid to benzene, or its complete degradation, and the production of diphenyl ether and tars. These tars, produced essentially at the expense of phenol, mainly appear in the liquid phase. They slow down its rate of formation considerably, and make it necessary to extract the reaction medium as rapidly as possible.

By contrast, water exerts a beneficial effect. Selectivity increases substantially with the water/benzoic acid ratio, whose optimal value lies at about 1.2 to 1.5 by weight.

B. Industrial manufacture

Two types of process have been developed, operating either in the liquid phase or the vapor phase. So far, only the former has reached the industrial stage:

a. The Dow/DSM liquid phase process (Fig. 10.4)

In this process, benzoic acid is converted at a temperature of about 230 to 250°C, under a pressure close to atmospheric (0.2 to $1 \cdot 10^6$ Pa absolute), but sufficient to maintain the feed and the catalyst system in the liquid phase. It takes place in the presence of cupric ions (1 to 5 per cent weight in relation to benzoic acid) and magnesium (5000 to 15,000 ppm), introduced in the form of soluble salts (benzoates), together with excess oxygen or air (0.4 to 0.5 weight ratio in relation to the feed, expressed as oxygen) and steam (1.2 weight ratio in relation to the feed) which perform several functions:

- (a) To enable the oxidation and hydrolysis reactions to develop.
- (b) To ensure effective agitation of the medium, which can also be achieved mechanically.
- (c) To favor stripping by vaporization of the phenol upon its formation, which has a dual effect: it limits the production of tars and hence avoids a drop in productivity, and removes the heat generated by the reaction by controlling the temperature.

A liquid phase side stream also serves to keep the tar concentration of the reaction medium at an acceptable level, by extracting with water the benzoic acid and catalysts it contains. These compounds are recycled after reconcentration and heating by passage through evaporators, simultaneously with the steam generated in this operation.

The gaseous stream leaving the reactor is cooled and partly condensed. The liquid phase obtained, consisting chiefly of phenol, water, unconverted benzoic acid and benzoates, is fractionated by distillation. The water/phenol azeotrope ($\text{bp}_{1.013} = 99.5^\circ\text{C}$, water content 90.8 weight per cent), recovered at the top, is sent to the dehydration column and the bottom recycled to the reactor. The residual gases (N_2 , O_2 , CO_2 , steam, phenol, benzene, etc.) are again cooled, causing the virtually complete condensation of the water, phenol and benzene. This condensate is extracted with toluene; the aromatic extract is sent to the dehydration column, and the aqueous raffinate is removed. Organic compounds still present in the incondensables are absorbed by passage over beds of activated charcoal.

The dehydrator is a column with about 30 trays, designed to separate the water from the phenol by heteroazeotropic distillation in the presence of benzene and feed- and make-up toluene. The benzene/water azeotrope ($\text{bp}_{1.013} = 69^\circ\text{C}$, water content 8.8 per cent weight) and toluene/water azeotrope ($\text{bp}_{1.013} = 84^\circ\text{C}$, water content 13.5 per cent weight) leaving at the top are cooled and condensed to yield two phases:

- (a) An organic fraction, which serves partly as reflux and is partly distilled, to purge the benzene and thus prevent its buildup in the toluene recycle, especially in the treatment of the phenolated gases leaving the reactor.
- (b) An aqueous fraction, which is removed.

A side stream, consisting mainly of phenol, but also containing toluene, benzoic acid, diphenyl ether, etc., is treated in two other columns, one for light end separation, in which the toluene separated at the top is recycled to the dehydrator, and the second for heavy end separation, designed to obtain a distillate with phenol meeting the required specifications, while the withdrawal, rich in benzoic acid, is rid at the top of the diphenyl ether it contains by azeotropic distillation in an auxiliary column.

The dehydrator bottom, consisting essentially of benzoic acid, is recycled to the reactor with the acid recovered from the side stream. In this type of process, once-through conversion is about 60 per cent, and the yield of the separation is 85 to 90 molar per cent.

b. Lummus vapor phase process

In this process, benzoic acid is converted at between 250 and 300°C , on a fluidized bed of supported copper and magnesium base catalyst, while the remaining operating parameters are substantially the same as in the liquid phase process. Once-through conversion is lower (50 per cent), but selectivity is higher (90 to 95 molar per cent) due to lesser production of tars.

Fluidization allows better removal of the heat generated by the reaction, by means of coils sunk in the catalyst mass, conveying a coolant fluid and producing high-pressure steam. However, it requires auxiliary units, including cyclone separators to recover entrained solid particles, reactant injection and distillation systems, etc.

The vapor phase process makes it possible to regenerate the solid catalyst continuously by controlled combustion of coke deposits. This operation takes place in a second

reactor, supplied from the first by pneumatic or gravity transport, while the removal and recycling of the regenerated catalyst system take place in similar conditions. Prior preheating and vaporization of the reactants are indispensable for gas phase conversion.

The total yield of the oxidation of toluene to phenol varies according to the technology and operating conditions, from between 75 and 80 molar per cent in the liquid phase to between 80 and 85 per cent in the vapor phase. Its economics in comparison with competing methods, including the cumene method, which is the most widespread and shows the highest performance, depends closely on the price differential existing between the raw materials employed (benzene and toluene).

10.1.6 Other industrial methods for manufacturing phenol

10.1.6.1 Oxidation of cyclohexane

This method, developed in particular by *DSM, ICI, IFP, Inventa, Zimmer*, etc., led *Scientific Design* to build a single industrial plant in Australia, which operated for a relatively short time. It uses benzene as the raw material, and comprises the following three main steps:

- Catalytic hydrogenation of benzene to cyclohexane (see Section 12.1), normally in the liquid phase, around 200°C, at $4 \cdot 10^6$ Pa absolute, in the presence of a nickel or platinum base catalyst, which is highly sensitive to the existence of sulfur compounds in the raw material.
- Oxidation in air of the cyclohexane in a mixture of cyclohexanol and cyclohexanone ($\Delta H_{298}^0 = -295$ kJ/mol) between 145 and 175°C, and between 0.8 and $1 \cdot 10^6$ Pa absolute. This operation takes place in the liquid phase in two versions:

- (a) In the presence of a soluble cobalt salt (naphthenate or octoate) as catalyst, in which case an alcohol/ketone mixture is obtained in the molar ratio 1/1.
- (b) With the addition of boric acid, capable of esterifying the cyclohexanol formed in the reaction and thus preventing its subsequent oxidation (Scientific Design option). Once they are isolated, the boric esters are easily hydrolysed and the acid recovered can be recycled. To prevent this reaction from taking place inside the oxidation reactor, however, the water formed must be removed as thoroughly as possible, and this is done by exploiting the azeotropy between water and cyclohexane. This method, derived from the research by Bashkirov, yields a cyclohexanol/cyclohexanone mixture in a molar ratio of between 9 and 10/1.

With cobalt salts, once-through conversion is 4 to 6 per cent and yield is about 80 molar per cent. The use of boric acid serves to raise these values to 10 and 90 per cent respectively.

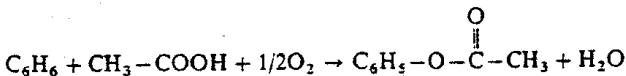
• Dehydrogenation of the cyclohexanol/cyclohexanone mixture to phenol. The alcohol forms with the phenol an azeotrope with a high phenol content (for example, 75 molar per cent at 12 kPa absolute). In order to employ distillation as a means of purification, this means that the reactor output must have a phenol content higher than that of the azeotrope. In practice, conversion takes place in the vapor phase with platinum base

catalysts deposited on alumina, between 250 and 350°C. Conversion is virtually complete, and phenol selectivity is 98 molar per cent. The by-product hydrogen can be used to hydrogenate benzene to cyclohexane.

10.1.6.2 Acetoxylation of benzene

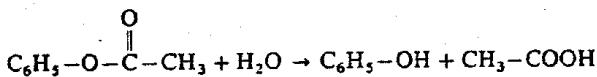
This method, developed in particular by *Mitsubishi*, comprises two main steps:

- Acetoxylation of benzene by acetic acid in the presence of air and a palladium base catalyst, by the following overall reaction mechanism:



The operation takes place in the liquid phase, around 150°C, with palladium nitrate and a selectivity of 72 molar per cent, but is accompanied by severe corrosion. It appears preferable to carry out the reaction in the vapor phase, with a catalyst deposited on alumina, promoted by gold and alkaline acetates, to prevent the formation of diphenyl or the direct production of phenol, which ultimately reduces selectivity. Between 180 and 200°C and at $0.5 \cdot 10^6$ Pa absolute, the yield is 75 molar per cent, with a once-through conversion of about 10 per cent.

- Hydrolysis of phenyl acetate by the following reaction:



This takes place at about 600°C and atmospheric pressure, with a once-through conversion better than 70 per cent and a selectivity of 99 molar per cent.

10.1.6.3 Direct oxidation of benzene

Many attempts have been made to achieve the direct oxidation of benzene, activated in various ways, including radiation. Although a number of experimental semi-industrial installations have been built, especially in the United States, the selectivities obtained were insufficient in most cases to envisage the large-scale implementation of this type of technology in the short or even medium term.

10.1.6.4 Treatment of coal tars

Phenol can be obtained from coal tars by two methods:

- (a) Directly by separation of the product contained in this type of feedstock, at the rate of 0.5 to 1.5 per cent weight.
- (b) Indirectly by hydrodealkylation of cresols, also present in a content comparable with that of phenol.

In the former case, tar treatment first involves the separation of phenolic and cresylic acids, which are then regenerated in the presence of a CO₂-rich gas and then isolated by distillation. In the second case, the cresols are converted in the vapor phase, around

(France conditions, mid-1986)

Phenol production route	Benzene sulfonation	Benzene chlorination	Benzene oxychlorination	Cumene method		Toluene oxidation
				Alkylation	Oxidation	
Typical technology	-	Dow	Hooker-Raschig	UOP	UOP	Dow
Production capacity (t/year)	50,000	50,000	50,000	70,000	50,000	50,000
Battery limits investments (10 ⁶ US\$)	33	55 ⁽¹⁾	32	9	30	37
Consumption per ton of product						
Raw materials						
Propylene (t)	-	-	-	0.375	-	-
Benzene (t)	1.1	0.95	0.97	0.685	-	1.20
Toluene (t)	-	-	-	-	-	-
Cumene (t)	-	-	-	-	1.35	-
By-products						
Sodium sulfite and sulfate (t)	1.7	-	-	-	-	-
Diphenyl (kg)	-	50	-	-	-	-
Diphenyl ether (kg)	-	50	-	-	-	-
Benzene (kg)	-	-	-	-	-	10
Hydrocarbons (kg)	-	-	-	50	-	-
Acetone (t)	-	-	-	-	0.61	-
Heavy products (kg)	-	-	-	-	0.10	-
Utilities						
Steam (t)	2.0	9.0	16.5	-	3.5	9.0
Electricity (kWh)	100	3,900	350	30	260	600
Fuel (10 ⁶ kJ)	15	5.5	14	4.5	(-)4.5	3.5
Cooling water (m ³)	80	250	50	50	350	650
Boiler feed water (m ³)	-	-	-	-	-	-
Chemicals and catalysts (US\$)						
Sodium chloride (t)	2	18 ⁽²⁾	8	6	9	25
Caustic soda (t)	-	0.20	-	-	-	-
Hydrochloric acid (t)	1.70	-	-	-	-	-
Sulfuric acid (t)	1.35	-	0.25	-	-	-
Labor (Operators per shift)	7	15	7	1	5	5

(1) Including sodium chloride electrolysis. (2) Including electrode consumption.

680°C, in tubular reactors designed for the simultaneous production of high-pressure steam using the heat generated by the reaction ($\Delta H_{298}^{\circ} \approx -110$ kJ/mol). The main by-products formed are toluene and benzene, derived from the dehydroxylation of cresols and the hydrogenation of phenol.

10.1.7 Economic data

Table 10.2 summarizes the main economic data about the synthesis of phenol by industrial processes today.

10.1.8 Uses and producers

Tables 10.3a and 10.3b give the average commercial specifications of cumene and phenol respectively (for chlorination).

TABLE 10.3a
AVERAGE COMMERCIAL SPECIFICATIONS OF CUMENE

Characteristics	Values
Purity (% Wt) min.	99.9
Butybenzenes (ppm) max.	500
n-propylbenzene (ppm) max.	500
Ethylbenzene (ppm) max.	500
Lower aromatics (ppm) max.	300
Higher aromatics (ppm) max.	500
Phenolic compounds (ppm) max.	10
Sulfur compounds (ppm) max.	2
$d_{40}^{20(1)}$	0.864 to 0.867
Acid wash color max.	2
Bromine number max.	100
Distillation range (°C) max.	1 around 152°C

(1) Specific gravity, 68.0/39.2.

TABLE 10.3b
AVERAGE COMMERCIAL SPECIFICATIONS OF PHENOL

Characteristics	Values
Crystallization temperature (°C) min.	40.6
Distillation range (°C) max.	1 around 190°C
Water (ppm) max.	200
Carbonyl compounds (ppm) max.	50
Bromination test (%) min.	97.5
Color (Apha) max.	20

Table 10.4 lists the main applications of phenol in 1984 in Western Europe, the United States and Japan, as well as the production, capacities and consumption figures for these three geographic areas.

TABLE 10.4
PHENOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Adipic acid	4	1	—
Aniline	—	1	12
Bisphenol A	21	24	26
Caprolactam	17	16	5
Phenolic resins	34	35	47
Salicylic acid	3	1	1
Xylenols	5	5	—
Miscellaneous ⁽¹⁾	16	17	9
Total	100	100	100
Sources (% product)			
Benzene sulfonation	—	—	2
Cumene oxidation	82	97	97
Toluene oxidation	17	2	—
Miscellaneous ⁽²⁾	1	1	1
Total	100	100	100
Production (10 ³ t/year)	1,070	1,310	275
Capacity (10 ³ t/year) ⁽³⁾	1,415	1,460	380
Consumption (10 ³ t/year)	945	1,275	255

(1) Alkyphenols (*p*-tert butylphenol, *o*-cresol, dodecylphenol, nonylphenol, *p*-tert-octylphenol), chlorinated phenols (2,4-dichlorophenol, pentachlorophenol), cyclohexanol, dyes, medicinals; solvents; picric acid,...

(2) Extraction from petroleum and coke oven tars or off-gas caustic wash streams.

The worldwide production capacity of phenol was about $4.7 \cdot 10^6$ t/year in 1984 and nearly $5.1 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	1.5	Western Europe	1.5	Middle East	—
Canada	<0.1	Eastern Europe	1.4	Japan	0.4
Latin America	0.2	Africa	—	Asia and Far East	0.1

10.2 ACETONE

About one-third of the acetone ($d_4^{20} = 0.790$ ⁽²⁾, mp = -94.6°C , bp_{1.013} = 56.1°C) produced worldwide is derived from the dehydrogenation of isopropanol (Table 10.5). However, it is also obtained by various other methods, mainly the following:

(2) Specific gravity, 68.0/39.2.

- (a) Oxidation of cumene and splitting of the hydroperoxide formed into phenol and acetone (see Section 10.1.4).
- (b) Direct oxidation of propane/butane mixtures, or, more generally, of a naphtha, into a wide variety of oxygen-containing compounds, including acetone (see Section 8.1.3). This is the case of *BP Chemicals*, whose Hull plant (United Kingdom) has a production capacity of 27,000 t/year.
- (c) Co-oxidation of propylene and isobutane to propylene oxide and tertiary butyl alcohol, by a technology industrialized by *ARCO Chemical* (formerly *Oxitane*) yielding acetone among the main by-products (see Section 7.2.4).
- (d) Oxidation of isopropanol to acetone and hydrogen peroxide, by a technique developed by *Shell* and used in one industrial plant until 1980.
- (e) Direct oxidation of propylene by air in the presence of a coordination complex, by a method similar to the one commercialized by *Wacker/Hoechst* for the manufacture of acetaldehyde (see Section 8.1.4).
- (f) Acetone-butanol fermentation (see Section 9.3.1.3).

TABLE 10.5
RELATIVE IMPORTANCE OF THE DIFFERENT INDUSTRIAL WAYS
FOR SYNTHESIZING ACETONE WORLDWIDE IN 1986

Routes	% Wt of capacity
Cumene oxidation.....	75
Isopropanol dehydrogenation.....	17
Propylene oxidation.....	4
Miscellaneous ⁽¹⁾	4
Total	100

(1) By-product of chemicals synthesis.

Of these various methods, the only ones discussed in this section are those not already dealt with in the previous chapters:

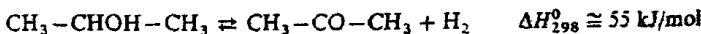
- (a) Isopropanol conversion by dehydrogenation or oxidation.
- (b) Direct oxidation of propylene.

The production of isopropanol, which is dealt with in Section 9.2, is not re-examined here.

10.2.1 Acetone production by dehydrogenation of isopropanol

10.2.1.1 Principle

This conversion takes place according to the following overall reaction mechanism:



The fraction x of isopropanol converted to acetone is expressed as a function of the operating pressure P (Pa) and the absolute temperature T , by the following formula:

$$x = \left(1 + \frac{10^5 P}{k_p} \right)^{-0.5}$$

where

$$\log k_p = -\frac{2758}{T} + 1.51 \log T + 1.76$$

From the thermodynamic and kinetic standpoints, dehydrogenation is favoured by an increase in temperature. At 325°C and atmospheric pressure, the theoretical conversion reaches nearly 98 per cent. It should be practically total at 525°C. In fact, a number of side reactions occur at these temperatures, including the dehydration of isopropanol to propylene.

This makes the use of catalysts indispensable. Copper, nickel, zinc based systems are used in the vapor phase, promoted or not, in metallic or oxide form, and possibly deposited on a support. The lower temperature ($\approx 150^\circ\text{C}$) reaction can be carried out in the liquid phase, in the presence of Raney nickel. The thermodynamic equilibrium in this case is shifted in the desired direction by the continuous removal of the hydrogen produced. It is also necessary to extract the acetone from the reaction medium upon its formation, by vaporization for example, owing to the inhibitory action it exerts on the activity of the catalyst.

10.2.1.2 Industrial manufacture

A. Liquid phase processes, the IFP process (Fig. 10.5)

This process applies not only to the production of acetone, but more generally to the conversion of aliphatic secondary alcohols to the corresponding ketones. It constitutes a highly flexible technique, making it possible to treat isopropanol and 2-butanol in the same plant, in successive runs.

Catalytic dehydrogenation takes place in the liquid phase at 150°C and atmospheric pressure, in the presence of Raney nickel. An inert high-boiling solvent is used to raise the reaction temperature and to keep the mixture in the liquid state. The catalyst remains in suspension by means of agitation, which is either mechanical or achieved by the circulation of fluids by a thermosyphon effect. The heat required for the reaction and the heat of vaporization of the products are provided by external heating and the introduction of the feed in the vapor state.

The reactor output enters a fractionation section, where the unconverted alcohol is first separated and recycled. The hydrogen strips a non-negligible amount of acetone, which is recovered by water scrubbing. The resulting aqueous solution is distilled to obtain acetone in a purity of over 99.5 per cent weight. Yield and selectivity are very high (98.5 molar per cent), and the hydrogen produced is extremely pure.

B. Vapor phase processes (Fig. 10.6)

In this type of technology, the reaction is conducted between 350 and 400°C, and $0.2 \cdot 10^6$ Pa absolute, in tubular units featuring the flow of a heat transfer fluid (steam,

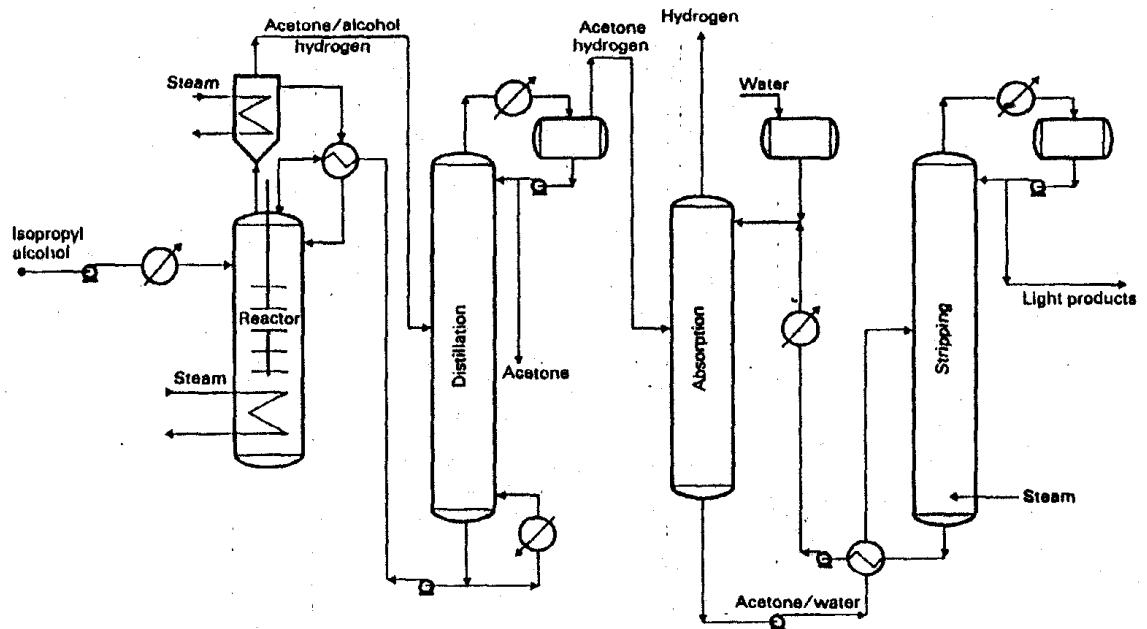


Fig. 10.5. Acetone manufacture by liquid phase dehydrogenation of isopropyl alcohol. IFP process.

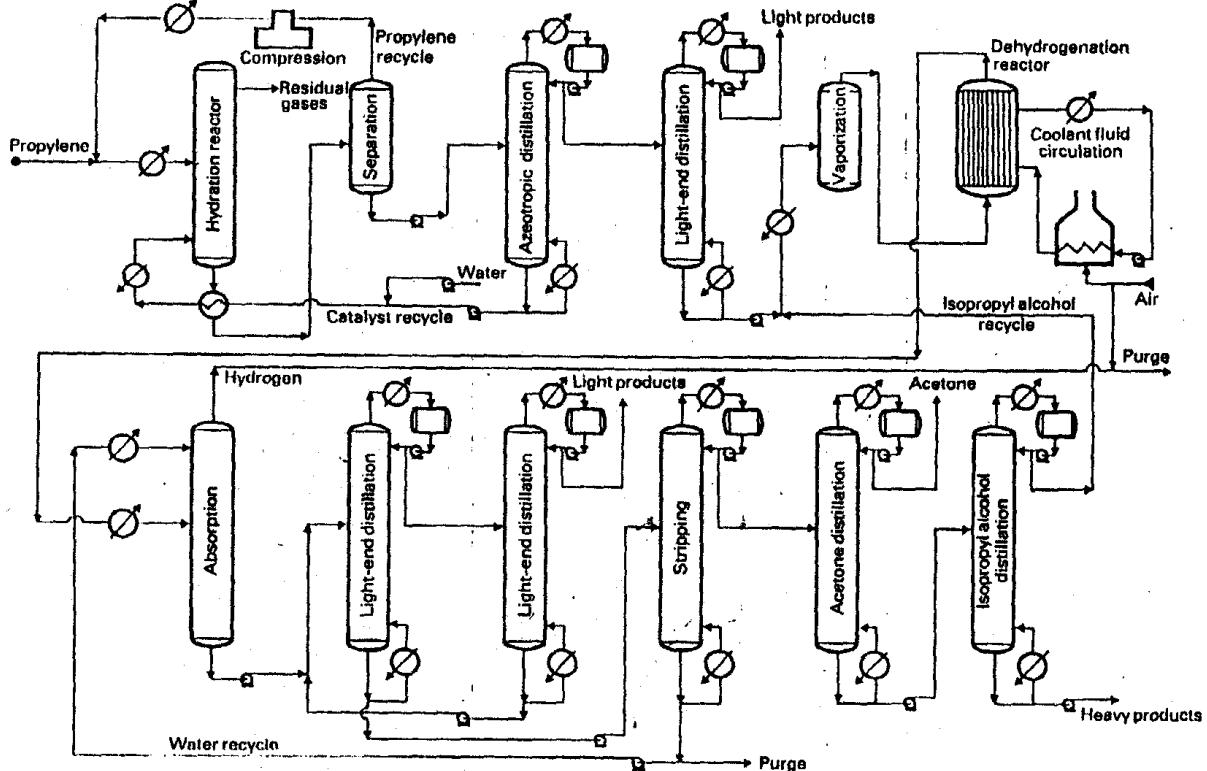


Fig. 10.6. Acetone manufacture by vapor phase dehydrogenation of isopropyl alcohol.

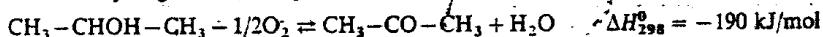
preheated air etc) on the shell side, designed to compensate for the endothermicity of the reaction, and the catalyst on the tube side. Good performance has been achieved with systems containing 7 to 8 per cent weight zinc oxide, promoted by zirconium oxide (0.5 per cent weight) and deposited on a pumice carrier. Isopropyl alcohol and hydrogen in a molar ratio of 1:1 are sent at 380°C on the catalytic bed operating with a LHSV of about 1.5 h⁻¹. Once-through conversion, as high as 98 per cent at the beginning of the runs, drops rapidly to less than 90 per cent owing to organic deposits which reduce the activity of the catalyst. Its regeneration by combustion at 500°C using a mixture of oxygen and nitrogen (2 and 98 per cent volume respectively) must be carried out at ten-day intervals. To guarantee continued production, it is therefore necessary to have several reactors in parallel, with a staggered operating schedule.

The operation presents a number of drawbacks, including the difficulty of temperature control in the neighborhood of 400°C. In the earliest versions, yields also failed to exceed 75 to 85 molar per cent. The latest technologies (*BP, Standard Oil* in particular) claim total yields approaching 98 molar per cent, with average once-through conversions above 90 per cent, for a reaction temperature ranging between 450 and 550°C.

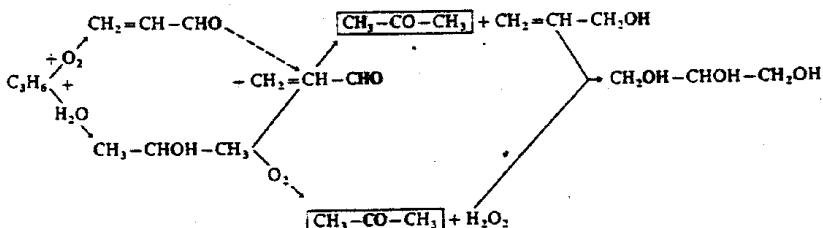
The reactor output is first cooled and then scrubbed with water to rid the hydrogen of entrained reactants and products, followed by light and heavy ends separation in a series of three distillation columns, the second producing acetone to specifications at the top, with the third column designed to recover unconverted isopropanol to be recycled. If the feed consists of the azeotrope containing 87 per cent weight alcohol, three additional columns are required for the purification of the acetone and the recycling of isopropanol in a sufficient concentration.

10.2.2 Acetone production by the oxydation of isopropanol (Shell process)

In theory, and in the presence of catalyst systems similar to those employed for alcohol dehydrogenation, this process involves the following exothermic conversion:



The practical application of this reaction, conducted by *Shell Chemical* on an industrial scale in its Norco, Louisiana, plant, shut down in 1980, is much more complex. Indeed, the initial objective was to synthesize glycerin from propylene, with the production of acetone (or methyl ethyl ketone) as a subsidiary product. The general scheme of this operation is as follows:



It comprises the following:

- Oxidation of propylene to acrolein. This conversion takes place in the vapor phase, in the presence of a copper oxide base catalyst.
- Simultaneous sulfuric hydration of propylene to isopropanol.
- Action of acrolein on part of the isopropyl alcohol, in the presence of a catalyst containing oxides of magnesium and zinc, to obtain acetone together with allyl alcohol.
- In parallel, oxidation of the remaining fraction of isopropanol to acetone and hydrogen peroxide. This reaction, a derivative of the theoretical transformation, takes place in the liquid phase between 70 and 160°C, at about $1 \cdot 10^6$ Pa absolute, in slightly acidic medium, always saturated with oxygen. It does not necessarily require any initiator or catalyst.
- The action of the hydrogen peroxide produced on allyl alcohol to convert it to glycerin, in the presence of a tungsten oxide base catalyst system.

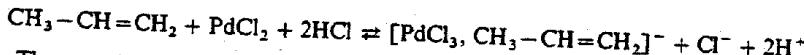
Methyl ethyl ketone can be obtained as a co-product instead of acetone, by replacing the isopropanol by secondary butyl alcohol.

10.2.3 Acetone production by the direct oxidation of propylene (Hoechst/Wacker process)

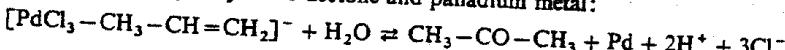
The first industrial plant using this method, developed jointly by *Wacker Chemie* and *Hoechst*, and currently commercialized by *Hoechst-Uhde*, dates from 1964 with the construction of a plant with a production capacity of 35,000 t/year of acetone in Yokkaichi, Japan, on behalf of *Kyowa Petrochemicals*.

10.2.3.1 Principle

The oxidation technique is applied to propylene, in the presence of palladium chloride and copper chloride, initially developed for the manufacture of acetaldehyde from ethylene (see Section 8.1.4). In principle, the transformation reaction comprises the formation of a complex with propylene, in the presence of palladium chloride and in hydrochloric acid medium:

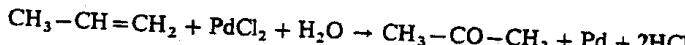


The complex is hydrolysed to acetone and palladium metal:

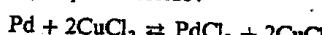


The degree of oxidation lost by the palladium must then be restored, so that the following reaction sequence is involved:

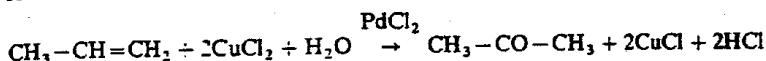
- Acetone production:



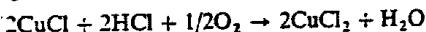
- Oxidation of palladium by cupric chloride:



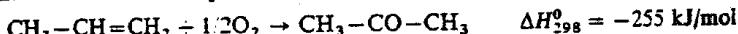
The combination of these two conversions constitutes the first step of the process:



(c) Regeneration of cupric chloride by air or oxygen:



This represents the second step of the process. On the whole, the following overall exothermic reaction takes place:



The reaction rate is directly proportional to the rate of formation of the complex between propylene and palladium chloride, in other words to the rate of absorption of the olefin in the PdCl_2 solution. The rate decreases with a rising number of carbon atoms in the feed, but is substantially the same for ethylene and propylene.

As a rule, the propylene is oxidized between 90 and 120°C, at low pressure (between 0.9 and $1.2 \cdot 10^6$ Pa absolute), and the catalyst is regenerated in the same conditions. The catalyst solution, whose pH is kept between 1 and 2, contains about 100 times more palladium chloride by weight than cupric chloride. In these conditions, once-through conversion reaches nearly 98 to 99 per cent and the yield is 92 to 94 molar per cent. This technique also applies to the oxidation of *n*-butenes to methyl ethyl ketone, with an olefin conversion of 95 per cent and a molar yield between 85 and 88 per cent.

10.2.3.2 Industrial manufacture (Fig. 10.7)

The installation comprises the vaporization and heating to 115°C of propylene, introduced at the base of an oxidation reactor to which the catalyst solution is also added, preheated to the same temperature, and operating at $1.2 \cdot 10^6$ Pa absolute. The exit streams leaving at 120°C are flashed at $0.5 \cdot 10^6$ Pa absolute, to enable the separation of the reactants and products of the reaction medium in gaseous form, and the regeneration of the catalyst kept in the liquid phase.

The latter operation takes place around 110°C, at $1.2 \cdot 10^6$ Pa absolute, in the presence of precompressed air. By flashing at $0.15 \cdot 10^6$ Pa absolute, the off-gases are separated from the catalyst system, which is sent to the oxidation reactor after the addition of make-up hydrochloric acid and chlorides to offset any losses. The organic compounds, including acetone, stripped in the gas phase, are recovered by water scrubbing in an absorption column operating at atmospheric pressure around 50°C, and recycled with the catalyst solution.

The crude acetone produced in the first step of the reaction is first rid of gaseous components (unconverted propylene, propane etc.). The small amounts entrained are absorbed by scrubbing with water at 50°C and atmospheric pressure. The acetone is then distilled to separate the light ends, particularly propionaldehyde, with heavy ends separation to remove the heavy products (water, acetic acid, chlorinated compounds such as mono- and dichloroacetones, mono- and dichloropropionaldehydes, etc.). Treatment with caustic soda, carried out in the same final column, facilitates the destruction of the chlorinated compounds and improves the final yield of the operation.

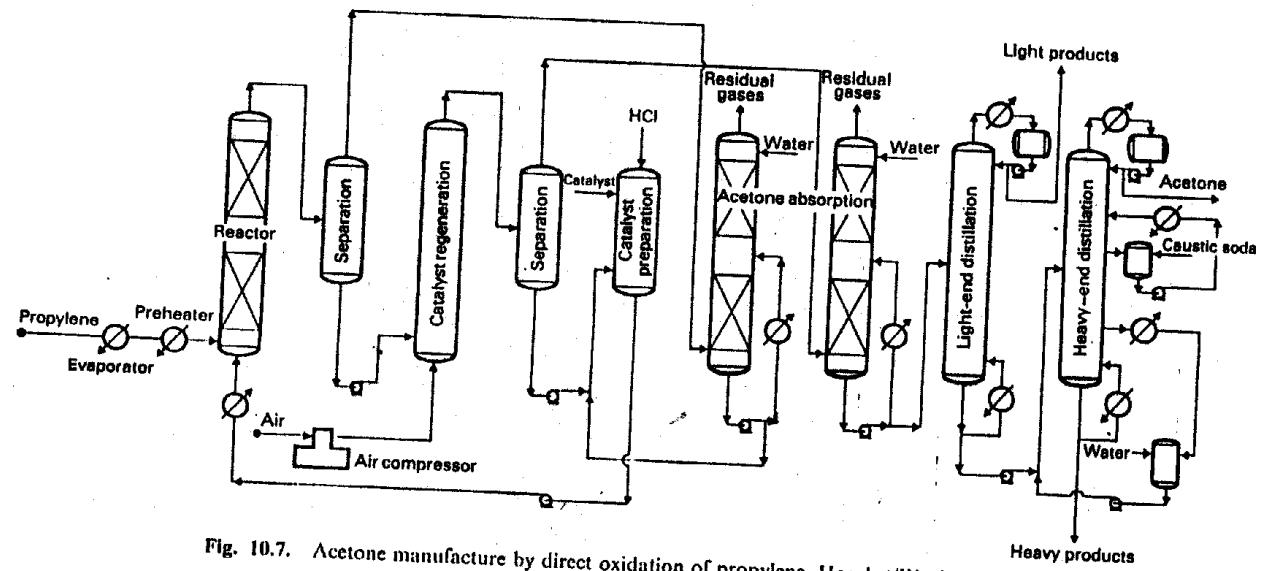


Fig. 10.7. Acetone manufacture by direct oxidation of propylene. Hoechst/Wacker process.

10.2.4 Economic data

Table 10.6 provides figures on investments and consumption, concerning the production of acetone by the dehydrogenation of isopropanol in the liquid and vapor phases, and also by the direct oxidation of propylene.

TABLE 10.6
ACETONE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Acetone production route	Isopropanol dehydrogenation		Direct oxidation of propylene
	Liquid phase	Vapor phase	
Typical technology	IFP	Standard Oil	Wacker/Hoechst
Production capacity (t/year)	25,000	80,000	80,000
Battery limits investments (10^6 US\$)	5	24	32
Consumption per ton of acetone			
Raw materials			
Propylene (t) (as 100%)	—	0.80	0.78
Isopropanol (t)	1.05	—	—
Utilities			
Steam (t)	3.8	6.0	7.5
Electricity (kWh)	55	330	380
Cooling capacity ($^{\circ}$ C) (10^6 kJ)	0.3	—	—
Cooling water (m^3)	150	340	590
Process water (m^3)	—	1	—
Treated water (m^3)	—	—	3
Chemicals and catalysis (USS)	3	12	7
Caustic soda (kg)	—	—	5
Hydrochloric acid (kg)	—	—	15
Labor (Operators per shift)	1.5	5	4

10.2.5 Uses and producers

The average commercial specifications of acetone are listed in Table 10.7.

Table 10.8 lists the applications of acetone in 1984 in Western Europe, the United States and Japan, together with the production, capacity and consumption figures for these three geographic areas at the time.

TABLE 10.7
AVERAGE COMMERCIAL SPECIFICATIONS OF ACETONE

Characteristics	Values
Purity (% Wt) (min.) d_{40}^{20} ⁽¹⁾	99.5
Distillation range (°C).....	0.791 to 0.793
Acidity (ppm) max. (expressed as acetic acid).....	1 between 55.8 and 56.8
Water (ppm) max.....	10
Non-volatile residue (ppm) max.....	3,000
Permanganate test (minutes) min.....	10
Color (Pt/Co) max.....	240
	5

(1) Specific gravity, 68.0/68.0.

TABLE 10.8
ACETONE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Aldol chemicals ⁽¹⁾	13	19	23
Bisphenol A.....	10	9	8
Methylmethacrylate.....	29	28	44
Solvent.....	38	23	25
Miscellaneous ⁽²⁾	10	21	—
Total	100	100	100
Sources (% product)			
Cumene oxidation.....	71	84	76
Isopropanol dehydrogenation.....	24	16	—
Propylene oxidation.....	—	—	10
Miscellaneous ⁽³⁾	5	—	14
Total	100	100	100
Production (10^3 t/year).....	730	855	245
Capacity (10^3 t/year) ⁽⁴⁾	1,015	1,310	355
Consumption (10^3 t/year).....	660	890	240

(1) Diacetone alcohol, hexylene glycol, isophorone, mesityl oxide, methylisobutylcarbinol, methylisobutylketone.

(2) Acetone — formaldehyde condensates, diphenylamine condensates, drugs, isoprene, methyl *n*-amylketone, methylbutynol, pharmaceuticals (cosmetics, toiletries), substituted *p*-phenylenediamines.

(3) Acetic acid manufacture by-product, cymene oxidation into cresol and acetone.

(4) The worldwide production capacity of acetone was more than $3.7 \cdot 10^6$ t/year in 1984 and 1986, with the following distribution:

United States	1.31	Western Europe	1.02	Middle East	—
Canada	0.04	Eastern Europe	>0.64	Japan	0.36
Latin America	0.16	Africa	0.08	Asia and Far East	>0.12

10.3 METHYL ETHYL KETONE

Most of the methyl ethyl ketone ($d_4^{20} = 0.805$ ⁽³⁾, mp = -85.9°C , bp_{1.013} = 79.6°C) manufactured worldwide is produced by the dehydrogenation of secondary butanol. Smaller quantities are obtained as a by-product of the oxidation of n-butane to acetic acid. This is the case in the United States of *Celanese* in its Pampa, Texas, plant (40,000 t/year) and of *Union Carbide* in Brownsville, Texas (35,000 t/year). Plants of this type built in Western Europe have been shut down, including the Konan plant in the Netherlands (20,000 year at Europoort) which was closed in 1979.

10.3.1 Processes for synthesizing methyl ethyl ketone

As a rule, all industrial methods for producing acetone can be adapted to manufacture methyl ethyl ketone, and most process licensors claim the advantage of this flexibility in their installations. The various possibilities will be reviewed briefly, with references to the chapters and sections dealing with these matters in greater detail.

10.3.1.1 Technologies already industrialized

- Dehydrogenation of secondary butanol, itself produced by the sulfuric or direct hydration of n-butenes (see Section 9.3.2). Two alternatives are available for carrying out this operation:
 - (a) In the liquid phase (IFP process), around 150°C , in the presence of a Raney nickel base catalyst, with a yield of about 98 molar per cent (see Section 10.2.1.2, paragr. A).
 - (b) In the vapor phase (Standard Oil process), around 400°C , at $0.2 \cdot 10^6$ Pa absolute, in the presence of zinc oxide base catalysts on pumice carrier, with a yield of about 95 molar per cent (see Section 10.2.1.2, paragr. B).
- Oxidation of n-butane (see Section 8.2.2.1, paragr. A).

10.3.1.2 Potential commercial technologies

- Oxidation of secondary butanol to methyl ethyl ketone and hydrogen peroxide, developed by *Shell* to produce glycerin (see Section 10.2.2).
- Direct oxidation of n-butenes by the Wacker/Hoechst process, in the presence of palladium and copper chlorides, around 110°C , at $1.2 \cdot 10^6$ Pa absolute, with a yield of 85 to 88 molar per cent (see Section 10.2.3).
- Splitting of 2-phenyl butane hydroperoxide into phenol and methyl ethyl ketone, this intermediate being itself obtained by the alkylation of benzene by means of n-butenes (see Section 10.1.4).

(3) Specific gravity, 68.0/39.2.

A number of differences nevertheless appear between the purification schemes of acetone and methyl ethyl ketone. The existence of a water/methyl ethyl ketone heteroazeotrope ($\text{bp}_{1.013} = 73.4^\circ\text{C}$, water content 11.3 per cent weight) complicates the separation of the products.

10.3.2 Economic data

Table 10.9 lists the main economic data available on the production of methyl ethyl ketone from *n*-butenes, in two steps involving the intermediate formation of secondary butyl alcohol by sulfuric hydration followed by dehydrogenation, or directly by the Wacker/Hoechst technology.

TABLE 10.9
METHYLETHYL KETONE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 50,000 t/year

Methyl ethyl ketone route	Sulfuric hydration/vapor phase dehydrogenation	Direct oxidation
Typical technology	Maruzen	Wacker/Hoechst
Battery limits investments (10^6 US\$).....	18	35
Consumption per ton of methyl ethyl ketone		
Raw materials		
C ₄ cut ⁽¹⁾ (t)	1.30	1.35
By-products		
C ₄ cut (t)	0.35	0.25
Hydrogen (kg)	33	—
Utilities		
Steam (t)	15	8
Electricity (kWh)	150	350
Fuel (10^6 kJ)	4.2	0.2
Cooling water (m ³)	750	400
Process water (m ³)	15	10
Treated water (m ³)	—	—
Chemicals and catalysts (US\$)	5	6
Hydrochloric acid (kg)	—	115
Sulfuric acid (kg)	10	—
Caustic soda (kg)	25	20
Sodium bisulfite (kg)	—	80
Labor (Operators per shift)	4	4

(1) Composition (% Wt): *n*-butenes = 73.5, isobutene = 2.0, C₅- = 2.0, butanes = 22.5.

10.3.3 Uses and producers

Methyl ethyl ketone is essentially intended for solvent uses, in direct or indirect form, chiefly in paints and resins, nitrocellulose varnishes, adhesives and inks, and also for lubricant dewaxing. Its average commercial specifications are listed in Table 10.10.

Table 10.14 gives the production, capacities and consumption of methyl ethyl ketone in Western Europe, the United States and Japan in 1984.

TABLE 10.10
COMMERCIAL SPECIFICATIONS OF METHYL ETHYL KETONE

Characteristics	Values
Purity (% Wt) min.	99.5
d_{4}^{20}/d_{4}^{10}	0.805 to 0.807
Distillation range (°C)	1.5 around 79.6
Acidity (ppm) max. (expressed as acetic acid)	30
Water (ppm) max.	1000
Non-volatile residue (ppm) max.	10
Color (Pt/Co) max.	10

(1) Specific gravity, 68.0 68.0.

TABLE 10.11
METHYL ETHYL KETONE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Chemical intermediate		5	2
Solvent		95	
Adhesives	15		
Dewaxing	5		
Paints and coatings	65		
Miscellaneous ⁽¹⁾	10		
Total	100	100	100
Production (10^3 t/year)	265	275	110
Capacity (10^3 t/year) ⁽²⁾	330	320	130
Consumption (10^3 t/year)	155	265	110

(1) Extractive solvent in hardwood pulping and ink production, magnetic tape solvent.

(2) The worldwide production capacity of methyl ethyl ketone in 1984 was around $0.82 \cdot 10^6$ t/year.

Chapter 11

VINYL MONOMERS

Vinyl monomers are well-known for their very high chemical reactivity and their specific ability to form polymers. Since the most direct and easiest synthesis method involved the addition of an acid to acetylene, this compound provided the ideal raw material for a long time. However, acetylene is an expensive raw material, so that, although it is still employed today to manufacture a number of vinyl monomers, a significant part of recent advances in petrochemicals manufacture has consisted in its replacement by ethylene and propylene.

While styrene, for example, can be considered a vinyl derivative, the term is generally used to include:

- (a) Actual vinyl compounds: vinyl acetate and chloride.
- (b) Acrylates and methacrylates.
- (c) Acrylonitrile.

The essential markets for the resulting polymers are fibers, elastomers and plastics.

11.1 VINYL ACETATE

Vinyl acetate ($d_4^{20} = 0.935^{(1)}$, mp = -100.2°C , bp_{1,013} = 72.7°C) is a colorless, flammable liquid in ambient conditions. It is manufactured industrially today by two principal methods:

- (a) The older method is the addition of acetic acid to acetylene in the vapor phase.
- (b) The latest method, which accounts for over 90 per cent of output in the United States and 60 per cent in Japan and Western Europe, is based on the vapor phase reaction of acetic acid and ethylene, in the presence of oxygen.

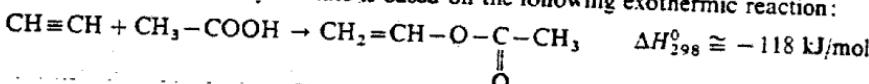
(1) Specific gravity, 68.0:39.2.

11.1.1 Production of vinyl acetate from acetylene

Although this type of reaction was initially developed in the liquid phase (1912), it is mainly the vapor phase processes, developed in particular by Wacker (1930), that have been industrialized. Until 1960, all existing manufacturing facilities worldwide employed this synthesis method. A number of these plants are still in operation, particularly in Western Europe.

11.1.1.1 Principle

The production of vinyl acetate is based on the following exothermic reaction:



In the liquid phase, this conversion takes place at low temperature (between 60 and 80°C), under low pressure (between 0.1 and $0.2 \cdot 10^6$ Pa absolute). Hence it requires a highly active catalyst, such as mercury salts (oxide, sulfate, phosphate, etc.), kept in suspension in an acid (preferably acetic acid) at the rate of 1 to 5 per cent weight. To prevent the formation of large amounts of ethylidene diacetate, the operating temperature must be kept as low as possible. The residence time of acetylene in the catalyst suspension can also be reduced, or a large excess employed. In this case, however, it is indispensable to use a polymerization inhibitor such as HF, BF_3 , etc. In these conditions, the molar yield is higher than 90 per cent.

The vapor phase reaction takes place between 180 and 210°C, at a pressure approaching atmospheric, in the presence of a supported metallic salt as a catalyst. The two components of the catalyst system (support and impregnated phase), which, considered separately, exert only a slight effect on the reaction, derive their influence from a synergistic effect. In practice, the support is activated charcoal and the ideal metals for the purpose are mercury, bismuth, zinc, cadmium etc., usually employed in the form of acetates, as well as benzoates, chlorides, sulfates, phosphates, etc. The reaction scheme is currently assumed to comprise three essential steps:

- (a) Activation of zinc acetate, for example, by activated charcoal, with the formation of a complex.
- (b) Chemisorption of acetylene on the catalyst with conversion of the complex.
- (c) Reaction of acetic acid and adsorbed acetylene.

The catalyst may be poisoned permanently by components such as AsH_3 , PH_3 , H_2S , etc., or temporarily by the formation of deposits of tars or polymers, or ultimately coke. This is corrected by prior scrubbing of the reactants (especially acetylene) by caustic soda, and by periodic regeneration with steam. The average gaseous VHSV, at standard temperature and pressure, is about 200 to 500 h^{-1} . Catalyst life is no longer than a few months (2000 h).

As in the liquid phase, a large excess of acetylene is used, with a molar ratio as high as 2 to 5 in relation to acetic acid, whose once-through conversion ranges between 30 and 70 per cent. The molar yields amount to over 97 per cent on acetic acid and 95 per cent

on acetylene. The main by-products are acetaldehyde (> 1 per cent weight), acetone, crotonaldehyde, ethylidene diacetate, acetic anhydride, acrolein, propionaldehyde, methyl vinyl ketone, etc., as well as unsaturated hydrocarbons (mono- and divinylacetylene, methylacetylene, etc.).

11.1.1.2 Industrial manufacture (Fig. 11.1)

The basic scheme of an industrial plant first comprises the passage of make-up and recycle acetylene through a vaporizer operating at $0.13 \cdot 10^6$ Pa absolute, around 70 to 80°C, into which a countercurrent stream of fresh and recirculation acetic acid is also introduced. This feed, preheated to between 170 and 190°C by heat exchange with the gaseous stream leaving the reaction zone and with steam, is then sent to the reactor, which operates with a fixed or fluidized catalyst bed. The catalyst consists of activated charcoal, impregnated to 20 to 30 per cent weight of zinc acetate. In the fixed bed system, it is placed in tubes 5 cm in diameter and 3.5 to 4 m high, around which the circulation of a fluid coolant serves to remove the heat generated by the reaction and to maintain temperature at about 200°C. In a fluidized bed, this control is achieved by means of coils sunk in the catalyst mass. Certain plants include a continuous loop for catalyst regeneration by steam, involving the withdrawal of the solid impregnated with the reactants. The acetylene recovered during this operation is recycled after boosting.

The gas stream leaving the reactor is cooled by heat exchange with the feed, and then partly condensed by scrubbing with cold liquids. This is achieved by using the condensation products themselves, acetic acid, or both in succession. Most of the residual gases, consisting mainly of acetylene, are recycled. A small proportion is purged to prevent the buildup of inert elements in the synthesis loop.

The condensates are purified by distillation in a sequence of columns. The light components are first separated (≈ 35 trays) including gaseous acetylene, which is recycled, and acetaldehyde, acetone, propionaldehyde, acrolein, etc. in the liquid state. An additional column may be used to purify the acetaldehyde contained in this mixture and to return the stripped vinyl acetate and acetic acid to the previous distillation stage. The sequence of operations includes the recovery of pure vinyl acetate (≈ 50 to 60 trays), the separation of divinylacetylene and crotonaldehyde (packed column), and the purification of unconverted acetic acid by heavy ends separation of the heavier components (≈ 30 trays).

To prevent the vinyl acetate from polymerizing during these distillations, it is necessary to operate in the presence of an inhibitor (hydroquinone, diphenylamine, etc.). The equipment used is made of high-alloy steels (Cr 15 to 20 per cent, Ni 10 to 15 per cent).

11.1.2 Manufacture of vinyl acetate from ethylene

The oxidation of ethylene in the presence of acetic acid to produce vinyl acetate can be achieved both in the homogeneous liquid phase and in the vapor phase. In both cases, palladium acts as a catalyst, either through the complexing properties of its chloride, or by means of a deposited metal. However, as with the conversion of acetylene, the liquid phase technology, the first to be developed, found its industrialization hampered in favor of the competitive method, due to the fact that it raises severe corrosion problems.

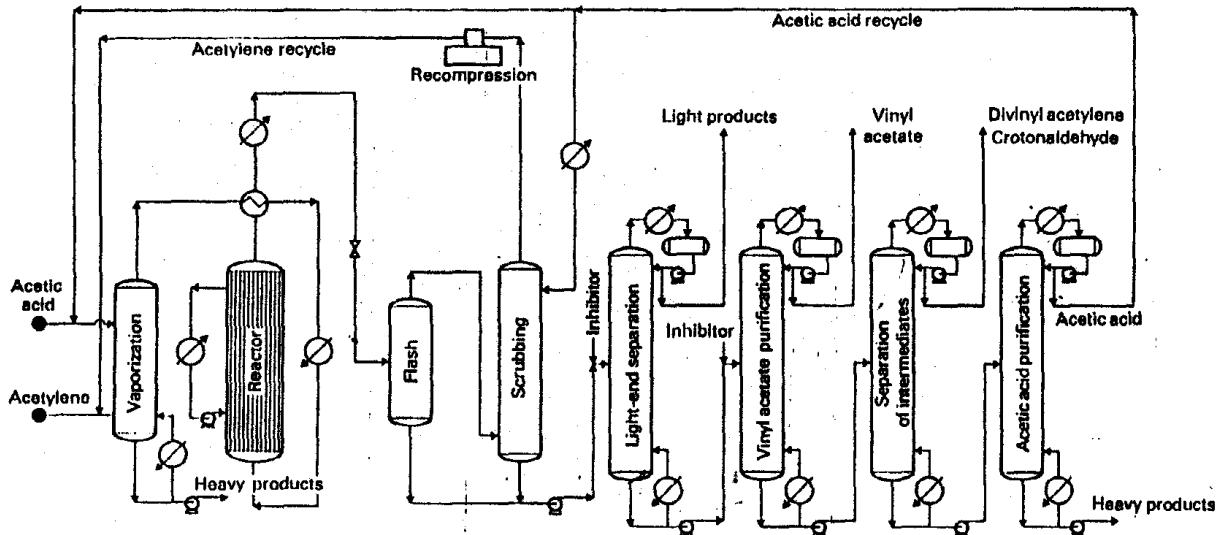


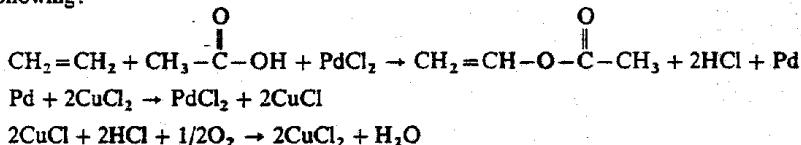
Fig. 11.1. Vinyl acetate manufacture from acetylene.

The principal liquid phase processes, currently abandoned, which saw considerable development, are those of *Hoechst*, *ICI (Imperial Chemical Industries)*, *Nippon Gosei*, etc. Their common feature is operation at moderate temperatures, in the presence of palladium chloride and hydrochloric acid. They are self-sufficient in terms of acetic acid, since they produce acetaldehyde as a by-product, which can be oxidized to the acid and recycled.

Two comparable vapor phase technologies currently share the market. They were developed by *Rhône-Höchst* and *USI (US Industrial Company) Chemicals*, and are distinguished by the large acetic acid make-up which they require, because of the production of too little acetaldehyde by-product. Self-sufficiency can be achieved, for example, by a combination with a polyvinyl alcohol production unit. On the other hand, these processes offer the decisive advantage of eliminating the need for special materials, such as titanium, and of limiting the use of high-alloy steels required to contend with corrosion problems.

11.1.2.1 Liquid phase processes (*Hoechst*, *ICI*, etc.)

This type of process is related in principle to those developed by *Hoechst/Wacker* to manufacture acetaldehyde (see Section 8.1.4) by the once-through oxidation of ethylene by oxygen, in the presence of a redox system, or to produce acetone (Section 10.2.3) from propylene. The main reactions involved in the synthesis of vinyl acetate are the following:



The low solubility of copper salts in acetic acid has led to the discarding of the two-step version in air used to manufacture acetaldehyde. This variant is only justified inasmuch as the reaction, which takes place in aqueous medium, allows the use of dilute ethylene and limits the risks of explosion.

In fact, one important parameter is the water content of the medium, which causes the undesirable production of acetaldehyde by its reaction with ethylene in the presence of palladium chloride, or by the hydrolysis of the vinyl acetate formed. This operating variable can be adjusted to make the acetate production plant self-sufficient in terms of acetic acid. In this case, the acetaldehyde co-produced is oxidized to the acid in a separate section. It is the water content of the acetic acid employed, controlled by the degree of purification of the by-product acid which is recycled, which ultimately serves to determine the vinyl acetate to acetaldehyde ratio. Longer residence time in the reactor or higher temperature also favors the formation of acetaldehyde.

Acetic acid once-through conversion is 20 to 30 per cent, and that of ethylene is 2 to 3 per cent. The molar yield in relation to ethylene is 70 to 80 per cent. The maximum oxygen content of the gases is set by the upper flammability limit (94.5 per cent ethylene, 5.5 per cent oxygen, at 130°C, and $3 \cdot 10^6$ Pa absolute). The oxygen is introduced directly into the catalyst solution, to prevent the precipitation of cupric chloride caused by a lack of oxygen in the medium.

The catalyst solution contains 30 to 50 mg/l of palladium ions. A higher concentration would favor the dimerization of ethylene to butenes. The copper ion content is 3 to 6 g/l. The presence of chlorine ions is necessary to maintain catalyst activity, but it leads to the formation of chlorinated by-products. The remaining by-products are mainly oxalic acid, which yields copper oxalate, esters (acetate), formic acid and carbon dioxide.

In the procedure originally planned for the operation of industrial plants employing this process, the reaction is carried out in a perforated plate column containing the catalyst, at between 110 and 130°C, under $3 \text{ to } 4 \cdot 10^6 \text{ Pa}$ absolute. The circulation gases (fresh and recycled ethylene, recycled oxygen) and acetic acid are introduced at the base of the reactor. Make-up oxygen is introduced directly into the solution. The stream leaving the reactor is cooled and partly condensed:

- (a) The gaseous fraction is recycled after purge and removal of carbon dioxide.
- (b) The liquid portion undergoes a series of fractionations: separation and recycle of unconverted acetic acid, distillation of light products and acetaldehyde, removal of water, purification of vinyl acetate.

Acetaldehyde is separated from the light products by scrubbing with water, concentrated, and then oxidized to acetic acid in the presence of manganese acetate. The intense corrosion implies the use of coatings of titanium, resin-impregnated graphite, ceramics, etc.

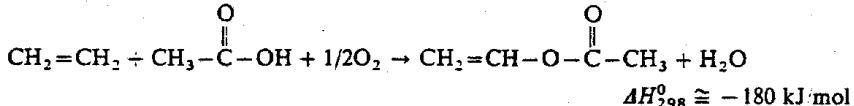
The ICI plant at Wilton in the United Kingdom, with a capacity of 30,000 t/year, had to be shut down on this account, and those belonging to Celanese (United States) and Showa Denka (Japan) under ICI license, had to be altered accordingly. Since then, no other commercial facilities have been built for the liquid phase oxidation of ethylene.

11.1.2.2 Vapor phase processes (Bayer/Hoechst, USI Chemicals)

Vapor phase processes, which were developed in the 1960s, led to the construction of the first industrial plant in 1968. Nearly all the new units built since then employ this method, which continues to supplant the acetylene method.

A. Principle

The following overall reaction is involved:



It takes place between 160 and 180°C, at between 0.5 and $0.8 \cdot 10^6 \text{ Pa}$ absolute, in the presence of a supported palladium base catalyst, on which ethylene and acetic acid are activated by dissociative adsorption thereby becoming capable of combining to form vinyl acetate.

Catalyst systems used today are in fact more complex. The performance of palladium, in a content between 1 and 3 per cent weight, is significantly improved by combining it with other metals such as platinum (USI Chemicals), cadmium and gold (Bayer/Hoechst).

as well as bismuth, barium, iron, noble metals in general etc., at the rate of 0.2 to 2 per cent weight. Catalyst activity is also easier to control by the addition of an alkaline acetate, of sodium (*USI Chemicals*), or potassium (*Bayer/Hoechst*), introduced either at each regeneration (*USI Chemicals*), or continuously (*Bayer/Hoechst*) to offset evaporation losses, in a concentration of 0.5 to 5 per cent weight of catalyst. The support is either a low surface area α alumina (*USI Chemicals*) or conditioned silica in 4 to 5 mm diameter spheres (*Bayer/Hoechst*). These improvements serve to multiply the productivity of supported palladium without adjuvants by a factor of 5. Residence time is about 10 s. Ethylene once-through conversion is 8 to 12 per cent, with a vinyl acetate molar selectivity of 92 per cent. 7.5 per cent is converted to carbon dioxide, 0.5 per cent to ethyl and methyl acetates and acetaldehyde. Acetic acid in sub-stoichiometric mixture (0.25 to 0.5 in moles in relation to ethylene) undergoes once-through conversion of 20 to 25 per cent, but nearly all to vinyl acetate.

To prevent excessive ethylene losses in the waste gas purge, it is preferable to use oxygen rather than air as the oxidizing agent. However, the O₂ content must be such that the composition of the reaction mixture remains outside the flammability range, that is to say less than 8 to 9 molar per cent. In these conditions, a typical feed gas composition, expressed as per cent volume, would be ethylene 50, acetic acid 15, oxygen 6, and inert gases 29.

The presence of water, resulting particularly from the recycling of dilute acetic acid, reduces the activity of certain catalysts, especially those with a silica support, and favors the formation of acetaldehyde. Reconcentration of the recycle streams is therefore necessary in this case. The overall molar yield of the vapor phase processes, in relation to the ethylene feed, is 88 to 90 per cent. It is about 98 per cent in relation to acetic acid.

B. Industrial manufacture (Fig. 11.2)

Industrial transformation takes place in tubular reactors, usually two reactors in parallel. The fresh and recycle acetic acid feed, to which are added make-up ethylene and recirculation ethylene previously heated by heat exchange with the reactor output, is first vaporized at about 140°C and $1 \cdot 10^6$ Pa absolute, and then raised to 160°C by passage through a heat exchanger. The oxygen (and any alkaline acetate) required is then added in proportions and dispersion conditions such that the composition of the mixture lies outside the flammability range. A coolant fluid flow on the shell side of the reactor removes the heat generated and produces low-pressure steam.

The gaseous stream leaving the reaction zone around 160°C, at $0.7 \cdot 10^6$ Pa absolute, is cooled to 130°C by heat exchange with the ethylene recycle, and partly condensed by supplementary cooling, absorption by acetic acid and scrubbing with water. This operation serves to recover the vinyl acetate formed and any unconverted acid. The residual gases, chiefly consisting of ethylene and carbon dioxide, are partly purged to prevent the accumulation of inerts in the synthesis loop, and mostly recompressed, and then rid of CO₂ by chemical absorption by potassium carbonate. This reagent is regenerated by stripping, and the purified ethylene is recycled.

The aqueous solution of vinyl acetate and acetic acid is fractionated and purified by distillation. A first column ($\cong 60$ trays) separates a 97 to 98 per cent weight acetic acid recycle stream at the bottom. The overhead units, condenser and settler, are common to two other columns ($\cong 25$ trays each), one for stripping, and the second for dehydration

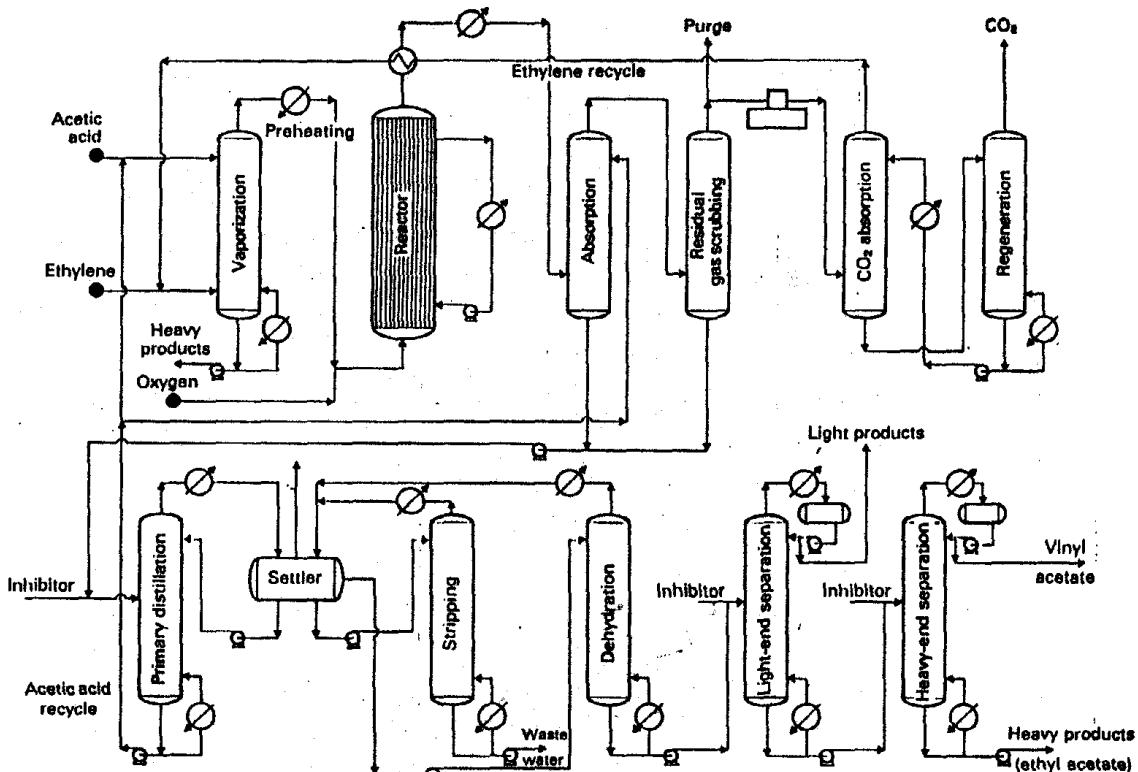


Fig. 11.2. Vinyl acetate manufacture from ethylene. Bayer/Hoechst and USI Chemicals vapor phase processes.

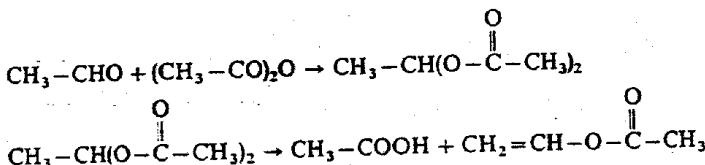
of vinyl acetate. They are fed partly with the distillate from the first separation, rich in vinyl acetate and incondensables (ethylene and oxygen) which, after recompression, are sent to the reaction section, and partly with a vinyl acetate/water heteroazeotrope ($\text{bp}_{1.013} = 66^\circ\text{C}$, water content 7.3 per cent weight) derived from the two other columns. Phase separation takes place in the settler: two-thirds of the organic phase is used as reflux for the first distillation and the remaining third as reflux for the third distillation, and the aqueous phase is sent to the stripper. The withdrawal contains few organic compounds (1000 to 2000 ppm). The dehydration bottom stream is first subjected to light ends separation (≥ 25 trays) followed by heavy ends separation (≥ 100 to 120 trays), to yield vinyl acetate to commercial specifications. This final separation is designed to remove ethyl acetate among the heavy products, and the previous separation to remove methyl acetate and acetaldehyde among the light components.

Vinyl acetate recovery and purification require operation in the presence of an inhibitor, which may be gaseous (such as a mixture of O_2 and CO_2). The various units must be built of high-alloy steels ($\text{Cr:Ni} = 18/8$).

11.1.3 Other industrial methods for producing vinyl acetate

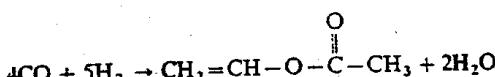
Among the various other methods for synthesizing vinyl acetate that have led to developments which may culminate in plant construction, the following techniques are worth mentioning:

- Reaction of acetic anhydride and acetaldehyde at above 300°C , in the presence of an acidic catalyst. The ethylidene diacetate formed decomposes to vinyl acetate and acetic acid:

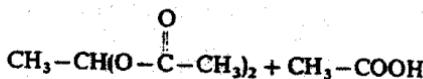
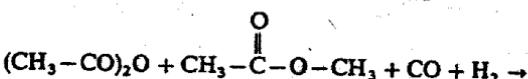
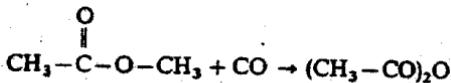


A 20,000 t/year capacity plant built in 1953 at Pampa, Texas, using this process (Celanese), was subsequently shut down.

- Carbonylation of methyl acetate, developed in particular by Halcon. This method is based on the use of synthesis gas to produce successively methanol, methyl acetate, and acetic anhydride jointly with ethylidene diacetate, which then decomposes to vinyl acetate and acetic acid, which is recycled to methyl acetate synthesis. The overall reaction is the following:

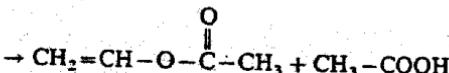
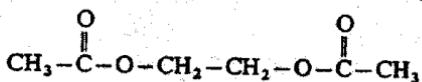


Carbonylation of methyl acetate is the essential step (molar yield ≈ 85 per cent):

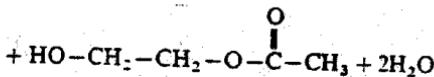
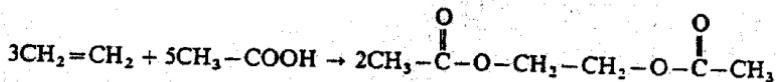


It takes place in the liquid phase around 130 to 160°C and between 4 and $7 \cdot 10^6$ Pa absolute, in the presence of a catalyst complex based on palladium or rhodium, methyl iodide, and an amine or phosphine as initiator. Acetic anhydride is formed as an intermediate. The conversion is directed toward the production of ethyldiene diacetate by increasing the proportion of CO in the synthesis gas.

- Pyrolysis of ethylene glycol diacetate (*Halcon*) around 500 to 550°C, with a molar yield of 85 to 87 per cent, by the following reaction:



Ethylene glycol diacetate is itself obtained by the acetoxylation of ethylene at about 400°C and $3 \cdot 10^6$ Pa absolute, in the presence of oxygen and a tellurium and bromine catalyst:



11.1.4 Economic data

Table 11.1 lists economic data concerning methods for the manufacture of vinyl acetate from acetylene and ethylene.

11.1.5 Uses and producers

Table 11.2 gives the average commercial specifications of vinyl acetate.

TABLE II.1
VINYL ACETATE PRODUCTION. ECONOMIC DATA
(France conditions mid-1986)

Process	From acetylene	From ethylene	
		Liquid phase ⁽¹⁾	Vapor phase
Typical technology	Wacker	ICI/Hoechst	USI Chem. Bayer-Hoechst
Production capacity (t/year)	50,000	100,000	100,000
Battery limits investments (10 ⁶ US\$)	18	46 ⁽²⁾	35
Consumption per ton of vinyl acetate			
Raw materials			
Acetylene (t)	0.32	—	—
Ethylene (t)	—	0.64	0.37
Acetic acid (t)	0.70	—	0.72
Oxygen (t)	—	0.70	0.28
Utilities			
Steam (t)	3.6	6	2.3
Electricity (kWh)	340	310	50
Cooling water (m ³)	220	580	150
Process water (m ³)	1	1	2
Inerts (Nm ³)	50	5	5
Chemicals and catalysts (US\$)	12	18	9
Labor (Operators per shift)	4	6	6

(1) Process abandoned.

(2) Including oxidation of acetaldehyde to acetic acid.

TABLE II.2 /
AVERAGE COMMERCIAL SPECIFICATIONS OF VINYL ACETATE

Characteristics	Values
Purity (% Wt) min.	99.9
$d_{20}^{20(1)}$	0.9335 to 0.9345
Distillation range (°C)	72.4 to 72.8
Water (ppm) max.	300
Acetic acid (ppm) max.	50
Acetaldehyde (ppm) max.	100
Non-volatiles (ppm) max.	10
Iron (ppm) max.	0.1
Methyl acetate (ppm) max.	20
Ethyl acetate (ppm) max.	30
Inhibitor (hydroquinone) (ppm) max.	7
Color (Pt/Co) max.	5

(1) Specific gravity, 68.0-68.0.

Table 11.3 lists the applications of vinyl acetate, expressed in per cent, in Western Europe, the United States and Japan, together with the production, capacity and consumption figures for these three geographic areas.

TABLE 11.3
VINYL ACETATE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Ethylene - vinyl acetate resins	4	7	11
Polyvinyl acetate	60	58	16
Polyvinyl alcohol	17	21	71
Polyvinyl butyral	3	7	-
Vinyl chloride copolymers	11	4	1
Acrylic fibers	3	3	1
Miscellaneous ⁽¹⁾	2		8
Total	100	100	100
Sources (% product)			
Acetylene	43	-	19
Ethylene	57	100	81
Total	100	100	100
Production (10^3 t/year)	495	920	425
Capacity (10^3 t/year) ⁽²⁾	560	1,130	575
Consumption (10^3 t/year)	570	655	505

(1) Barrier resins, polyvinyl formal...

(2) In 1984 and 1986 the worldwide production of vinyl acetate was about $2.7 \cdot 10^6$ t/year. In 1986 the distribution was the following:

United States	1.15	Western Europe	0.56	Middle East	-
Canada	0.05	Eastern Europe	> 0.16	Japan	0.58
Latin America	0.09	Africa	-	Asia and Far East	> 0.15

11.2 VINYL CHLORIDE

Vinyl chloride monomer ($d_4^{-20} = 0.9834^{(2)}$, mp = -153.8°C , bp_{1.013} = -13.4°C) is a colorless gas in standard conditions, essentially employed in liquid form to manufacture polyvinyl chloride which, together with polyethylene, polystyrene and polypropylene, is one of the most widely used plastics. After having witnessed tremendous growth in the 1960s, especially in the building sector, with average annual growth rates of 15 to

(2) Specific gravity, 4.0/39.2.

20 per cent in the leading industrial countries, it suffered in the subsequent period from the repercussions of the oil crises and the economic recession, the extremely sharp competition from other plastics, and the enforcement of anti-pollution regulations aimed at the hydrocarbon emission associated with its manufacture. As a result, with total world capacity of nearly $17 \cdot 10^6$ t/year, very high overcapacity existed in 1986, with plant utilization factors in the neighborhood of 60 per cent. About 96 per cent of this capacity was based on the use of ethylene as the raw material, with the intermediate production of ethylene dichloride, with the remaining 4 per cent employing acetylene.

The essential disadvantage of vinyl chloride monomer is associated with the presence of chlorine in its molecule, which, directly and often indirectly in the event that hydrochloric acid is used, results from the electrolysis of sodium chloride, a process known to be highly energy-intensive.

If acetylene is the raw material, the hydrochloric acid by-product can be used as an addition. In fact one mole of this acid is produced when starting with ethylene, by the decomposition of the ethylene dichloride obtained by chlorination, and per molecule of vinyl chloride. The chlorine atom in this acid was originally obtained by the electrolysis of sodium chloride. To overcome this drawback and make maximum use of an expensive reactant, it has been proposed to employ equal part mixtures of ethylene and acetylene, or to perform the oxychlorination of ethylene.

In these conditions, the main methods currently industrialized are the following:

- Addition of hydrochloric acid to acetylene, commercialized for the first time in 1930.
- Addition of chlorine to ethylene, followed by cracking of the ethylene dichloride formed to vinyl chloride and hydrochloric acid, a method developed in the 1950s.
- The combined use of ethylene and acetylene, in so-called "balanced" schemes, to avoid the formation of hydrochloric acid as a by-product.
- Oxychlorination of ethylene, developed since 1955, possibly combined with its chlorination in so-called "integrated" schemes.

11.2.1 Manufacture of vinyl chloride by the addition of hydrochloric acid to acetylene

Processes for manufacturing vinyl chloride from acetylene, which, for many years, were the only ones employed, offer the advantage of simplicity. Hence they benefit from lower capital expenditures, but, on the other hand, require the use of a much more expensive hydrocarbon raw material. This explains why they have been supplanted by technologies employing ethylene, and why they enjoyed a revival as the price of crude oil increased, although ethylene produced from gas-field ethane is ultimately the most advantageous economic alternative.

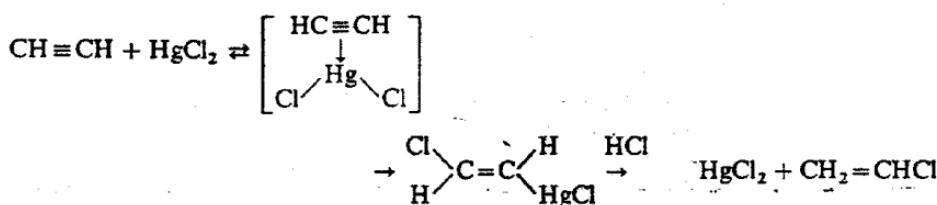
11.2.1.1 Principle

The reaction is a simple exothermic addition of hydrochloric acid to acetylene as follows:



The transformation takes place in the gas phase, in the presence of a supported mercuric chloride base catalyst in general, at a temperature between 100 and 170°C, and a pressure of about $0.3 \cdot 10^6$ Pa absolute. The support is activated charcoal, but this can be replaced by graphite, aluminum and sodium silicate etc.

From the kinetics standpoint, the reaction rate is of the first order in relation to each of the reactants employed. It implies the formation of a π complex, by the addition of mercuric chloride to acetylene, followed by transformation to mercuric chlorovinyl chloride. The action of hydrochloric acid then regenerates the mercuric chloride with the formation of vinyl chloride:



The development of the reaction, in a fixed bed, and in a reaction tube (5 cm diameter, 3 m high) is characterized by the temperature profile which is established. This exhibits a hot spot, which cannot exceed 200°C, and which shifts with time in the direction of the gas stream, making it possible to measure the aging of the catalyst. For a height of 3 m, a suitable adjustment achieves a path time longer than 200 h. In these conditions, and even at high conversions, yields in relation to acetylene and hydrochloric acid reach 98 molar per cent. Catalyst life is about five months in this case. This displacement of the hot spot reflects the progressive sublimation of mercuric chloride and its entrainment in the gaseous stream which is accordingly polluted, and also in the wastes. Mercury losses may be as high as 0.5 to 0.6 kg/t of vinyl chloride produced, so that highly elaborate recovery treatment is required to prevent environmental pollution. This can be minimized by operating in a fluidized bed, so as to allow better removal of the heat generated by the reaction, and thus to obtain a more uniform temperature profile (BASF, USSR : Badische Anilin und Soda Fabrik, etc). It has also been proposed to operate in the liquid phase in the presence of a solvent (Distillers, Knapsack, Shell, etc).

The main by-products are acetaldehyde, formed from traces of water present in the reactants, and 1,1-dichloroethane, obtained by the reaction of hydrochloric acid with vinyl chloride, according to the following reaction:



11.2.1.2 Industrial manufacture (Fig. 11.3)

The scheme of an industrial plant involves three main aspects:

- (a) Feedstock preparation. Acetylene and hydrochloric acid, in slight excess (about 10 molar per cent) to avoid undesirable polymerizations, are first dried, and then mixed together and with the recycle gas. At this stage, the presence of traces of chlorine is liable to cause an explosion hazard. This is the risk incurred when the acid used is prepared by the reaction of dry hydrogen with chlorine, and if the conversion of the reactants is incomplete.

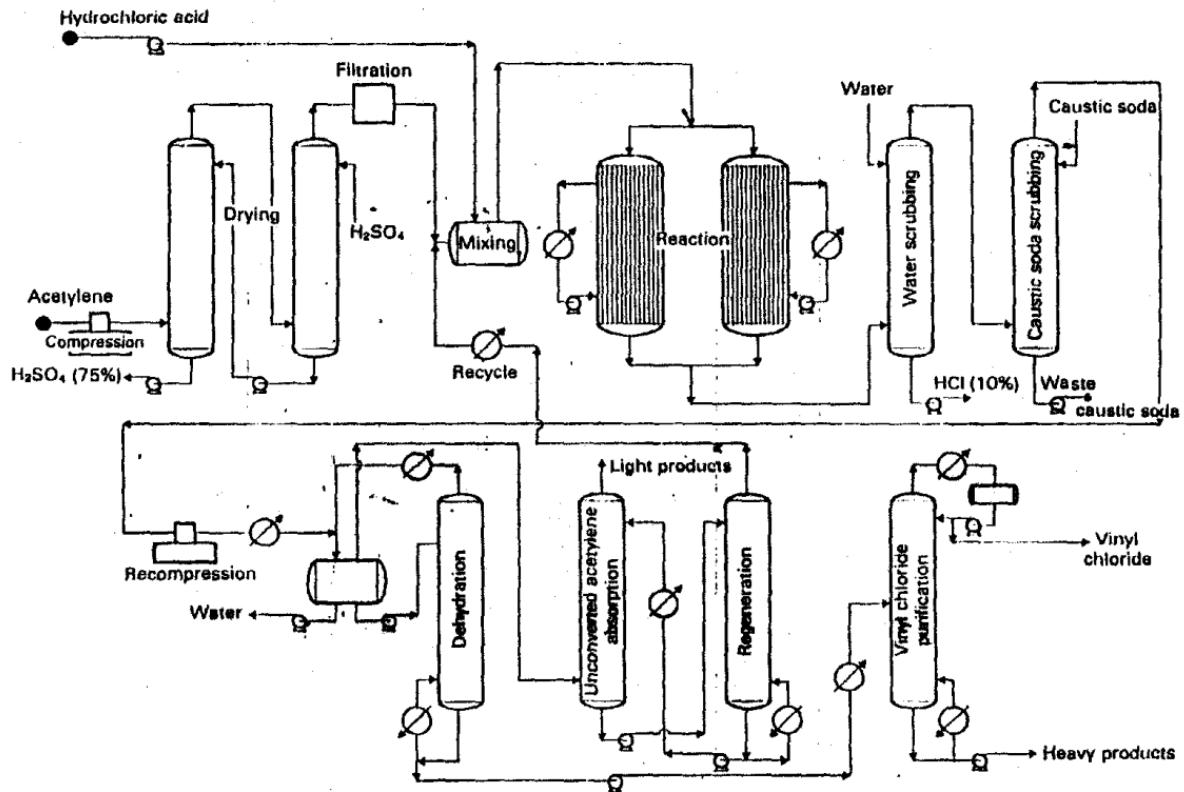


Fig. 11.3. Vinyl chloride manufacture by addition of hydrochloric acid to acetylene.

- (b) Reaction. The gas mixture obtained then enters a set of multi-tube reactors placed in parallel, of which each bundle may comprise 1500 to 2000 tubes, and whose unit dimensions are in the neighborhood of 2 m in diameter, 4 m in height, for a shell containing 1500 tubes. The heat generated by the reaction is removed by the circulation of a coolant fluid, which is cooled externally by passage through a heat exchanger.
- (c) Effluent treatment. The gases leaving the reaction zone are scrubbed with caustic soda and water to eliminate excess hydrochloric acid, and then compressed to $0.7 \cdot 10^6$ Pa absolute and cooled. Most of them are condensed in this way. Residual water is separated by settling. The gases dissolved in the organic fraction are liberated by stripping at moderate temperature, to prevent the decomposition of crude vinyl chloride. This is purified by low-temperature distillation at between 0.4 and $0.5 \cdot 10^6$ Pa absolute. Unconverted acetylene, which accounts for the bulk of the recovered gases, is purified by absorption and stripping, and then recycled to the reactors. All these operations take place in the presence of a polymerization inhibitor.

This type of process, which has been known for a long time, has been developed and industrialized by many companies (*Allied, BASF, Distillers, Hoechst, Hüls, ICI, Lonza, Monsanto, Péchiney-Saint-Gobain, Shell, Solvay, etc.*) It employs pure concentrated acetylene. More recently, certain techniques, such as those proposed by *Japan Gas Chemical*, have been developed to utilize dilute acetylene, such as that obtained directly by the cracking of a naphtha.

11.2.2 Production of vinyl chloride by chlorination of ethylene and cracking of the ethylene dichloride formed

Ethylene has so far appeared to be a much less expensive raw material than acetylene. It is likely to remain so for some time, even if the price of crude oil rises, if, simultaneously, reservoir chemistry based on liquefied petroleum gas, and ethane in particular, develops at the expected rate. This means that the most widespread methods will continue to rely on chlorination or oxychlorination of ethylene, either alone or, more generally, combined in integrated schemes, each one followed by the cracking of the ethylene dichloride produced.

Even in combination with oxychlorination (see Sections 11.2.4 and 11.2.5), the chlorination of ethylene, and the cracking of the ethylene dichloride common to both methods, constitute distinct stages which merit separate examination.

11.2.2.1 Manufacture of ethylene dichloride by ethylene chlorination

1,2-ethylene dichloride ($d_4^{20} = 1.253$ ⁽³⁾, mp = -35.3°C , bp_{1.013} = 83.7°C) is a colorless, volatile, but stable liquid at standard temperature and pressure.

(3) Specific gravity, 68.0/39.2

A. Conditions of its production

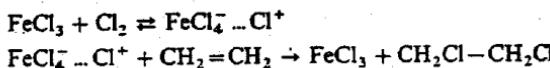
It is obtained chiefly as a captive intermediate of vinyl chloride manufacture and, in the case of ethylene chlorination, it results from the following exothermic reaction:



This transformation can be conducted in the liquid or vapor phase and, selectively, in the presence of catalysts based mainly on metallic chlorides. Ferric chloride is the ideal catalyst for the liquid phase, and supported calcium chloride, or systems containing lead derivatives, for the vapor phase process.

Most industrial processes operate in the liquid phase, at a temperature ranging between 50 and 90°C, and at low pressure (between 0.3 and $0.5 \cdot 10^6$ Pa absolute). The reaction temperature is determined by the choice of the method for recovering ethylene dichloride: 50 to 60°C if it is withdrawn in the liquid state, and 85 to 90°C if it leaves the reaction zone in gaseous form.

The present interpretation of the mechanisms of the action of ferric chloride is based on a polar mechanism, and particularly on its ability to polarize chlorine, which attacks the double bond of the ethylene:



At higher temperature, the catalyst acts according to a free radical mechanism.

In the liquid phase, ferric chloride can be added to the medium, consisting mainly of ethylene dichloride, into which ethylene and chlorine are injected. In certain cases, however, it is generated *in situ* by the action of chlorine on the reactor walls.

Once-through conversion of the reactants is very high, approaching 100 per cent, and molar selectivity is also high at more than 99 per cent, both in relation to ethylene as well as chlorine. The main by-product is 1,1,2-trichloroethane, but, at higher temperature, various chloroethanes and chloroethylenes may also be formed. The presence of oxygen in the chlorine feed is an interesting impurity, because it inhibits the free radical reactions giving rise to these derivatives, and accordingly improves the ethylene dichloride selectivity.

B. Industrial manufacture (Figs. 11.4 a and 11.4 b)

In the production schemes of the most widespread units, the gases, rich in chlorine and ethylene, are introduced into a set of reactors placed in parallel, through a medium consisting of ferric chloride in solution in ethylene dichloride. The removal of the heat generated by the reaction, as well as temperature control, together with the dispersion of the gaseous reactants, is achieved by means of the external forced circulation of a fraction of this medium and its passage through heat exchangers.

- If the conversion takes place around 50 to 60°C (Fig. 11.4 a), the unit operates with a slight excess of ethylene (about 5 molar per cent). The products are withdrawn in a mixed phase and sent to a gas/liquid separator operating in an inert atmosphere (nitrogen) to limit the explosion hazard. The composition of the gases recovered is adjusted by the addition of ethylene, and the mixture is sent to a finishing reactor, whose product is used to feed the initial set of reactors with reaction medium and to prepare the ferric

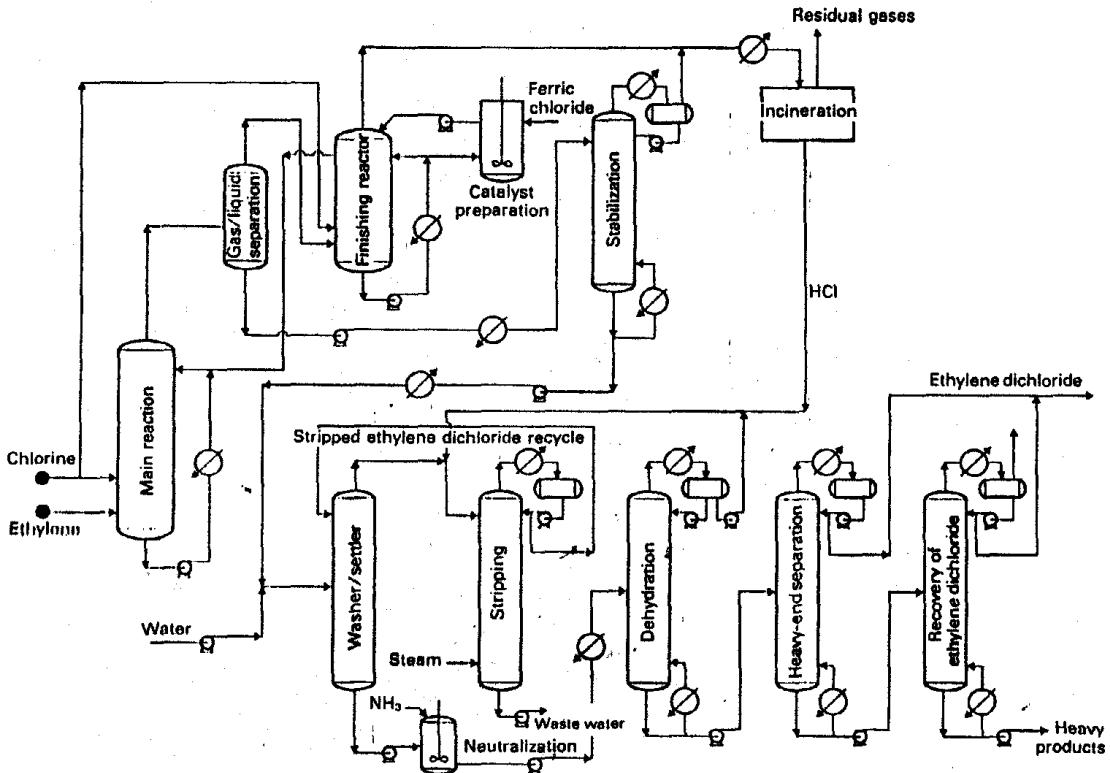


Fig. 11.4 a. Ethylene dichloride manufacture by ethylene chlorination, with mixed-phase effluent withdrawal.

chloride solution. The liquid fraction leaving the separator is heated and then stabilized by distillation. The various residual gases obtained are incinerated, while the crude ethylene dichloride is purified to 99.8 per cent weight. This is achieved by first adding water designed to facilitate the separation of ferric chloride. An upper aqueous phase is obtained by settling, which can be purified of the small amounts of dissolved ethylene dichloride which it contains, by stripping and recycling, together with a lower organic layer rich in ethylene dichloride. This phase is neutralized with ammonia, dried by heteroazeotropic distillation (≥ 15 trays), with the ethylene dichloride recovered at the top after settling being used as a reflux, and then subjected to heavy ends separation (≥ 15 trays). The heavy products, consisting of trichloroethane, perchloroethane, chloroethylene and ethylene dichloride, can be separated, and possibly utilized as solvents, by vacuum distillation (7 kPa absolute, 20 trays).

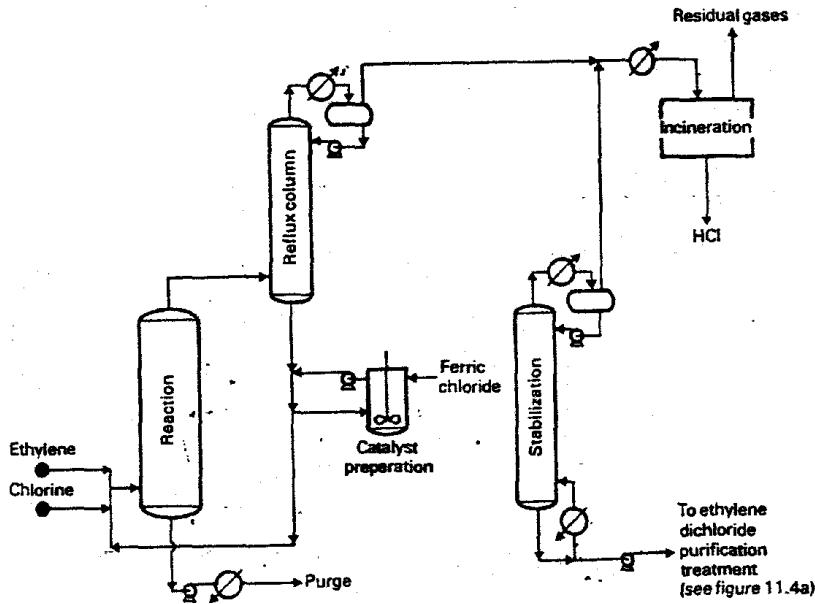


Fig. 11.4 b. Ethylene dichloride manufacture by ethylene chlorination, with vapor phase effluent recovery.

- If the conversion takes place around 85 to 90°C (Fig. 11.4 b), in other words at a temperature close to the boiling point of ethylene dichloride, the products are withdrawn from the reaction medium in the vapor phase. This procedure offers the advantage of avoiding entrainment of the catalyst, allowing the removal of the heat generated by the reaction by partial vaporization, and considerably simplifying the scheme of the installation. However, a slight drawback is associated with the lower yield of high-grade ethylene dichloride, part of which (5 per cent weight) must be purged at the same time as the catalyst system. In this case, the reactors are surmounted by packed reflux columns to

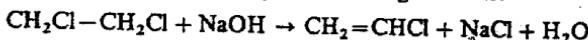
maintain the necessary liquid phase hold-up and simultaneously separate and recycle the heavy products, which are present in the purge making up the withdrawal stream (75 to 80 per cent weight ethylene dichloride). The distillate consists partly of residual gases which are incinerated, and the remainder, crude ethylene dichloride, is stabilized by distillation, while the gaseous fraction recovered at the top is added to the light ends.

In certain processes currently being developed, it is proposed to withdraw the ferric chloride by adsorption on alumina or activated charcoal to avoid excessive product losses. As a rule, most of the equipment is built of carbon steel. The main license holders are *Dow*, *Ethyl Goodrich*, *Höchst*, *Hüls*, *Mitsui Toatsu*, *Monsanto*, *PPG (Pittsburgh Plate Glass Company)*, *Rhône-Poulenc*, *Solvay*, *Stauffer*, *Toa Gosei*, *Tokuyama Soda*, *Toyo-Soda*, etc. In the 1970s, *Diamond Alkali* and *Oronzo de Nora* developed a process for the chlorination of dilute ethylene called *Dianor*.

More than 90 per cent of the ethylene dichloride is used captively for the manufacture of vinyl chloride. The remainder forms part of the composition of antiknock additives or is used as an intermediate in the production of amines and chlorinated solvents.

11.2.2.2 Ethylene dichloride pyrolysis to vinyl chloride

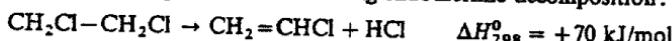
This operation was previously carried out by hot caustic soda (6 per cent weight) around 150°C, at $1 \cdot 10^6$ Pa absolute, by the following reaction:



It is carried out thermally today in tubes which are empty (*Allied*, *BASF*, *BP*, *Goodrich*, *Höchst*, *Hüls*, *Knapsack*, *Kureha*, *PPG (Pittsburgh Plate Glass Company)*, *Solvay*, *USSR* processes, etc.) or filled with catalysts (*SBA : Société Belge de l'Azote*, *USSR*, etc.) and placed in a furnace.

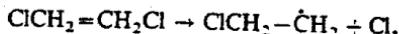
A. General conversion conditions

The objective is to implement the following endothermic decomposition:

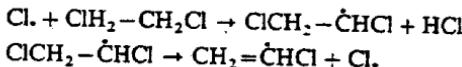


This is feasible at atmospheric pressure above 300°C, but the rate only becomes significant between 400 and 550°C, provided that the presence of hydrocarbons does not shift the transformation towards the production of ethylene. It obeys a chain free radical type of reaction mechanism, of which the overall rate is of the first order in relation to ethylene dichloride, and which can be expressed as follows:

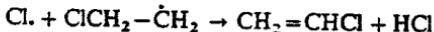
(a) Initiation:



(b) Propagation:



(c) Termination:



As in steam cracking, a large number of by-products is produced. Some of them result from the consecutive reactions of the chlorination of vinyl chloride and of its derivatives obtained by dehydrochlorination (tri-, tetra-, pentachloroethane, perchloroethane, di-, trichloroethylene, perchloroethylene), and the others from the hydrochlorination of vinyl chloride (1,1-dichloroethane), while others result from decomposition reactions (acetylene, coke) or conversion of impurities initially present (hydrocarbons such as ethylene, butadiene and benzene, chlorinated derivatives such as chloroprene, methyl and ethyl chlorides, chloroform, carbon tetrachloride, etc., and hydrogen).

The main conversion is favored by the presence of certain accelerators (chlorine, bromine, iodine, carbon tetrachloride, and oxygen to a lesser degree). However, it is inhibited by chain splitters such as olefins (ethylene, propylene, etc.).

On the whole, industrial processes operate between 500 and 550°C, at between 2.5 and $3 \cdot 10^6$ Pa absolute, in the absence of catalyst, with the highest possible once-through conversion compatible with an acceptable carbon deposit in the tubes, in other words about 50 to 60 per cent. In these conditions, molar selectivity exceeds 95 per cent, and may even be as high as 99 per cent.

The catalyst systems available (activated charcoal, metallic chlorides, etc.) help to perform the conversion at lower temperature. Their short life and the technological constraints connected with their use, particularly the loss of production caused by periodic shutdowns, have hitherto prevented their use on an industrial scale.

B. Industrial manufacture (Fig. 11.5)

Industrial manufacture starts with preheating and vaporization of make-up and recycle ethylene dichloride at about 215°C. This mixture is then introduced into a set of tubular furnaces placed in parallel, based on a similar operating principle to those employed for steam cracking. They comprise a convection zone in which the materials are brought to temperature and a radiation zone in which the actual reaction takes place, and in which the tubes are of high-alloy steel, given the high temperature to which they are raised by the radiation from the refractory walls, heated by means of burners normally operating on natural gas. The product gases, which exit at about 500°C, are quenched to prevent any subsequent change, by passage through a tower, in countercurrent contact with condensed products cooled to 50°C. This lowers their temperature to about 200°C. Supplementary cooling then condenses most of the unconverted ethylene dichloride, a fraction of which is used as a quenching fluid, after coke and tars are removed by filtration.

The remainder, as well as the residual gases, enter a series of distillation columns designed to perform the following operations:

- Separation of hydrochloric acid by-product in gaseous form ($\cong 20$ trays).
- Production of crude vinyl chloride ($\cong 60$ trays).
- Purification of vinyl chloride ($\cong 15$ trays) to reduce its hydrochloric acid content from 500 to 10 ppm, and its neutralization with caustic soda.
- Recovery of unconverted ethylene dichloride and its recycle from the heavy fraction resulting from the production of crude vinyl chloride. This requires:
 - . light ends separation (70 to 75 trays) to remove the light products;
 - . heavy ends separation in two stages, first at atmospheric pressure (20 to 25 trays) to separate most of the ethylene dichloride, and then under vacuum (70 kPa

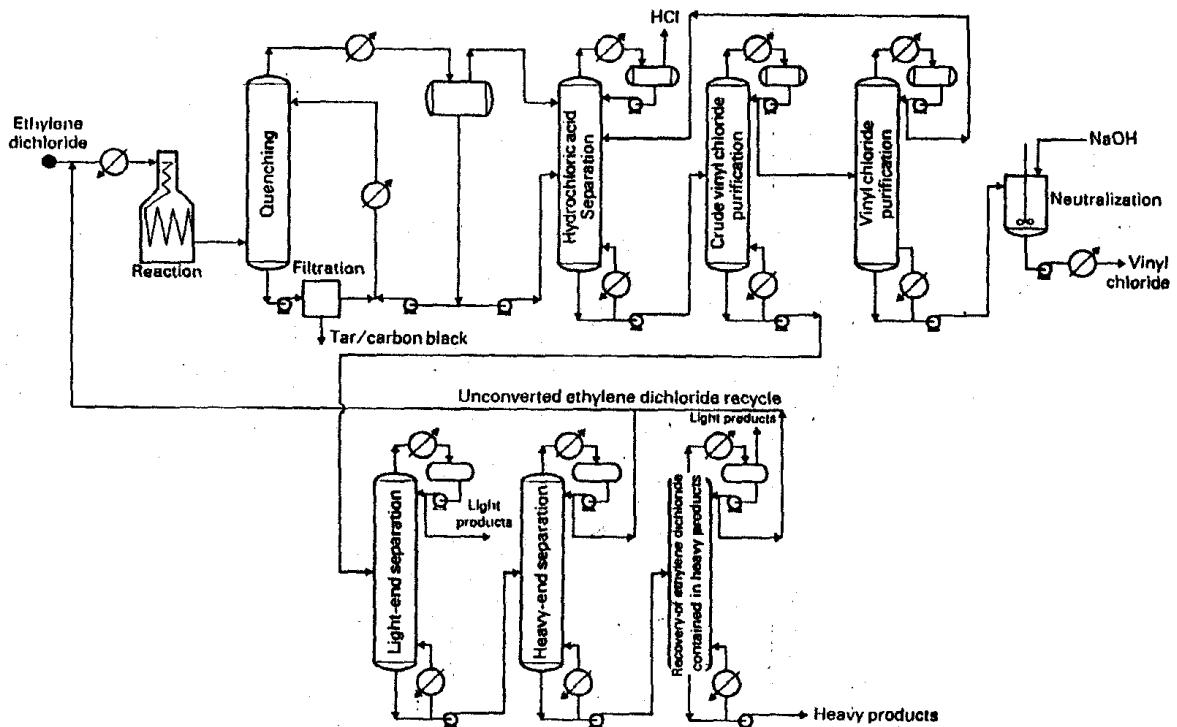


Fig. 11.5. Vinyl chloride manufacture by ethylene dichloride cracking.

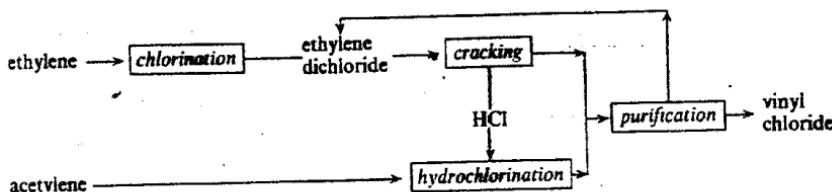
absolute, 25 trays) to intensify ethylene dichloride recovery, especially from the quantities remaining in the heavier components, and thus improve the total conversion yield.

11.2.3 Joint production of vinyl chloride from acetylene and ethylene in so-called "balanced" schemes or processes

11.2.3.1 Main industrial situations encountered

To avoid the by-production of hydrochloric acid inherent in processes that start with ethylene alone, or resulting from the cracking of ethylene dichloride, one method consists of combining them with the hydrochlorination of acetylene. In these conditions, depending on the types of reactant available, three typical situations can be considered, as described schematically below:

a. Availability of equimolecular amounts of ethylene and acetylene

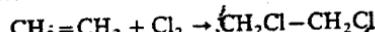


The reactions are as follows:

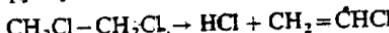
(a) Hydrochlorination of acetylene:



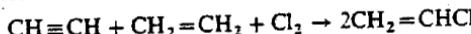
(b) Chlorination of ethylene:



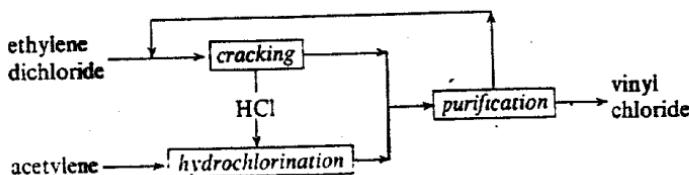
(c) Ethylene dichloride pyrolysis:



yielding the overall reaction:

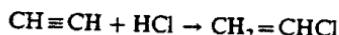


b. The reactants available in equimolecular quantities are ethylene dichloride and acetylene



The reactions involved are as follows:

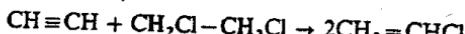
(a) Hydrochlorination of acetylene:



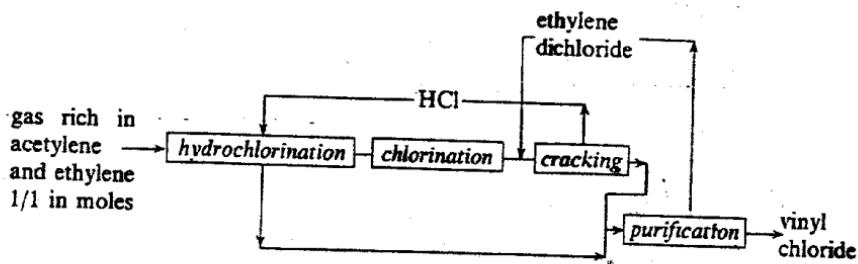
(b) Ethylene dichloride pyrolysis:



making the overall reaction:



c. Availability of a gas containing acetylene and ethylene in equimolecular amounts



For several years, a number of companies with resources of acetylene and ethylene and even dichloroethane, from different sources, have balanced their manufacture of vinyl chloride without the net production of hydrochloric acid. They have achieved this by using operating schemes of the first two types. These firms include *Monsanto*, *Pechiney-Saint-Gobain*, *Union Carbide*, etc.

Although they have not experienced substantial industrial development, processes have also been developed to produce an ethylene/acetylene mixture of a suitable composition directly, and by the type (c) scheme, to perform the rest of the operations to produce vinyl chloride, without separation or purification of the components of the stream produced. These techniques have been proposed by *SBA* and especially *Kureha*. This type of method, which uses a dilute gas mixture, avoids costly fractionation of acetylene and ethylene, replacing them by the easier fractionation of vinyl chloride and ethylene dichloride.

11.2.3.2 The Kureha process

In its original version, this process operates on naphtha, which is cracked by injection into a hot medium, achieved by the combustion of the same naphtha with oxygen in the presence of steam. The latest technological developments, achieved jointly with *Union Carbide* and *Chiyoda*, are designed to convert crude oil in a reactor whose operation can be directed towards the preferential production of ethylene (see Section 2.1.3.4), or towards that of an acetylene/ethylene mixture in a molar ratio close to 1 (see Section 5.4.2). This possibility is exploited to produce vinyl chloride monomer in a process (Fig. 11.6) whose main stages are discussed below:

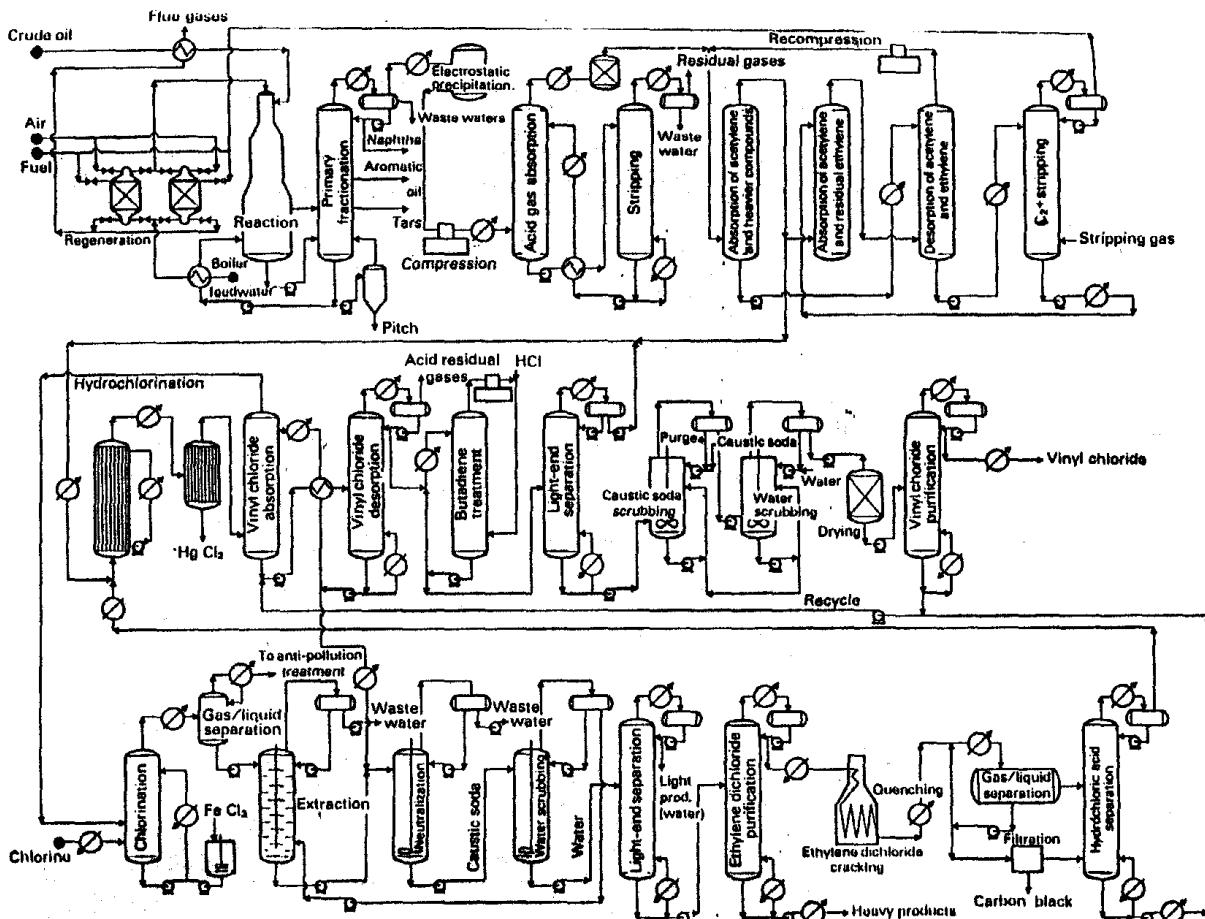


Fig. 11.11. Process flow diagram for the production of vinyl chloride monomer.

- Cracking of crude oil in the presence of steam superheated to 2000°C. with the formation, in addition to acetylene and ethylene, of various co-products (fuel gas, propylene, benzene, naphthalene, tars, pitches, etc.). This operation is followed by quenching and primary fractionation.

- Treatment of the gaseous fraction in the following successive steps:

- Removal of solid particles.
- Compression to between 0.6 and $0.7 \cdot 10^6$ Pa absolute.
- Cooling to -20°C . yielding a condensate consisting mainly of benzene.
- Separation of acid gases (CO_2 and H_2S) by absorption in the presence of alkaline carbonates, with regeneration by stripping.
- Drying.
- Fractionation of C_3 - by primary absorption using kerosene, and recovery of the stripped acetylene and ethylene, by secondary absorption using fresh solvent: the absorbent is regenerated by stripping.

- Hydrochlorination of the acetylene/ethylene mixture, in the presence of mercuric chloride supported on activated charcoal, around 120 to 170°C, using recycle hydrochloric acid introduced at 96 to 98 per cent of stoichiometry. Control of the reaction is facilitated by the dilution of the gas which, by heating, absorbs a large part of the heat liberated, although operation takes place under pressure to bring the partial pressure of acetylene to about $0.6 \cdot 10^6$ Pa absolute. After cooling and filtration, the vinyl chloride formed is absorbed in a stream of cold ethylene dichloride, and then released by stripping in a unit which is also designed to treat the crude product obtained from the subsequent cracking stage.

- Addition of chlorine to the residual ethylene contained in the effluent resulting from the absorption of vinyl chloride, by passage through a solution of ferric chloride in ethylene dichloride. The temperature is maintained at between 50 and 70°C, under pressure between 0.4 and $0.5 \cdot 10^6$ Pa absolute. The chlorine is injected in sub-stoichiometric quantities in relation to ethylene (96 to 98 per cent) to eliminate the risks of explosive reactions due to the presence of hydrogen. The ethylene dichloride produced is rid of the catalyst by extraction with water. Added to that employed as a solvent in the previous stage, it is neutralized with caustic soda, filtered, washed with water, separated from the light components (especially water) and heavy components by azeotropic or conventional distillation.

- Cracking of preheated ethylene dichloride, at between 450 and 550°C. at $1.5 \cdot 10^6$ Pa absolute, followed by quenching, first indirectly for the production of steam, and then directly by the in-line injection of cold product, and then by the separation by distillation of the hydrochloric acid co-produced, which is recycled to the acetylene hydrochlorination stage.

- Purification of crude vinyl chloride produced by cracking and hydrochlorination, including the lowering to about 5 ppm of the butadiene content by means of liquid/liquid countercurrent contact with hydrochloric acid, separation by distillation of the light products returned to hydrochlorination, followed by neutralization with dilute caustic soda, scrubbing with water, drying on molecular sieves, and finally the removal of heavy compounds by distillation.

• Treatment of residual gases produced by the hydrochlorination and chlorination stages. These gases, which contain practically no acetylene or ethylene, are rich in hydrogen and methane, and can be used as a fuel in crude oil and ethylene dichloride cracking furnaces, provided that they are previously rid of the chlorinated compounds they contain by means of absorption by kerosene.

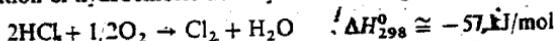
11.2.4 Production of vinyl chloride by oxychlorination

Balanced processes, which combine hydrochlorination with chlorination, offer an answer to the problem of the by-production of hydrochloric acid. In so far as they include the production of acetylene using cheap energy (nuclear-generated electricity for example) or by operating on dilute streams (Kureha process), they may prove economically attractive. In fact, they involve a high capital expenditure, their operation is sometimes delicate, and the utilization of many of their by-products is uncertain.

Another solution, proposed for a long time, consists in reconverting the hydrochloric acid to chlorine by the Deacon process, which can be improved and inserted into the installation scheme (variant suggested by *Shell*). The past two decades, however, have witnessed the simultaneous development of many processes for the direct oxychlorination of ethylene, designed to perform such an operation *in situ*. They have led to the construction of most of the large plants currently in operation worldwide.

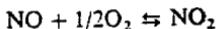
11.2.4.1 Processes including the reconversion of hydrochloric acid to chlorine

The hydrochloric acid produced during the cracking of ethylene dichloride can be converted to chlorine by electrolysis. *Bayer*, *De Nora*, *Dow*, *Hoechst/Uhde*, etc. use a technique of this type. However, the method proposed more generally involves the catalytic oxidation of hydrochloric acid by the following overall reaction:



This reaction, which is exothermic, has been implemented industrially by the following two main technologies:

- (a) The earlier, that of *Deacon*, is based on the use of a copper chloride catalyst. Despite various improvements, made in particular by *Shell*, it has only given rise to the construction of a single plant in the United States, currently shut down.
- (b) The latest, that of the *Kel-Chlor* process developed jointly by *Pullman/Kellogg* and *Du Pont*, performs the conversion by means of nitrogen oxides in sulfuric acid medium, on the basis of the following main reaction mechanism:



This technique has itself undergone several improvements. In its original version, called *Kel-Chlor I*, it has been practised industrially by *Du Pont* at Corpus Christi, Texas, since 1974.

The integration of a vinyl chloride plant is above all the achievement of *Shell* (Fig. 11.7), who developed a more active catalyst than the earlier systems, by depositing copper chloride containing rare earth chlorides on a support. At the outset, to offset the lack of activity, it was necessary to operate around 500°C, an unfavorable temperature from the thermodynamics standpoint, and also raising problems of corrosion resistance of the materials employed. The use of additives served to lower the temperature to about 350 to 400°C, with a once-through conversion of 75 per cent. The catalyst can be used in a fixed or fluidized bed. Given the exothermicity of the reaction, hot spots appear in a fixed bed, with the risk of sublimation of the active elements of the catalyst system. In the fluidized bed, greater temperature uniformity eliminates this drawback, but isothermality is an unfavorable factor for the reaction. *Shell* nevertheless selected the fluidized bed and its process operates around 365°C at between 0.1 and 0.2 . 10⁶ Pa absolute.

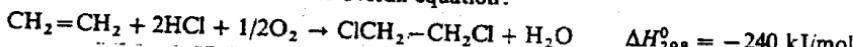
The flow sheet in Fig. 11.7 provides an indication of the Deacon/*Shell* plant. Unconverted hydrochloric acid is extracted with water, recovered by stripping and recycled. The chlorine is dried by sulfuric acid.

11.2.4.2 Oxychlorination processes

These processes perform the oxidation of hydrochloric acid *in situ*. Their principle is similar to the one implemented to produce phenol from benzene by the Hooker/Raschig process (see Section 10.1.3). The first industrial ethylene oxychlorination plant was built by *Dow* in the United States in 1955.

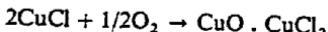
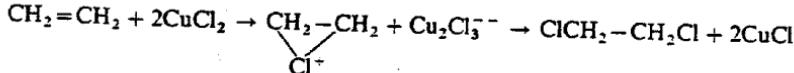
A. General conversion conditions

The main reaction follows the overall equation:



This highly exothermic reaction normally takes place at about 300 to 350°C, between 0.1 and 0.3 . 10⁶ Pa absolute. At this temperature, however, it is accompanied by the formation of a large number of by-products: ethyl chloride (above 250°C), vinyl chloride, 1,2-dichloroethylene, 1,1-dichloroethane, 1,1,2-trichloroethylene, 1,1,2-trichloroethane, chloral, perchloroethylene, vinylidene chloride, carbon dioxide, carbon monoxide, etc. Above 300°C, the impurities contained in the ethylene, especially ethane, produce methyl and methylene chlorides, chloroform, carbon tetrachloride, etc. On the whole, the exothermicity of the conversion is even greater because it reaches nearly 260 kJ/mol.

Copper chloride catalysts are used to operate at lower temperature, and to improve selectivity. Their action mechanism can be explained by the formation of a complex with ethylene, which is then capable of being converted to ethylene dichloride. In these conditions, the usual reaction scheme is as follows:



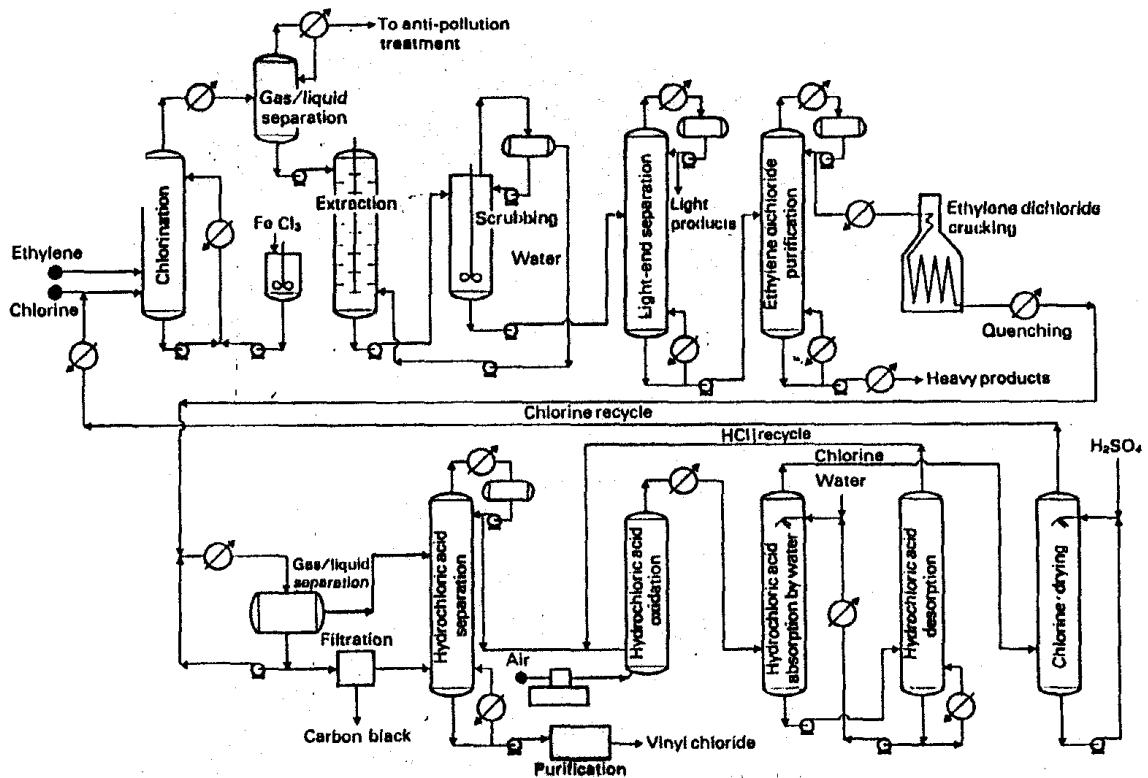


Fig. 11.7. Vinyl chloride manufacture from ethylene and chlorine, incorporating Deacon oxidation of by-product hydrochloric acid.

Many catalytic formulations have been proposed to enhance the performance of cupric chloride, the only active phase developed to the industrial stage. Hence other metallic chlorides are combined with it (potassium, rare earths, etc.) to increase the selectivity of the reaction, reduce the volatility of the copper compounds, prolong catalyst life, etc. Various supports are also used, generally based on alumina, but also kieselguhr, silico-aluminates and diatomaceous earths.

Transformation can take place in the presence of either air or oxygen. In both cases, it is important to avoid direct oxidation of the hydrocarbon, and this is achieved by introducing excess hydrochloric acid or ethylene. In fact, the latter appears to be preferable, because it generates smaller amounts of by-products owing to the increase in temperature, a parameter to which the reactions involving HCl are more sensitive.

In practice, with air, a slight excess is maintained of both ethylene and oxidant, to guarantee high conversion of hydrochloric acid (96 to 99 per cent), and the conversion of the hydrocarbon must also be very high (95 to 99 per cent) to minimize raw material losses in the residual gases. The molar selectivity of ethylene dichloride is as high as 93 to 96 per cent.

The use of oxygen facilitates the achievement of these performance levels. To begin with, operations can be performed at a lower temperature, reducing the rate of formation of by-products. Furthermore, it is possible to use a large excess of ethylene, whose conversion is limited, but which can be separated easily and recycled. The only losses are those of the purge, which is necessary to prevent the buildup of inert (carbon oxides, nitrogen, argon, hydrocarbons, etc.) in the synthesis loop, and which accounts for 1 to 5 per cent of the purge consisting of the residual gases resulting from air treatment.

B. Industrial manufacture

At the present time, all industrial plants operate in the vapor phase, although certain developments have been conducted to achieve the oxychlorination of ethylene in the liquid phase, particularly by Kellogg. In this case, transformation takes place around 170 to 185°C, at between 1.5 and $2 \cdot 10^6$ Pa absolute, in the presence of a catalyst system based on promoted cuprous and cupric chlorides, with more efficient temperature control by vaporization of part of the reaction medium and better performance, but with acid corrosion problems that are more difficult to solve.

Among the various commercial technologies deriving from the vapor phase conversion of ethylene are the following main alternatives, which can be distinguished according to the method of using the catalyst and the type of oxidant employed:

- (a) Fixed bed reactor processes using as reactant:
 - . Air: Dow, Ethyl, ICI, Solvay, Stauffer, Tokuyama Soda, Toyo Soda, Vulcan, etc.
 - . Oxygen: Stauffer, etc.
- (b) Fluidized bed reactor processes using:
 - . Air: Allied, Goodrich, Hoechst, Monsanto, Rhône-Poulenc, Tokuyama Soda, etc.
 - . Oxygen: Goodrich, Mitsui Toatsu, Monsanto, Pittsburgh Plate Glass, etc.

a. Fluidized bed technologies (Fig. 11.8)

The reactors employed in this type of process are vertical cylinders of high-alloy steel, equipped with internal coils sunk in the catalyst mass, designed to remove the heat

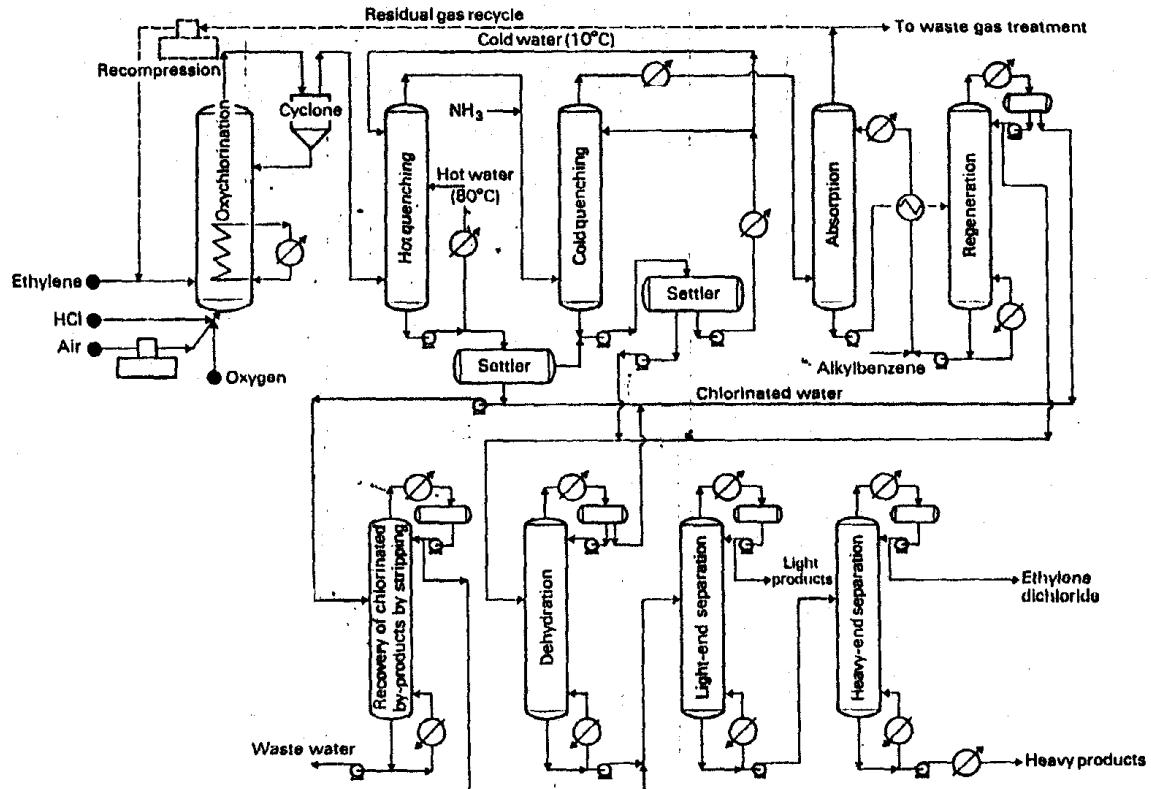


Fig. 11.8. Ethylene dichloride manufacture by ethylene oxychlorination. Fluidized bed processes
 (— Air. - - - Oxygen).

generated by the reaction, while producing steam directly from a boiler feedwater circulation, or indirectly by means of a heat transfer fluid. Fluidization is ensured by the reactants themselves, from the feed or recycle streams, and particularly by precompressed air. The fluidized bed process offers the advantage of favoring the uniformity of the temperature in the catalyst system, at about 220 to 230°C (at between 0.2 and $0.5 \cdot 10^6$ Pa absolute), and avoiding the appearance of hot spots which favor the sublimation of the active phases and the premature aging of the catalyst.

In processes based on the use of air, the installation scheme includes the following stages:

- **Efluent cooling and treatment.** At the exit of the reaction zone, the gaseous products are first rid of the solid particles they contain by passage through a cyclone separator. The stream is then rapidly cooled to about 90°C in a quenching tower using dual hot water (80°C) and cold water (10°C) recirculation, which is also designed to dissolve residual hydrochloric acid. This helps to limit acid corrosion to the smallest possible number of items of equipment. The streams are then neutralized with ammonia, again cooled in a second quenching tower by means of cold water (10°C) which, in alkaline medium, helps to recover certain by-products such as chloral.
- **Liquid separation.** The liquid fractions obtained in these two successive quenches are settled separately. Two phases are formed each time, one organic and the second aqueous. The former, which is rich in ethylene dichloride, is combined and sent to the purification stage. The latter is stripped to recover dissolved chlorinated compounds, or recirculated after cooling as a quenching fluid.
- **Gas separation.** The residual gaseous fraction still contains a significant amount of ethylene dichloride. It is recovered from a previously cooled effluent by absorption in a solvent (alkyl benzene) and regeneration by stripping. The remaining gases are incinerated and the fumes rid of the hydrochloric acid formed by scrubbing with dilute caustic soda.
- **Purification.** The crude ethylene dichloride is then purified. It is first dehydrated by heteroazeotropic distillation (10 trays). With water, ethylene dichloride in fact forms an azeotrope ($bp_{1.013} = 72.3^\circ\text{C}$, water content 9.2 per cent weight) which settles to yield an organic phase that serves as a reflux, and an aqueous phase added to that produced by the hot quench. It is then rid of the light components (ethylene dichloride, dichloroethylene, trichloroethylene, etc.) and heavy components (1,1,2-trichloroethane, pentachloroethane, perchloroethylene, etc.) in two distillation columns with 45 and 55 actual trays respectively. This operation also produces a small amount of ethylene dichloride, which forms an azeotrope with trichloroethylene ($bp_{1.013} = 82.1^\circ\text{C}$, ethylene dichloride content 56.5 per cent weight).

In processes using oxygen as the reactant, the only changes to the flow sheet concern the recycling of the remaining gases leaving the absorber. These gases, which are rich in unconverted or excess ethylene, are essentially recompressed and returned to the reaction zone.

b. Fixed bed technologies (Fig. 11.9)

The reactors employed in this case are of the multi-tube type with coolant flow on the shell side, to remove the heat generated by the reaction and to produce steam. The

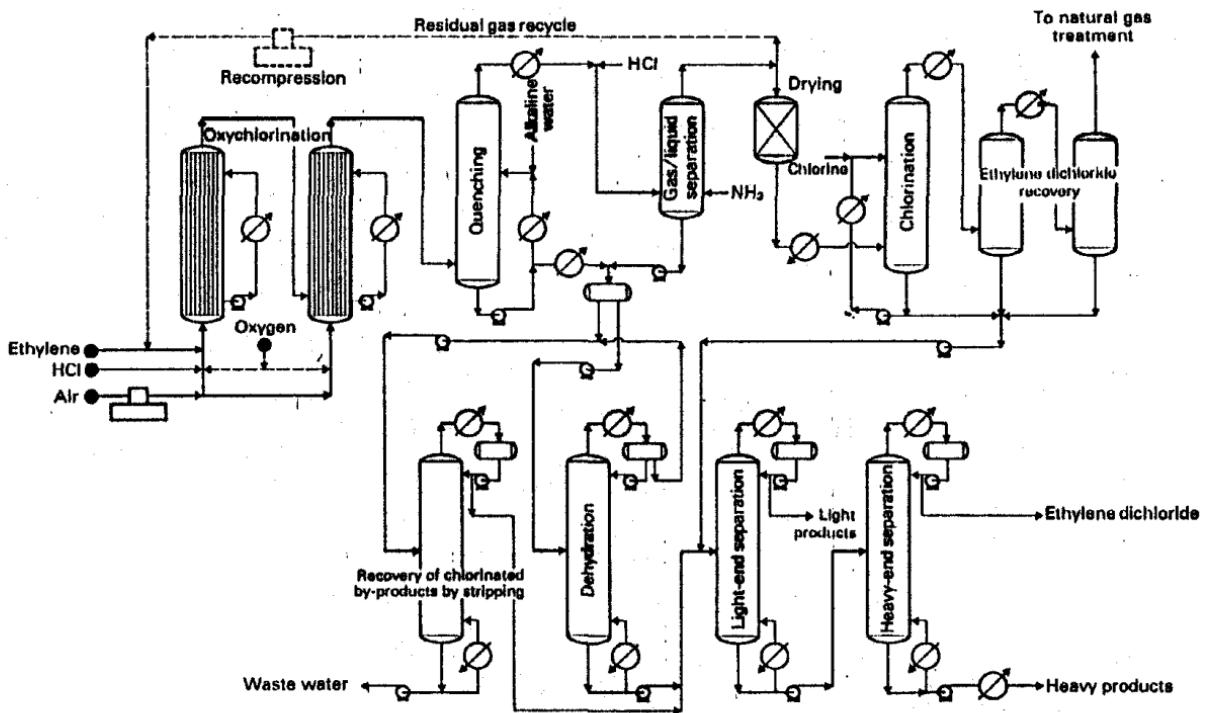


Fig. 11.9. Ethylene dichloride manufacture by ethylene oxychlorination. Fixed bed processes
 (— Air. - - Oxygen).

vertical tubes must be filled uniformly by the catalyst in order to guarantee comparable pressure drops, flow rates and contact times in each, thus avoiding non-uniform temperatures, an overall drop in selectivity, and accelerated aging of the catalyst system. As a rule, temperature control is more delicate than in fluidized bed reactors. This operation is facilitated and the formation of hot spots avoided by various expedients:

- (a) Reduction of the volumetric activity of the catalyst by diluting it with an inert solid.
- (b) Production of a concentration gradient in the active phase (cupric chloride) during filling.
- (c) Limitation of the advancement of the reaction by using several reactors placed in series, packed with catalysts with increasing cupric chloride contents, fed in parallel with air or oxygen.

The operating conditions are also more severe. As a rule, the temperature and pressure are higher (230 to 300°C, 0.3 to $1.5 \cdot 10^6$ Pa absolute). This results in greater corrosion problems, requiring the use of high-alloy or Inconel steel tubes, and nickel-coated distribution boxes, while the shell continues to be built of carbon steel.

The use of reactors in series is the most widespread industrial method. It forms part of a flowsheet which, in its principle and in the case of air, comprises the following main stages in addition to the auxiliary compressor:

- Quenching of the gaseous products leaving the reaction zone in a tower provided with precooled water recirculation, to which ammonia is added for the absorption of chloral. The liquid fraction withdrawn is essentially recirculated and partly settled to recover the ethylene dichloride which is also entrained.
- Supplementary cooling of the gaseous fraction leaving the quenching tower and its partial condensation, by passage through heat exchangers. This operation is supplemented by gas/liquid separation, followed by settling of the condensate which is previously neutralized with ammonia. The aqueous phase thus obtained is combined with that produced by quenching. The organic phase, rich in ethylene dichloride, is sent to the purification stage similar to the one already described for the fluidized bed technologies.
- Treatment of the residual gases, comprising first drying, followed by conversion of the excess ethylene they contain by chlorination. This reaction takes place in the presence of ethylene dichloride as a solvent, in a reactor equipped with external circulation of the medium through a heat exchanger, to remove the heat generated and to control the temperature. Ethylene dichloride entrained in the gaseous phase is recovered by multiple effect cooling to -25°C , by means of a series of units with alternating heat exchangers and separating drums. The rest of the gas is incinerated and the flue gases treated before discharge to the atmosphere, to rid them of the hydrochloric acid formed during this operation.

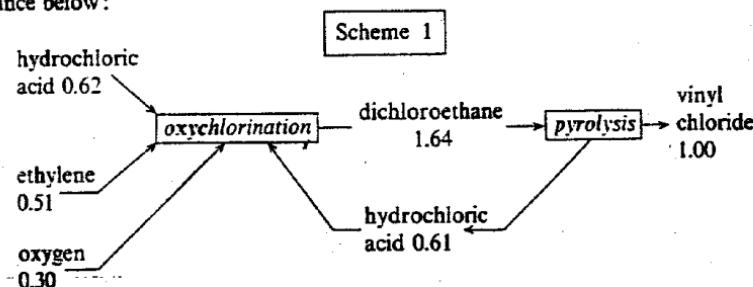
In installations operating in the presence of oxygen, the flowsheet is substantially the same. It differs in the recycling, after recompression, of a large fraction of the stream leaving the gas/liquid separator which follows the quenching stage. Given the large excess of ethylene employed in this type of unit, the natural gas is consequently very rich in unconverted hydrocarbons and contains very few inerts.

C. Integrated schemes

Integrated schemes are designed to deal with the following different situations.

a. Scheme 1. The only chlorinated raw material available is hydrochloric acid

Like chlorination, oxychlorination culminates in the production of ethylene dichloride, which generates hydrochloric acid by pyrolysis. Its recycle to the ethylene conversion stage serves to optimize the make-up required, as shown by the diagram and material balance below:

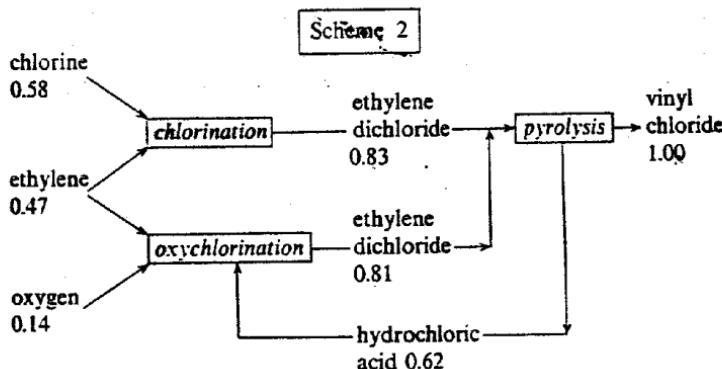


This situation is characteristic of producers who have only hydrochloric acid, resulting in particular from the manufacture of chlorinated solvents.

b. Schemes 2 and 3. The only chlorinated raw material available is chlorine

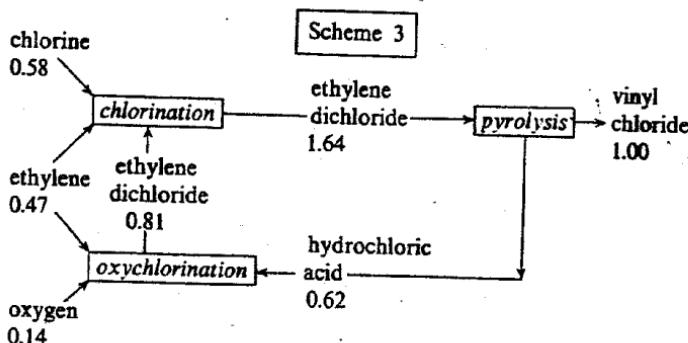
By combining oxychlorination, which consumes hydrochloric acid, with the direct chlorination of ethylene, the by-production of chlorinated wastes can be limited and the production of vinyl chloride adjusted to the chlorine availabilities. Different variants can be considered, including the following two:

- Scheme 2. The hydrochloric acid by-product is entirely recycled. This scheme is currently the most widespread industrially. The ethylene feed is divided into more or less equal amounts between chlorination and oxychlorination:



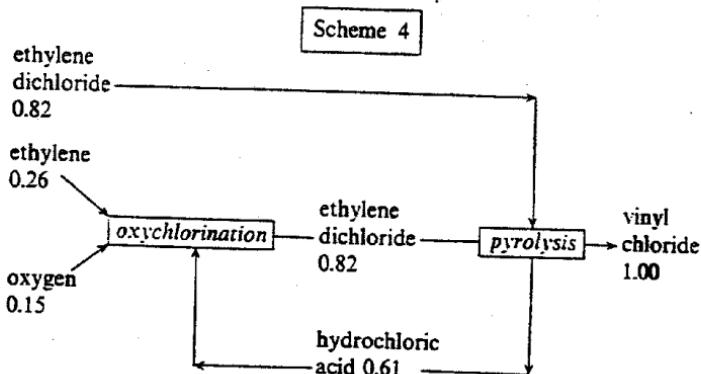
Scheme 3. Hydrochloric acid is entirely recycled and the energy balance is optimized. This solution was proposed recently by *Stauffer*, with the development of their High-Temperature Chlorination process (HTC process). This variant is based on the design of a "boiling" reactor, directly combined with the purification of ethylene dichloride by distillation. This U-shaped equipment allows liquid phase chlorination to take place in one of the two branches, and the removal of the heat generated, not by indirect cooling in the other branch, particularly of the ethylene dichloride, which is then introduced directly into the heavy product fractionation column. This arrangement guarantees substantial savings in the energy usually required to purify ethylene dichloride (0.4 to 0.5 t steam/t). Since it avoids the introduction of acidic or basic scrubbing liquors for the effluents, it also limits corrosion.

It offers the maximum advantage when the ethylene dichloride obtained by oxychlorination also passes through the chlorination reactor as a solvent. This case corresponds to the following scheme:



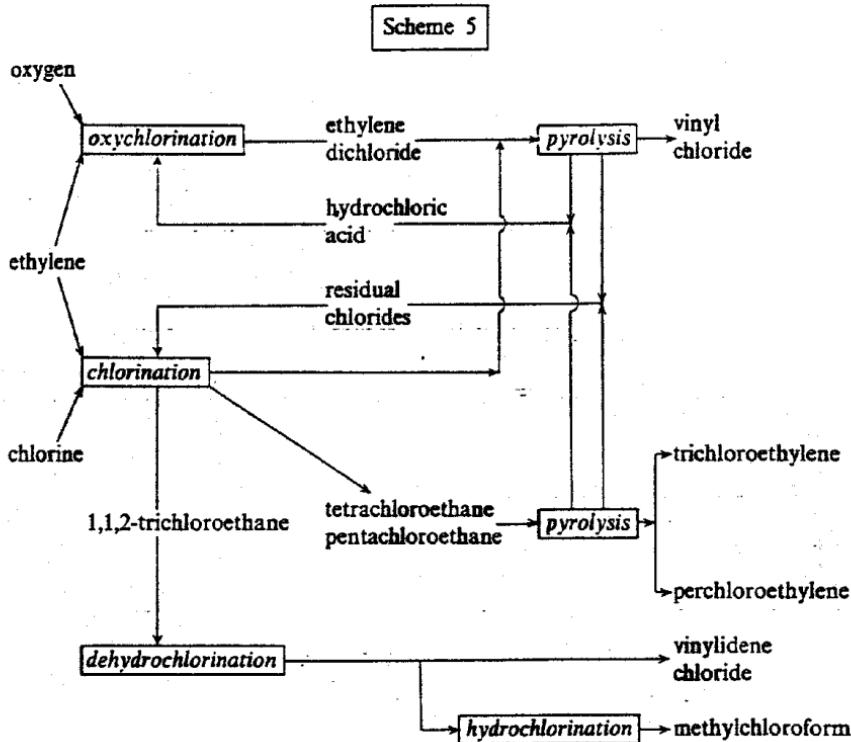
c. Scheme 4. Excess ethylene dichloride is available

In this situation, chlorine and hydrochloric acid are unavailable. The available ethylene dichloride may be obtained, for example, from an installation producing chlorinated solvents:



d. Scheme 5. The production of vinyl chloride forms part of a complex also manufacturing chlorinated solvents

This situation is that of the Chloe process of *Pechiney/Saint-Gobain* and the Vinyclene process of *Toa Gosei*, etc., which simultaneously produce vinyl chloride, trichloroethylene, perchloroethylene, etc. This results in the following typical scheme:



11.2.5 Chlorine manufacture

11.2.5.1 The importance of chlorine in petrochemistry

Chlorine is used in significant amounts in the manufacture of vinyl chloride, which is one of its principal outlets, along with chlorinated solvents. It is essentially produced by the electrolysis of sodium chloride, which also yields sodium hydroxide. In terms of availability and price, this production implies constraints connected with market fluctuations and changes in the economic situation. Until the 1970s, chlorinated products thus represented the driving force for the development of electrolysis facilities. This trend has been

reversed, to the extent that the shortage of available caustic soda has led to a substantial rise in the price of this basic material, so that alternative solutions are being developed to supplant it by sodium carbonate, lime or ammonia in certain applications (chemicals, paper industry, etc.). Small amounts of chlorine are also obtained as a by-product of the manufacture of sodium, magnesium and potassium, and also generally as a captive substance by the transformation of residual hydrochloric acid (see Section 11.2.4).

Although these technologies are associated with the field of inorganic chemistry and consequently have no theoretical link with petrochemical processes, it appeared to be indispensable to discuss briefly the technical and economic problems of chlorine manufacture in connection with the production of vinyl chloride. In fact, any complex of even average size, which considers this outlet for ethylene, must include chlorine-producing facilities, if only because of storage and transport problems.

11.2.5.2 Technological aspects of chlorine production by the electrolysis of sodium chloride

At first glance, three industrial methods exist for the simultaneous production of chlorine and sodium hydroxide by the electrolysis of sodium chloride. By order of importance in terms of installed capacity worldwide (per cent weight), these technologies involve the following electrolytic cells:

Diaphragm cells	56
Mercury cathode cells	43
Membrane cells	1
Total	100

A. Diaphragm cells (Fig. 11.10)

In this type of cell, a diaphragm is used to separate the anode and cathode compartments, to prevent the chlorine evolved at the anode and the caustic soda formed at the cathode from combining to produce sodium hypochlorite, followed by sodium chlorate.

The previously purified brine (anolyte), introduced into the anode compartment, diffuses through the diaphragm under the effect of the hydrostatic pressure differential, in other words the liquid levels on either side of the wall. The optimal diffusion rate results from a compromise between the need for a high sodium hydroxide content in the catholyte (low rates) and the need to limit the reverse migration of hydroxyl ions toward the anolyte (high rates). The consequences of this process (production of oxygen which contaminates the chlorine) can be controlled partly by the addition of small amounts of hydrochloric acid to the brine feed.

The earliest anodes used were of graphite, but the electrolytic decomposition of water and hypochlorous acid produces hydroxyl ions, and consequently oxygen, which gradually consumes the anodes to yield CO_2 . This results in an increase in the electrode spacing, the need to raise the voltage at the terminals, accelerated clogging of the diaphragm by free carbon particles, and ultimately, the limitation of the life of this type of equipment to a few months (4 to 8). The current preference is for expanded titanium base anodes, activated and protected by a coating of a precious metal oxide (RuO_2) or a TiO_2 -noble metal oxide system possibly with a third metallic oxide component (Co, Zr, Mg, Zn,

etc.). The cathodes, which were initially of steel, are now made of nickel or steel coated with nickel or cobalt. Their life is 15 to 20 years, whereas that of the new anodes is shorter (3 to 8 years).

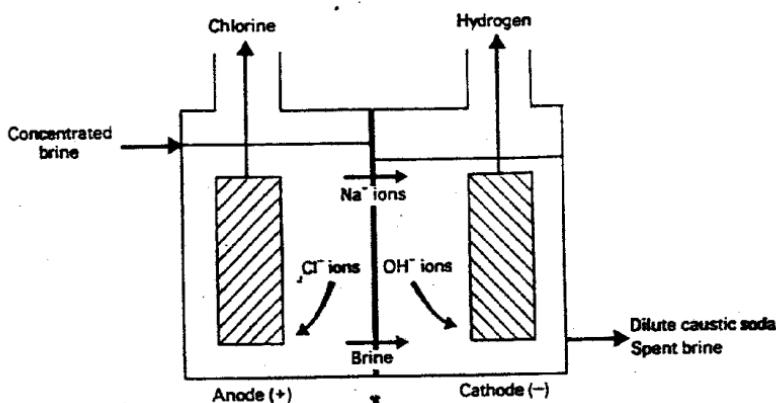


Fig. 11.10. Chlorine manufacture. Schematic diagram of diaphragm type electrolytic cell.

The diaphragms, initially of asbestos, are now based on a polymer (polytetrafluoroethylene) mixed with asbestos or used alone, or are formed of resins (Nafion by *Du Pont*, for example), in order to obtain lives comparable to those of metallic anodes, namely increased from less than one year to five years. They are generally located close to the cathode which acts as their support.

Industrial electrolytic cells are of two types, monopolar and bipolar, depending on the design of the electrodes. In the latter case, one side of the electrode is the anode of one cell, while the other is the cathode of adjacent cell. Bipolar systems allow box-type assemblies, like the monopolar systems, but also filter-press-type assemblies offering a gain in size and weight, etc. These electrolytic cells operate in similar conditions of voltage and current density, parameters that are related by the following equation:

$$V = a + bi$$

where

$$a = 2.4 \text{ to } 2.6,$$

$$b = \approx 0.4 \text{ to } 0.8,$$

$$i = \text{in kiloamperes per square meter such that: } 1.3 < i < 2.8.$$

Passage of the current helps to offset the endothermicity of the conversion, which amounts overall to $\Delta H_{298}^{\circ} \approx 225 \text{ kJ/mol}$ of NaCl. It also causes overheating of the electrolyte to 80 to 100°C. The boiling point of the anolyte is between 106 and 107°C, and that of the catholyte between 109 and 110°C.

The brine introduced is usually saturated with NaCl (25.5 per cent weight). It contains various impurities (Ca, Mg, K, SO₄, Fe, Ti, Mo, Cr, V and W ions) which should be removed as thoroughly as possible by chemical pretreatment (with sodium carbonate and/or caustic soda) or passage on ion exchange resins. In conventional cells, once-through conversion is up to 50 per cent (55 per cent in the most efficient equipment), so that the cathode compartment can yield a solution containing 145 to 160 g/l of sodium hydroxide, which can then be concentrated in multiple effect evaporators to obtain a product containing 50 per cent weight of NaOH. The other components are NaCl (1 to 2 per cent), Na₂CO₃ (1000 to 3000 ppm), NaClO₃ (500 to 1000 ppm). Most of these impurities are removed by physical or chemical treatment (extraction with ammonia, hydrogenation, crystallization, etc.).

The crude chlorine obtained at the anode is in a purity of 97 to 98 per cent volume. It also contains (in per cent volume): 0.1 to 0.5 H₂, 0.2 to 0.3 CO₂, 1 to 2 O₂, and 0.7 to 1 N₂. It is cooled to around 12 to 15°C (the hydrates crystallize below this temperature), dried with sulfuric acid, usually compressed to 0.3 to 0.4 · 10⁶ Pa absolute in order to liquefy it. During these operations, it is important to avoid the explosive combination of Cl₂ and H₂, by keeping the hydrogen content below 4 per cent volume by means of a diluent (such as air or nitrogen). Furthermore, the presence of ammonia in the brine feed leads to the formation of NCl₃, an impurity in chlorine which must be removed before compression, in view of its explosive character.

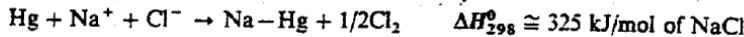
The main industrial diaphragm cell plants are due to:

- (a) *Diamond Shamrock*: DSA type (Dimension-Stable Anode), MDC, etc.
- (b) *Hooker*: S, H, MX, HA (Happ diaphragm) types, etc.
- (c) *Glanor electrolyser*, developed jointly by *De Nora* and *PPG*, *Dow*, *Nippon Soda*, *Showa Denko*, *Uhde* (modified *Hooker*), etc.

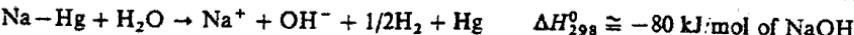
B. Mercury cathode cells (Fig. 11.11).

Processes employing cells of this type operate in two stages:

- In the first stage, sodium chloride in a 25.5 per cent weight aqueous solution is converted by electrolysis at the mercury cathode into chlorine and a sodium amalgam, by the following endothermic reaction:



- In the second stage, the amalgam is decomposed by water into caustic soda and hydrogen, and the mercury regenerated, according to the following exothermic reaction:



a. Electrolysis

The electrolytic cell consists of an elongated trough (average dimensions, 1 to 2.5 m wide, 10 to 25 m long), slightly inclined to the horizontal (slope adjustable between 1.5 and 2.5 per cent), equipped with a gastight cover from which the anodes are suspended. The side walls are lined with a protective and insulating coating. The ends are equipped with compartments and weirs designed for the distribution, separation and removal of the different flows circulating in the trough. The steel bottom is the cathode over its

entire surface. It supports a shallow layer of mercury in motion. Its surface must be as smooth as possible to prevent any breakage of this film. Direct contact with the brine, which is in co-current flow above the mercury, has the effect of causing significant corrosion, as well as the premature decomposition of the amalgam formed, with the liberation of hydrogen, which is detrimental to the mercury itself and also to the purity of the chlorine obtained at the anode (especially due to the explosive nature of the H_2/Cl_2 mixtures during subsequent compression).

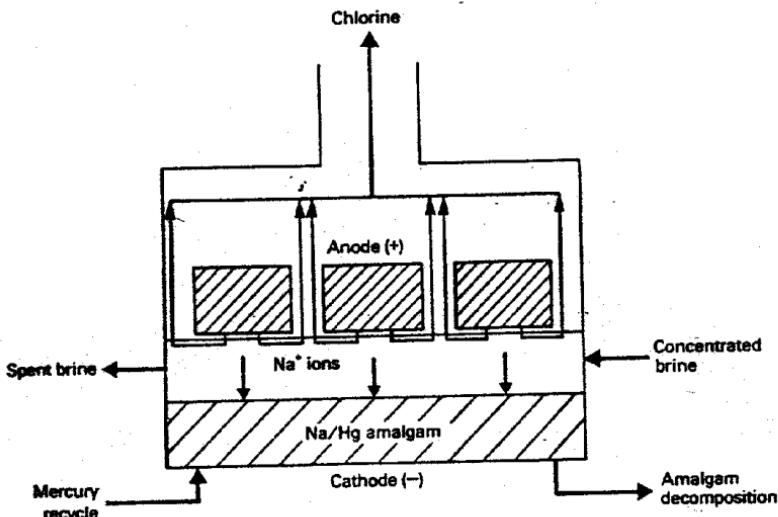


Fig. 11.11. Chlorine manufacture. Schematic diagram of mercury cathode electrolytic cell.

The anode consists of blocks of graphite or preferably of metal activated by a metal oxide coating (TiO_2), which offer better performance (current densities 9 to 13 kA/m^2 instead of 7 to 11), and longer life. The spacing is adjustable, and the blocks are placed immediately next to the cathode, and above it along its entire length, in order to minimize the voltage to be applied at the terminals. As a first approximation, this voltage is given by the following formula:

$$V = 3.1 + 0.1i$$

with i in kiloamperes per square meter.

The disadvantages of graphite are similar to those encountered in diaphragm cells: premature wear due to combustion by oxygen liberated by the secondary electrolysis of water, contamination of chlorine by carbon dioxide, pollution of the amalgam and brine by carbon particles, resulting in the formation of a sludge. Metallic anodes are not entirely devoid of drawbacks, moreover, because if they accidentally come into contact with the cathode, their protective coating is attacked and their life reduced to 1 to 2 years. This means that the stringent control of the spacing between the electrodes is an important

technological parameter. This drawback explains why graphite continues to be very widely used, with improvements under way concerning the quality of the anodes and also the use of diaphragms and ion exchange membranes (Memmer cell by *Technidas Reunidas*, for example) placed on the mercury surface to prevent accidental contact.

The entire trough is insulated from the ground to limit current losses. Once-through conversion of sodium chloride is up to 15 to 16 per cent, so that the spent anolyte, at a temperature between 85 and 90°C, contains 20 to 22 per cent weight of NaCl. It is recycled after the addition of sodium chloride to saturation.

b. Decomposition

Decomposition takes place separately, usually in a vertical column (vessel) containing a packing, generally graphite, which serves as a catalyst. The amalgam flows by gravity in countercurrent contact with an ascending stream of deionized water. Horizontal equipment also exists. In the transformation, the entire system is treated as an electrolytic system, in short-circuit between the graphite and the amalgam, capable of producing electric power. The caustic content of the solution obtained at the top is up to 50 per cent weight, but can theoretically be as high as 70 per cent weight. The regenerated mercury leaving at the bottom is recycled by a pump, whose shutdowns must be as rare as possible to prevent its fouling by the sludges or foams formed by the impurities or the degradation reactions.

c. Contamination and pollution problems associated with the use of mercury

The brine employed must have a purity even higher than that required by diaphragm cells, to avoid contaminating the mercury and causing the formation of sludges. Hence, independently of the Ca, Mg and SO₄ ions (10 ppm maximum), it must not contain more than 1 ppm of strontium ions and 0.02 ppm of vanadium, chromium, nickel ions, etc., metals that can normally be removed by pretreatment with sodium carbonate and caustic soda, at the same time as calcium, magnesium, etc.

Due to its high vapor pressure at the operating temperature of the electrolysis, mercury, whose circulating tonnage represents 700 to 2400 kg/t per day of chlorine production capacity, pollutes the different gaseous streams produced (chlorine, hydrogen). Similarly, it contaminates the different liquids produced by the operation (spent brine, caustic soda, etc.). This results in substantial losses, which must be limited for economic as well as environmental reasons. Whereas small amounts of mercury in the chlorine (0.1 to 0.2 g/t) are not detrimental to its subsequent uses, the same cannot be said of caustic soda, especially for food applications, in which it is removed by filtration (up to 15 ppb), for hydrogen, from which it is removed (up to 3 to 5 ppb) by absorption in sodium hypochlorite, adsorption on activated charcoal, etc., and aqueous wastes, from which it is removed (up to 5 to 10 ppb) by precipitation, adsorption, reduction or extraction. The spent brine, which normally contains 1 to 10 ppm mercury and occasionally 1000 ppm, is usually recycled and therefore does not require treatment.

The total mercury loss is thus up to 2 to 3 g/t of chlorine produced. US regulations stipulate that the daily release must not exceed 2.3 kg, corresponding to the normal operation of a plant with a chlorine production capacity of 1000 t/day. This regulation is expected to be even more stringent in the future (maximum daily release about 1.1 kg).

The main mercury cathode electrolytic cells used in the industry were developed chiefly by *De Nora* and *Uhde*, and to a lesser extent by *ICI*, *Krebs*, *Kureha*, *Olin* and *Solvay*.

C. Membrane cells (Fig. 11.12)

This type of cell, developed more recently, is based on the separation of the anode and cathode compartments by means of an insoluble cationic polyelectrolyte, in other words by means of a cation exchange membrane. This membrane displays the essential property of preventing the passage of Cl^- ions produced by the brine introduced at the anode side, towards the cathode, which operates with water as electrolyte. However, it must allow the migration of the positive Na^+ and H_3O^+ ions. It cannot totally prevent the transfer to the anode of the OH^- ions resulting from electrolysis of the water. To limit this side effect, which results in the production of oxygen in the anode compartment, 1 to 1.5 per cent weight of hydrochloric acid is added at the same time as the brine, in order to maintain the pH at 1 to 2. In this way, the oxygen content of the chlorine does not exceed 0.1 per cent volume, but, in this case, 90 to 93 per cent of the chlorine is obtained from sodium chloride and 7 to 10 per cent from the added acid. At the cathode, the production of one mole of sodium hydroxide causes the consumption of 3 moles of H_2O . This is compensated by the continuous addition of water. Owing to this permanent dilution, the caustic soda concentration is not higher than 30 to 35 per cent weight. It is then raised to 50 per cent by single-effect or double-effect evaporation.

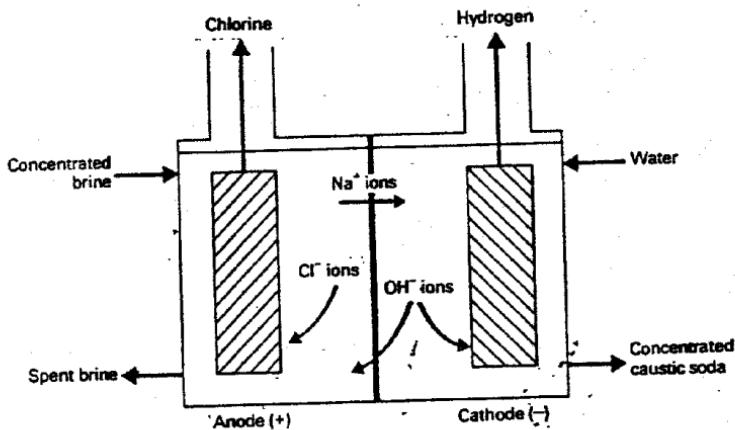


Fig. 11.12. Chlorine manufacture. Schematic diagram of membrane electrolytic cell.

The membranes employed must be able to resist the action of caustic soda, chlorine and acids, at a temperature generally between 85 and 100°C. They must offer good selectivity to Na^+ ions and poor selectivity to OH^- ions, a property that is directly related to the absorbent capacity of the membrane in water. They must also exhibit high electrical conductivity, must be thin, withstand abrasion, exhibit good dimensional stability and mechanical strength, and withstand fouling, thus offering fairly long life. In addition, they must be as inexpensive as possible.

Commercial membranes today meet only some of these requirements. These are based on perfluorinated hydrocarbon polymers (copolymer of tetrafluoroethylene and perfluoro-

sulfonyl-ethoxypropylvinyl ether) containing sulfonic and carboxylic groups. The first membranes were developed by *Du Pont* under the name of *Nafion*. Gradually improved, they gave rise to different variants, which are known by their serial numbers: 100, 200, 300, 400 and 900. They are available in films measuring 2.5×1.5 m. *Asahi Glass* offers the membrane *Fremion* (series 230, 430, 250, 330, DX and 273).

Du Pont membranes are mainly used in cells built by *Diamond Shamrock*, *Hoechst*, *Hooker*, *Ionics*, etc. *Asahi Glass* membranes are used in their own electrolyzers, and in those of *Diamond Shamrock*, *Hoechst*, *ICI*, *Uhde*, etc. *Tokuyama Soda* uses its own membranes. Many developments are also under way, especially by *Allied*, *Bayer*, *Dow*, *General Electric*, *Kanegafuchi*, *Krebskosmo*, *De Nora*, *Olin*, *PPG*, *Toyo Soda* etc.

Like the diaphragm cells, membrane cells (≈ 12 m long, 5 m wide and 3 m high) are of two types, monopolar and bipolar, and usually mounted as a filter press. They operate at low pressure (0.15 to $0.2 \cdot 10^6$ Pa absolute) to facilitate ion transfers and thereby the removal of hydrogen and chlorine. Slight overpressure is sometimes maintained in the cathode compartment to balance the membrane.

The purity of the brine feed must be as high as that employed in the other types of electrolysis. Ca and Mg ions are detrimental to the efficiency of the membrane. Their content, which must not be higher than 10 ppm in diaphragm cells, should not exceed 3 ppm in membrane cells. This can be achieved by adding phosphoric acid to the brine (*Diamond Shamrock*) or passing it on a chelating resin (*Asahi* method, which lowers the content to 0.5 ppm). Once-through conversion of the brine, which remains in the anode compartment only and from which it flows continuously after depletion, does not exceed 70 per cent in the absence of recycling. If recycling is practised, which is often done to maintain a high NaCl concentration, once-through conversion is up to 50 per cent.

11.2.6 Other methods under development

Despite an economic situation that was unfavorable to the establishment of new vinyl chloride plants, considerable research was conducted to improve the existing processes, especially in the following directions:

- (a) Elimination of the ethylene dichloride pyrolysis section, by converting the ethylene to vinyl chloride directly.
- (b) Reduction of material cost and consequently of the number of reaction stages, by operating on ethane.
- (c) Lower energy expenditures, by avoiding the preparation of the chlorine required by hydrolysis of sodium chloride, and employing chemical methods that are generally less endothermic.

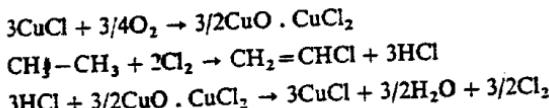
Of these improvements, the latter two appear to be the most promising from the economic standpoint.

11.2.6.1 Production of vinyl chloride by ethane oxychlorination

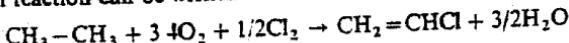
This method, investigated in 1965/1967 in the pilot plant stage jointly by *Lummus* and *Armstrong Cork* (Transcat process), continues to instigate research and development, particularly by *ICI*.

A. Lummus/Armstrong Transcat process

This process is based on the use of molten copper oxychloride as an intermediate oxidizing agent, whose action can be explained by means of the following reaction mechanism:



The overall reaction can be written:



Many by-products appear during this conversion, which takes place between 450 and 550°C. at about $1 \cdot 10^6$ Pa absolute. These by-products include ethyl chloride, ethylene dichloride, ethylene, carbon dioxide, etc. Hence the molar selectivity for vinyl chloride ranges between 65 and 70 per cent in relation to ethane and 50 per cent in relation to chlorine, for once-through conversions of 50 and 100 per cent respectively.

In this process, which applies to a wide variety of chlorinated feeds to which ethane is added, the molten salt plays the role of a heat transfer fluid between the oxychlorination reactor and the pyrolysis reactor, which operates at a lower temperature, and is necessary to convert the substantial amounts of ethylene dichloride by-product (molar selectivity in relation to ethane $\cong 25$ per cent).

B. ICI process

This process carries out the vapor phase oxychlorination of ethane, in the presence of oxygen or air enriched with oxygen, between 350 and 450°C, and between 0.1 and $10 \cdot 10^6$ Pa absolute. It employs a catalyst system based on silver doped by derivatives of manganese, cobalt or nickel, and possibly of rare earths (such as lanthanum), and which is employed in mass form or supported on a Y-type zeolite (offretite).

At 400°C and $0.1 \cdot 10^6$ Pa absolute, in the presence of a mass catalyst containing silver, manganese and lanthanum in the atomic ratio 1/2/0.1, once-through conversion of ethane reaches 100 per cent for a contact time of about 2 s. With excess air and chlorine in the molar ratio of 5/1 and 3/1 respectively, molar selectivity for vinyl chloride is about 40 per cent, and the main by-product is ethylene dichloride (33 per cent).

At 365°C and $0.1 \cdot 10^6$ Pa absolute, in the presence of zeolite impregnated with silver and manganese in the atomic ratio 20/1, ethane conversion is up to 50 per cent for a contact time of about 3 s. In an excess air ratio of 5/1, but with a molar chlorine deficiency of 0.5/1, selectivity for vinyl chloride is over 45 per cent, the main by-product being ethylene ($\cong 23$ per cent) and, to a lesser extent, cis and trans dichloroethylenes (14 per cent).

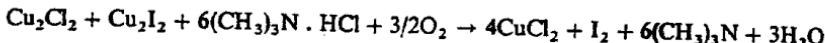
11.2.6.2 Ethylene chlorination by means of chlorine obtained chemically

Akzo proposes a process to produce vinyl chloride that eliminates the need for the production of chlorine by the electrolysis of sodium chloride. The successive conversions are as follows:

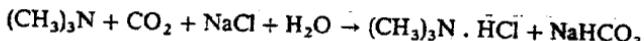
- Chlorination of ethylene in the liquid phase in the presence of cupric chloride and iodine and an aprotic solvent (such as adiponitrile):



- Regeneration of the catalyst system by oxidation in air in the presence of trimethylamine hydrochloride.



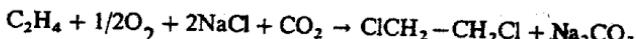
- Regeneration of triethylamine hydrochloride by stripping by CO_2 and the addition of sodium chloride:



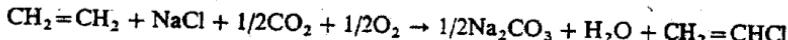
- Calcination after separation of sodium bicarbonate with the generation of CO_2 :



The overall reaction is as follows:

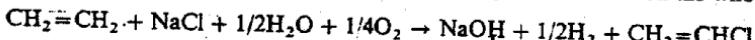


Recent improvements consist in producing the trimethylamine hydrochloride from the hydrochloric acid by-product of the pyrolysis of ethylene dichloride, so that the inclusion of this final step leads to the following overall exothermic conversion:



$$\Delta H_{298}^{\circ} \cong -115 \text{ kJ/mol}$$

This method should be compared with the standard method, which includes the electrolysis of sodium chloride and which is highly endothermic on the whole:



$$\Delta H_{298}^{\circ} \cong +65 \text{ kJ/mol}$$

11.2.7 Economic data

Table 11.4 lists economic data on the main methods for producing ethylene dichloride and vinyl chloride. Table 11.5 gives data on the three main types of process for manufacturing chlorine by the electrolysis of sodium chloride.

11.2.8 Uses and producers

Table 11.6 gives the average commercial specifications of vinyl chloride monomer.

TABLE 11.4
PRODUCTION OF ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER. ECONOMIC DATA
(France conditions, mid-1986)

Process	Acetylene hydro-chlorination	Ethylene chlorination		Ethylene dichloride pyrolysis	Balanced acetylene/ethylene process	Crude oil pyrolysis and chlorination	Ethylene oxychlorination to ethylene dichloride		Integrated schemes				
		Effluent recovery					Air	Oxygen	Air	Oxygen			
		Mixed phase	Vapor phase										
Typical technology	BASF	Rhône-Poulenc	Monsanto	PPEI-Hoechst	Höls	Koreha	Goudrech	Stenfert	Ciba-Geigy-Schaeffer				
Production capacity (t/year)	200,000	330,000	330,000	200,000	200,000	200,000	330,000	330,000	330,000	200,000			
Boundary limits investments (10 ⁶ US\$) ⁽¹⁾	24	10	6	16	32	70	35	26	40	31			
Consumption per ton of product													
Raw materials													
Crude oil (t)	—	—	—	—	—	1.33	—	—	—	—			
Acetylene (t)	0.42	—	—	—	0.22	—	—	—	—	—			
Ethylene (t)	—	0.29	0.30	—	0.23	—	0.31	0.30	0.31	0.31			
Chlorine (t)	—	0.74	0.75	—	0.58	0.61	—	0.07	0.03	0.58			
Hydrochloric acid (t)	0.62	—	—	—	—	—	0.76	0.77	0.72	0.80			
Ethylene dichloride (t)	—	—	—	1.66	—	—	—	—	—	—			
Oxygen (t)	—	—	—	—	—	—	—	0.17	—	0.19			
Hy-products													
Hydrocarbons (kg)	—	10	—	—	—	530	20	25	40	35			
Ethylene dichloride (77% Wt) (kg)	—	—	50	—	—	—	—	—	—	—			
Hydrochloric acid (kg)	—	—	1	590	—	20	—	—	—	—			
Utilities													
Steam (t)	0.1	0.5	(+ 0.1)	2.8	1.2	2.0	0.2	0.3	0.3	2.0			
Electricity (kWh)	120	25	10	80	20	500	80	50	150	100			
Fuel (10 ⁶ kJ)	—	—	—	4.0	2.2	6.0	—	—	—	4.5			
Cooling water (m ³)	50	70	60	180	150	200	100	150	110	240			
Process water (m ³)	0.5	0.5	—	—	1.0	5.0	0.5	0.5	0.5	1.0			
Nitrogen (Nm ³)	1.0	—	—	—	1.0	2.0	—	—	—	—			
Chemicals and catalysts (US\$)	5.5	1	—	1	3.5	2.5	3.5	2.5	3.5	4.5			
Labor (Operators per shift)	4	2	1	2	7	10	3	3	4	4			

(1) Due to corrosion, general services and storage facilities account for 60% of boundary limits investments as a first approximation.

TABLE 11.5
CHLORINE PRODUCTION BY SODIUM CHLORIDE ELECTROLYSIS. ECONOMIC DATA.
(France conditions mid-1986)
CAPACITY 250,000 T/YEAR OF CHLORINE

Electrolysis cell	Diaphragm	Mercury cathode	Membrane
Typical technology	Diamond Shamrock/ Hooker	de Nora/Uhde	Diamond Shamrock/ Hooker/Asahi
Battery limits investments (10 ⁶ US\$)	90	96	87
Consumption per ton of chlorine			
Raw material			
Sodium chloride (t)	1.71	1.71	2.43
By-products			
Hydrogen (100%) (Nm ³)	315	315	320
Sulfuric acid (98%) (kg)	9	9	10
Caustic (50%) (t)	2.26	2.24	2.29
Chemicals			
Sodium carbonate (kg)	—	40	35
Calcium chloride (kg)	14	15	—
Hydrochloric acid (kg)	55	40	12
Sulfuric acid (kg)	9	9	9
Miscellaneous (US\$)	1	1	8.5
Utilities			
Steam (t)	2.4	2.0	0.9
Electricity (kWh)	2,900	3,600	2,800
Cooling water (m ³)	70	210	150
Process water (m ³)	—	—	3
Labor (Operators per shift)	9	10	8

TABLE 11.6
AVERAGE COMMERCIAL SPECIFICATIONS OF VINYL CHLORIDE

Characteristics	Values (ppm) max.
Acetylene	2
Ethylene	4
Propylene	8
1-butene	3
2-butenes	0.5
Butadiene	6
Vinyl acetylene	1
Acetaldehyde	1
Ethylene dichloride	10
Chlorinated compounds (total)	15
Water	200
Iron	0.3
Non-volatile residue	150
Acidity (expressed as HCl)	0.5
Alkalinity (expressed as NaOH)	0.3

Table 11.7 lists the applications and sources of vinyl chloride in 1984, in Western Europe, the United States and Japan, together with the production, capacity and consumption figures for these three geographic areas.

TABLE 11.7
VINYL CHLORIDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Flexible PVC	38	42	39
Rigid and semi-rigid PVC	62	56	53
Miscellaneous ⁽¹⁾	—	2	8
Total	100	100	100
Sources (% product)			
Acetylene	6	2	2
Ethylene	94	98	98
Total	100	100	100
Production (10 ³ t/year)	4,425	3,360	1,695
Capacity (10 ³ t/year) ⁽²⁾	5,860	4,015	1,995
Consumption (10 ³ t/year)	4,160	3,100	1,140

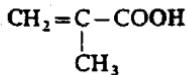
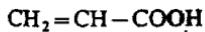
(1) Adhesive applications, specialized protective coatings...

(2) The worldwide production capacity of vinyl chloride was about $16.3 \cdot 10^3$ t/year in 1984 and $17.0 \cdot 10^3$ t/year in 1986, with the following distribution:

United States	3.8	Western Europe	5.9	Middle East	0.5
Canada	0.4	Eastern Europe	2.4	Japan	2.0
Latin America	0.9	Africa	0.2	Asia and Far East	0.9

11.3 ACRYLIC ACID, ACRYLATES AND METHACRYLATES

Industrial acrylic compounds are derivatives of acrylic and methacrylic acids:



The most widely used terms are acrylic acid itself, acrylamide, and, above all, acrylates and methacrylates. They are essentially used to manufacture polymers for many applications, including plastic films, molding powders, paint emulsions, etc. The most widely used polymer is polymethyl methacrylate (Plexiglas).

11.3.1 Acrylic acid

The earliest industrial developments of acrylic acid ($d_4^{20} = 1.051$ ⁽⁴⁾, mp = 13.5°C, bp_{1.013} = 141.6°C) date from 1925/1930. It is largely used as an intermediate in the manufacture of low molecular weight esters, especially the ethyl, butyl and 2-ethyl hexyl acrylates. As a rule, the same synthesis methods, with slight variations, serve to produce the acid itself, or its esters directly. The most widespread and most economical, based on propylene conversion, nevertheless requires the intermediate production of acrylic acid before obtaining its derivatives by esterification, in a distinct step.

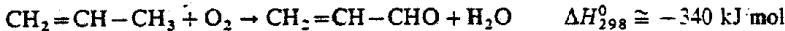
The main methods for manufacturing this acid are as follows:

- (a) Vapor phase oxidation of propylene, carried out in two steps, with passage through acrolein as an intermediate in all industrial plants currently in operation, despite an attempt by *Japan Catalytic Chemicals* in 1970/1971 to achieve single-step conversion. This technology was first developed by *Distillers*, and then by *BASF*, *Sohio*, *Toyo Soda*, *Union Carbide* and by *Japan Catalytic (Nippon Shokubai)*, *Rohm and Haas*, etc.
- (b) Hydrolysis of ethylene cyanohydrin, chiefly employed during the First World War and the postwar period, in Germany and the United States. This process is no longer in use.
- (c) Polymerization of β -propiolactone, achieved by the reaction of formaldehyde with acetene, followed by the destructive distillation of the polymer in the presence of water. This synthesis, commercialized by *Celanese* and *Goodrich*, was stopped because of the carcinogenic properties of β -propiolactone.
- (d) Oxidative carbonylation of ethylene, developed by *Union Oil of California*, mainly for the production of esters.

11.3.1.1 Production of acrylic acid by propylene oxidation

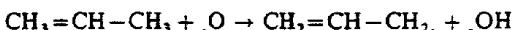
A. Conversion principle

The industrial process is based on the following exothermic reactions, carried out in two stages:



It is assumed that they take place according to a free radical chain reaction:

(a) Initiation:



(4) Specific gravity, 68.0/39.2.

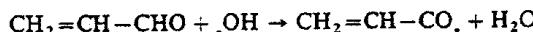
(b) Propagation:



(c) Termination:



and



Various by-products are formed during these transformations, deriving chiefly from partial and complete combustion reactions (acetaldehyde, acetic acid, carbon monoxide, carbon dioxide) and polymerization reactions. To favor the production of acrolein and acrylic acid, shorten the induction period, and operate at lower temperature (<400 to 500°C), highly selective catalysts must be employed.

Originally based on copper oxide or heavy metals deposited on silica or alumina, catalyst systems employed today for the first stage are preferably mixtures of mixed oxides prepared from salts of bismuth, potassium, cobalt, iron, nickel, tin, tellurium, tungsten, etc., molybdic or silico-molybdic acids. They operate around 300 to 350°C, at about 0.1 to $0.3 \cdot 10^6$ Pa absolute, in the presence of steam (water to propylene molar ratio about 4/5) and air, or possibly oxygen diluted with nitrogen (oxygen to propylene molar ratio about 2/1). The water and nitrogen act as diluents and serve to obtain a uniform temperature in the medium. They also limit the risks of explosion of gaseous mixtures, enhance the activity of the catalyst by facilitating the desorption of the reaction products, and maintain catalyst life at a high level (10 to 24 months). The LHSV is 0.5 to 4 (average 2) with once-through conversion better than 90 to 95 per cent, and molar yields of acrolein and acrylic acid of 80 to 90 per cent.

Acrolein conversion takes place in the presence of catalysts based on mixed oxides of molybdenum and vanadium, doped by compounds of tungsten, copper, chromium, tellurium, arsenic, etc., and designed to improve low-temperature activity, productivity, and mechanical performance. They operate around 250 to 280°C, at between 0.1 and $0.2 \cdot 10^6$ Pa absolute, also in the presence of steam (water to acrolein molar ratio about 5 to 7) and air or dilute oxygen (oxygen to acrolein molar ratio close to 2/1). The LHSV is generally about 2, with once-through conversion better than 95 to 97 per cent, and a molar yield of acrylic acid of more than 90 per cent in relation to acrolein.

B. Industrial manufacture (Fig. 11.13)

The latest technologies (especially *Toyo Soda*) do not include the separation and intermediate purification of acrolein. They employ two trains of reactors in series, operating in different conditions, with catalysts of distinct compositions based on molybdenum oxide, and through which the reaction medium flows. These are multitube systems with molten salt circulation (sodium and potassium nitrites and nitrates) on the shell side, to remove heat generated by the transformation, ensure effective temperature control, and the production of low-pressure steam. The catalyst is placed in a fixed bed in the tubes.

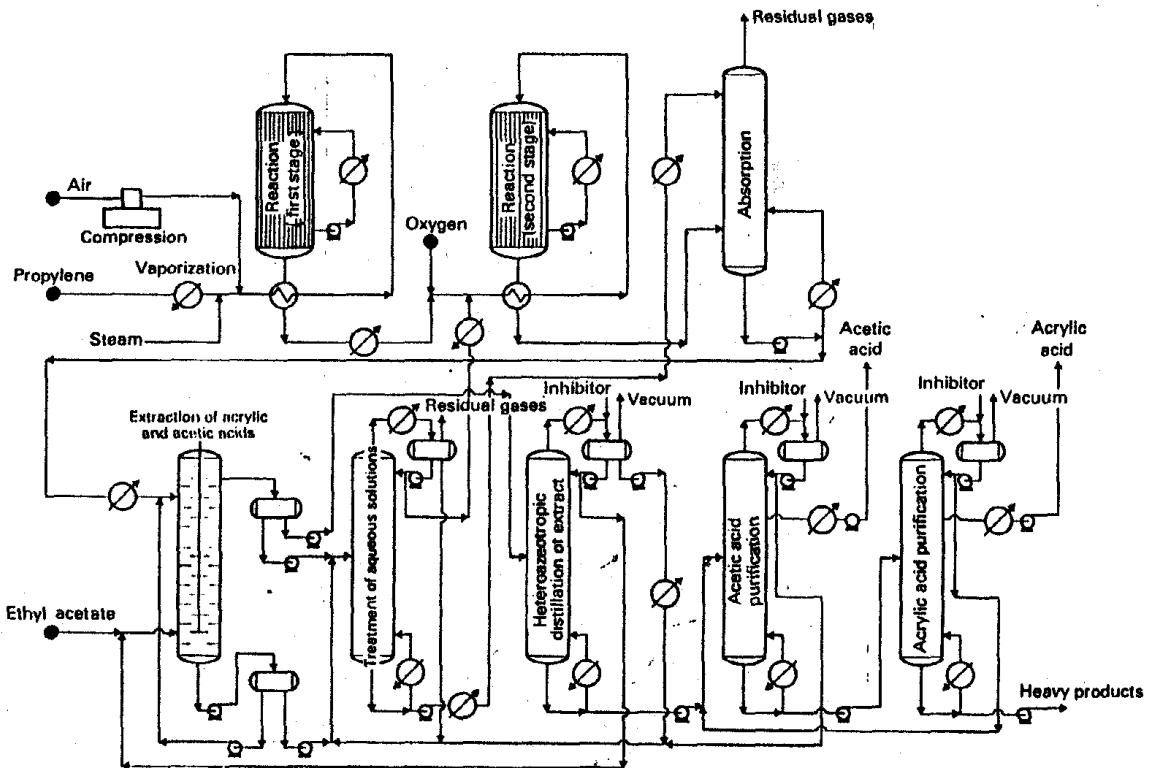


Fig. 11.13. Acrylic acid production by propylene oxidation. Two-stage process.

distributed in each as homogeneously as possible in order to achieve uniform pressure drops, flow rates, conversions, etc., and ultimately uniform catalyst life. The reactants descend through the catalyst, which is surmounted by a feed temperature preheating zone, containing inert solids.

Make-up propylene, in a purity higher than 90 per cent volume and with a propane content lower than 4.5 per cent volume, is first vaporized by heat exchange with the hot effluents issuing from subsequent cooling treatment. Steam and air are then added to it, so that the final mixture contains an average of 4 to 5 per cent volume of propylene, 30 to 40 per cent volume water, and 55 to 65 per cent volume air. It is then raised to the requisite temperature by countercurrent contact with the effluent coming from the first step of the reaction.

This effluent, whose oxygen and steam content is adjusted, is sent directly to the second transformation step after heating by heat exchange with the exiting products. During the various cooling steps undergone by the converted gases, it is essential to make sure that their temperature remains below their dew-point, to avoid excessive corrosion.

To prevent subsequent changes, the products formed are quenched and absorbed. This operation, which lowers the temperature from 140 to 150°C to between 65 and 70°C, takes place by recirculation at 20 to 30°C of water or an organic solvent with a boiling point higher than that of acrylic acid (such as diethylphthalate). This solution tends to simplify the subsequent purification operations, but is not widely used commercially. The operation is supplemented by the recycling of a fraction of the absorption liquid previously cooled to between 40 to 50°C.

The waste gases are burned. The acrylic acid, recovered in an aqueous solution (20 per cent weight), is separated from the other components (particularly acrolein and acetic acid) by means of the following treatment:

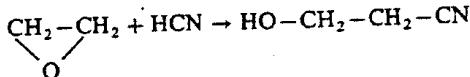
- (a) Extraction of acrylic and acetic acids, usually by ethyl acetate (and possibly butyl acetate, xylenes, diisobutyl ketone, methyl, ethyl and butyl acrylates, or more elaborate solvents, alone or in mixtures). This operation takes place in countercurrent flow in a system of the "Rotating Disk Contactor" type, a central shaft fitted with disks (8 to 10) rotating in a series of baffles.
- (b) Vacuum distillation of the extract (12 trays, 20 kPa absolute) to recover a water/solvent heteroazeotrope at the top, which is settled to recycle the ethyl acetate to the extractor and separate an aqueous phase.
- (c) Purification of the withdrawal rich in acrylic acid by vacuum distillations (7 to 10 kPa absolute) in two columns (55 and 30 trays) yielding acetic and glacial acrylic acids in succession at the top (purity higher than 99 per cent weight). These columns operate with a moderate bottom temperature (70°C) and in the presence of a polymerization inhibitor (especially hydroquinone), to prevent losses of acrylic acid by dimerization to 3-acryloxy propionic acid.
- (d) Treatment of the different aqueous streams to recover the acrolein and ethyl acetate they contain by simple atmospheric distillation (65 trays).

The overall recovery rate of the initial acrylic acid is about 95 per cent.

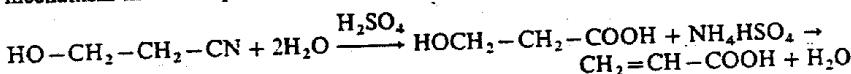
11.3.1.2 Other industrial methods for producing acrylic acid

The following methods are among the processes that have led to industrial plants or to extensive pilot development:

- Hydrolysis of ethylene cyanohydrin, of which the last installation in activity (*Union Carbide Institute*, West Virginia) was shut down in 1971 (see Section 11.3.2.2); it is based on the production of cyanohydrin by the reaction of hydrogen cyanide with ethylene oxide:

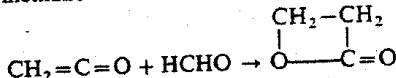


This is followed by its hydrolysis to acrylic acid, in sulfuric medium, by a reaction mechanism in two steps which are carried out simultaneously in practice:

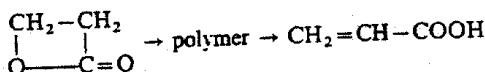


The total yield does not exceed 60 to 70 molar per cent.

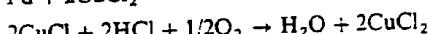
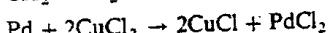
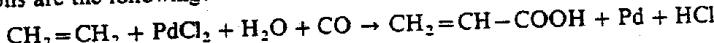
- Polymerization of β -propiolactone and destructive distillation with water of the polymer obtained: this method involves the production of ketene from acetic acid, followed by the action of formaldehyde in the presence of aluminum chloride, or of zinc chloride in solution in acetone or methanol:



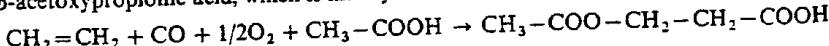
β -propiolactone is then hydrolysed by water in two steps by heating at about 100 to 150°C and then up to 260°C, or directly (Celanese process) at 50°C under partial vacuum in the presence of phosphoric acid:



- Oxidative carbonylation of ethylene: this process, developed by *Union Oil*, operates in the liquid phase, between 135 and 150°C, at $7.5 \cdot 10^6 \text{ Pa}$ absolute, with a high ethylene and low carbon monoxide partial pressure, and in the presence of a catalyst system similar to the one used in the Wacker process for manufacturing acetaldehyde. The main reactions are the following:



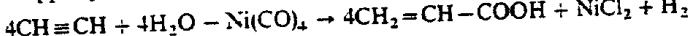
The catalyst system contains several additives, including chlorides of lithium, sodium, rhenium, etc., and lithium or sodium acetate dihydrate. The main by-products are β -acetoxypropionic acid, which is mainly formed if acetic acid is employed as a solvent:



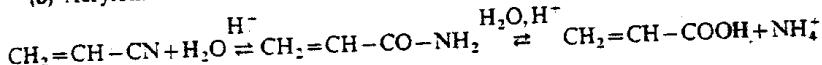
This compound can be thermally redecomposed into acetic and acrylic acids, carbon dioxide, polymers, propionic acid, vinyl acetate and acetaldehyde.

Among the other technologies still employed for the direct production of acrylic esters, and formerly used or considered for the manufacture of acrylic acid, are the following:

(a) The Reppe synthesis from acetylene, modified by BASF (see Section 11.3.2.3);



(b) Acrylonitrile route:



11.3.2 Acrylates

The esters of acrylic acid, of more recent industrial development, are used to manufacture polymers and copolymers. A distinction must be drawn between low molecular weight acrylates obtained by direct synthesis whose physical properties are given in Table 11.8 for the most important commercially, and the higher esters produced by transesterification from methyl acrylate in particular.

TABLE 11.8
PHYSICAL PROPERTIES OF SOME ACRYLATES

Ester	Boiling point (°C under P in kPa)	$d_4^{20(1)}$
Methyl acrylate	80 at 101	0.9535
Ethyl acrylate	43 at 13.7	0.9234
<i>n</i> -butyl acrylate	35 at 1.1	0.8998
Isobutyl acrylate	62 at 6.7	0.8896
2-ethylhexyl acrylate	85 at 1.07	0.8852

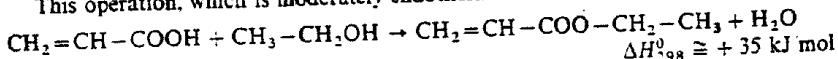
(1) Specific gravity, 68.0-39.2.

The main processes for manufacturing low molecular weight acrylates are the following:

- (a) Acrylic acid esterification.
- (b) Hydrolysis and esterification of ethylene cyanohydrin.
- (c) Reppe reaction using acetylene, carbon monoxide and an alcohol.
- (d) Condensation between ketene and formaldehyde.
- (e) Acrylonitrile hydrolysis and esterification of the product obtained.

11.3.2.1 Acrylate manufacture by acrylic acid esterification (Fig. 11.14)

This operation, which is moderately endothermic:



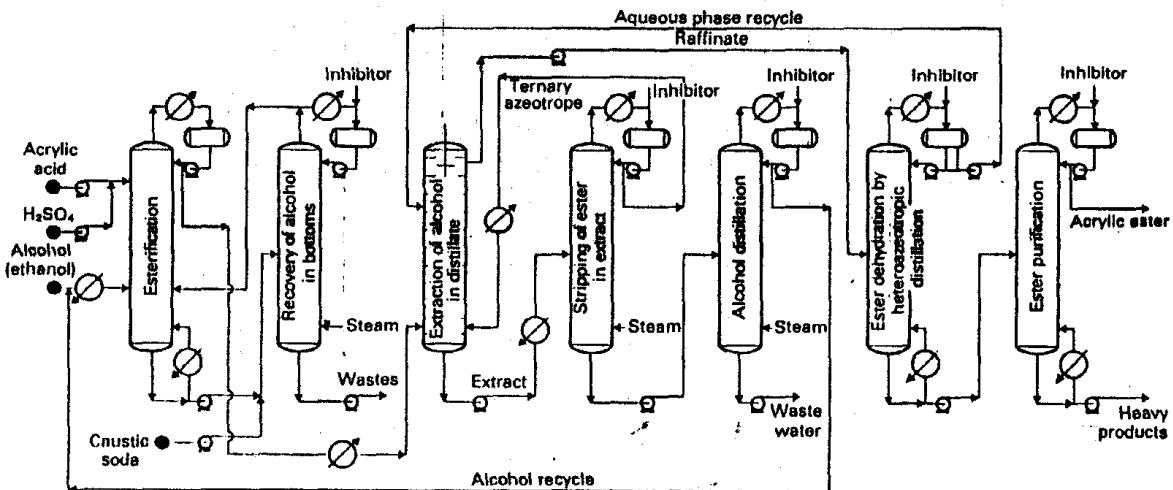


Fig. 11.14. Acrylate production by acrylic acid esterification.

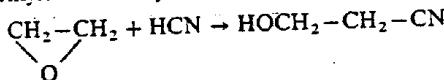
takes place industrially in the liquid phase, at moderate temperature (50 to 80°C), and low pressure (between 20 and 100 kPa absolute), in the presence of an acid catalyst (usually sulfuric acid, but sometimes ion exchange resins). It is carried out in an esterification column containing approximately 30 trays, supplied with acrylic acid, sulfuric acid and make-up and recycle alcohol (methanol, ethanol, etc.). The reaction itself takes place in the lower part of the column, which is adjusted to recover an acrylate/alcohol/water mixture at the top containing a minimum of acrylic acid, and, at the bottom, a purge rich in sulfuric acid and heavy compounds, which is neutralized by caustic soda. The alcohol content is recovered and recycled to esterification by stripping at about 110 to 120°C, at low pressure (between 40 and 120 kPa absolute).

The distillate is scrubbed with water, and caustic soda added if necessary to neutralize the traces of acrylic acid, in order to extract the alcohol. This is obtained by countercurrent contact in a "Rotating Disk Contactor" type system (series of 8 to 10 disks attached to a central shaft rotating between baffles). The ester recovered in the raffinate is dehydrated by heteroazeotropic distillation (20 trays, 50 to 80°C at the top depending on the type of ester, at 20 to 100 kPa absolute). The upper organic phase obtained by settling the distillate is used as reflux, and the lower aqueous layer is recycled to the extraction stage. The withdrawal is treated in a finishing column (20 trays, 40 to 100°C at the top, at 15 to 100 kPa absolute), to obtain the acrylate to specifications at the top (minimum purity 98.5 to 99 per cent weight). The bottoms may be subjected to supplementary stripping to recover its ester content.

All these distillations are conducted in the presence of a polymerization inhibitor (200 ppm of hydroquinone or its monoethyl ether), introduced at the reflux level, and in moderate bottom temperature conditions (100 to 110°C maximum), and hence under reduced pressure if necessary. The different aqueous phases, especially the water extract of the alcohol, are stripped to recover the ternary acrylate/alcohol/water azeotrope at the top, which is recycled to the extraction step (case of butanol in particular), and a water/alcohol mixture at the bottom, which may be separated by azeotropic distillation. The molar yield of esterification is 90 to 95 per cent in relation to acrylic acid.

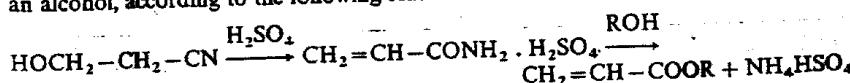
11.3.2.2 Acrylate manufacture from ethylene cyanohydrin

This operation takes place in two steps by a process developed originally by *Rohm and Haas*, and then by *Union Carbide*, and abandoned since 1971. The cyanohydrin is first obtained from ethylene oxide by the following reaction:



This reaction takes place between 55 and 65°C, in the presence of an alkaline catalyst consisting of an aqueous solution of caustic soda and diethylamine. The crude product is purified by vacuum distillation.

This is followed by hydrolysis and esterification in the presence of sulfuric acid and an alcohol, according to the following reactions:



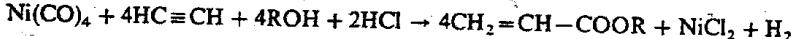
These reactions are conducted simultaneously in the liquid phase, at atmospheric pressure, around 150°C, in a lead-lined reactor, with a cyanohydrin/alcohol/acid molar ratio of 1/2/2. After the effluent is cooled and scrubbed with hot water, the unconverted methanol is recovered and recycled. The other components are fractionated and purified by distillation. The molar yield of acrylate is up to 80 per cent in relation to cyanohydrin.

11.3.2.3 Acrylate manufacture from acetylene

Processes involving the addition of carbon monoxide and alcohol to acetylene, to produce acrylates, are derived from the Reppe reaction, in which nickel carbonyl, used in stoichiometric amounts, produces the CO required by itself. In these variants, the nickel carbonyl is used in semi-catalytic proportions (Rohm and Haas process) or in effective catalytic proportions (BASF process).

A. Reppe synthesis

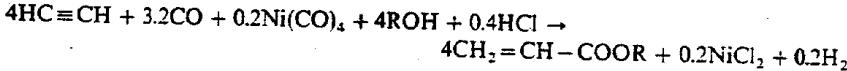
The reaction using $\text{Ni}(\text{CO})_4$ in stoichiometric amounts takes place according to a free radical chain mechanism. It is auto-catalytic, and fast, even at low temperature, normally occurring between 25 and 70°C, at atmospheric pressure. The presence of a small amount of carbon monoxide in the medium prevents initiation and acts as a poison. The overall transformation is written:



It is highly exothermic; $\Delta H_{298}^0 \approx -250 \text{ kJ/mol}$ of acrylate (ethyl acrylate). The hydrogen formed does not appear. It is immediately consumed by side reactions leading in particular to the production of propionate, methanol, etc.

B. Rohm and Haas process

In this case, the stoichiometric and catalytic reactions develop simultaneously. The first ensures startup, and the second subsequently predominates, so that only 20 to 30 per cent of the carbon monoxide consumed is obtained from nickel carbonyl, with the rest supplied by make-up CO. The overall conversion is written:



The reaction accordingly takes place in two stages. In steady-state conditions, it takes place at atmospheric pressure, around 30 to 50°C, with an acetylene to carbon monoxide molar ratio of about 1/1 in an agitated reactor provided with a circulation of coolant fluid designed to control the temperature by removing the heat generated. Excess alcohol (20 per cent) is also used to reduce the viscosity. It is injected after having been used to scrub the gases leaving the reaction zone.

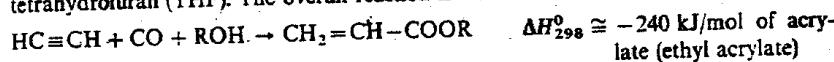
The liquid withdrawn from the reactor is cooled, and the unconverted alcohol and salts are extracted by a nickel chloride solution. The extract is purified and the alcohol recovered is recycled. The raffinate is neutralized by sodium carbonate to remove the acids formed (hydrochloric and acrylic acids especially), and then fractionated in a series

of three distillation columns operating under vacuum in the presence of a polymerization inhibitor. The first removes the water and light compounds at the top, the second produces the acrylate to commercial specifications, and the third recovers the residual acrylate which is recycled to the previous separation step.

The Deer Park, Texas, plant employing the Rohm and Haas technology was shut down in 1977.

C. BASF process (Fig. 11.15)

If nickel carbonyl is employed in effective catalytic proportions, the reaction must take place in more severe operating conditions, i.e. between 150 and 290°C (average 225°C), and 3×10^6 Pa absolute (preferably 10×10^6 Pa absolute), in order to maintain the medium in the liquid phase, most of which consists of a solvent, generally tetrahydrofuran (THF). The overall reaction is written:



Industrial operations take place in two steps with the initial production of acrylic acid, followed by esterification to the acrylate in a separate facility. The flow sheet of the acid production section comprises the following main operations:

- Catalyst preparation from nickel and copper bromide or chloride and acrylic acid recycle, in an agitated jacketed reactor.
- Acetylene dissolution in tetrahydrofuran and its pressurization.
- Implementation of the reaction itself, by the injection of make-up and recycle carbon monoxide, previously recompressed, into the acetylene solution to which the catalyst is added, in a multi-tube reactor with coolant flow on the shell side and low-pressure steam production. Once-through conversion of acetylene is virtually total, and the molar yield in relation to acetylene is up to 70 to 75 per cent.
- Gas separation by flashing and recovery of the stripped acrylic acid by THF scrubbing.
- Treatment of the liquid fraction (18 per cent weight acrylic acid solution in THF) comprising stripping of the CO and water scrubbing before recycling, vacuum distillation of the solvent, acrylic acid extraction by an auxiliary solvent (methyl ethyl ketone), recovery of the new solvent and final purification of acrylic acid by vacuum distillation in the presence of a polymerization inhibitor (hydroquinone). The BASF plant at Freeport, Texas, using this modified Reppe synthesis, was shut down in 1982 and superseded by a unit employing the Nippon Shokubai propylene oxidation technology. The Ludwigshafen plant is apparently still in operation.

11.3.2.4 Acrylate manufacture from ketene and formaldehyde

This method, industrialized by Celanese, one of the world's leading producers of ketene, in its Pampa, Texas, plant, and by Goodrich in Calvert City, Alabama, is now abandoned, both for the manufacture of acrylates and for that of acrylic acid.

For the production of esters, the overall conversion is written:

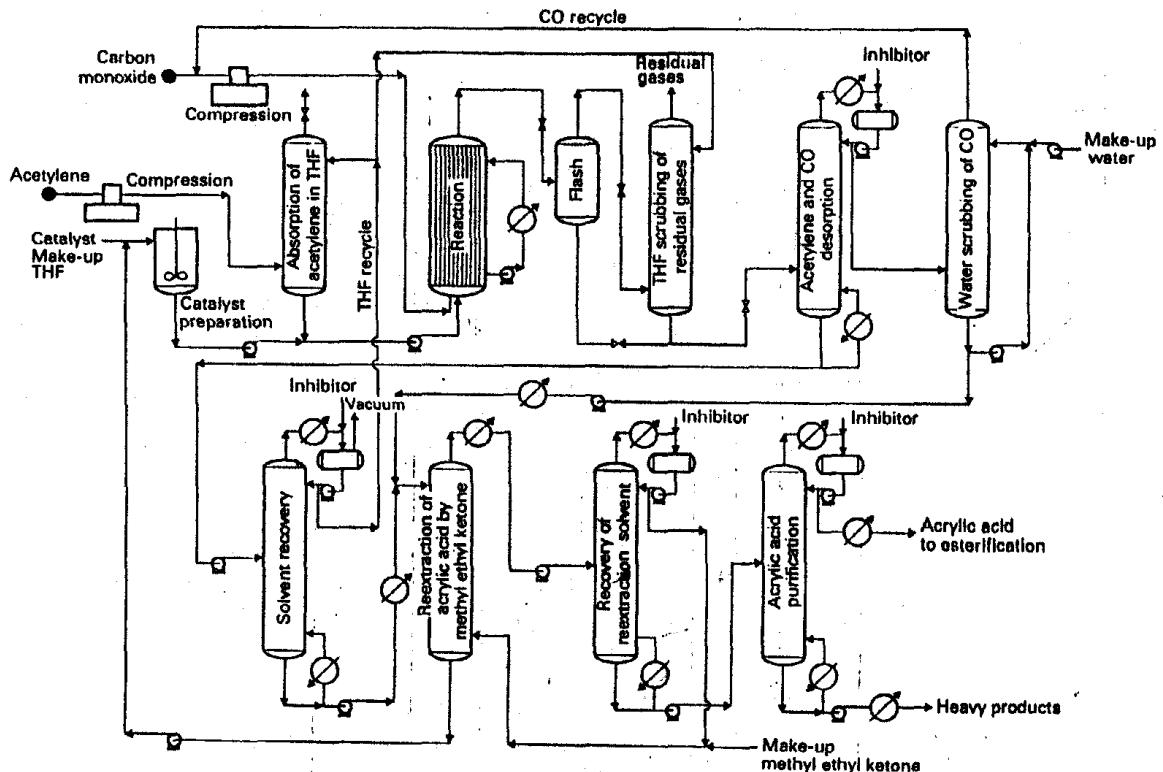
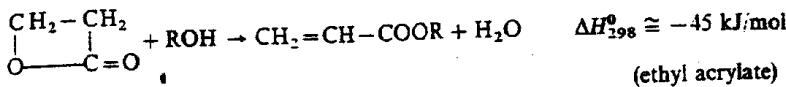
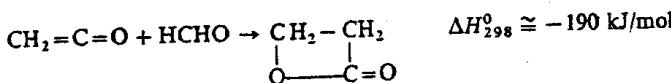


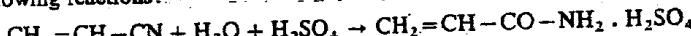
Fig. 11.15. Production of acrylic acid and acrylate from acetylene. BASF process.



11.3.2.5 Acrylate manufacture from acrylonitrile (Fig. 11.16)

This process, which involves the indirect oxidation of propylene, developed initially by *Sohio* and *Ugine*, and then by various Japanese companies such as *Asahi*, *Osaka Gas*, *Showa Denka* and *Toyo Koarsu*, is only used industrially today in Japan and Mexico. The main reasons restricting its commercialization are its low total yield compared with the direct oxidation of propylene, and the by-production in large quantities of sulfuric wastes that can be converted to ammonium sulfate, amounting to nearly 2 t/t of acrylate.

It is based on the hydrolysis of acrylonitrile to acrylamide sulfate in sulfuric acid medium, followed by esterification to the acrylate in the presence of an alcohol by the following reactions:



Although the transformation of acrylonitrile to acrylamide sulfate is carefully controlled by limiting the water content of the medium and the residence time (5 to 10 min) in the reactor, a small fraction is hydrolysed to acrylic acid. This reaction takes place at atmospheric pressure, between 145 and 155°C, in the presence of 85 per cent weight sulfuric acid solution, in an agitated jacketed reactor, with a once-through conversion of more than 95 to 97 per cent.

The effluent obtained at the outlet is directly esterified around 160 to 180°C, a temperature at which the by-product acrylic acid can also be converted in a packed column operating at atmospheric pressure. A mixture of acrylate, excess alcohol and water is recovered at the top, and another mixture at the bottom, consisting of sulfuric acid, ammonium bisulfate and heavy organic by-products, such as 3-alkoxypropionates, which can be thermally decomposed to allow the use of the ammonium sulfate as fertilizer.

The light ends stream is fractionated to recover the by-product ether, the formation of which is limited by adjusting the water content and recycling it to esterification, in order to achieve steady-state concentration conditions. The alcohol is then separated by extractive distillation, and the withdrawal consists of a mixture of water and alcohol, purified by distillation, which may or may not be azeotropic, before recycling and the production at the top of an acrylate/water heteroazeotrope (with ethyl acrylate bp_{1,013} = 81°C, water content 15 per cent weight). Two phases are formed by settling. The lower aqueous phase is used as reflux, and the acrylate-rich organic fraction is dehydrated and then purified in a finishing column. These distillations take place in the presence of a polymerization inhibitor (hydroquinone) and at moderate temperature.

The total yield of the operation in relation to acrylonitrile is 85 to 90 molar per cent. A number of companies, including *Mitsubishi*, have developed techniques for manufacturing acrylamide which correspond to the first stage of the flowsheet considered.

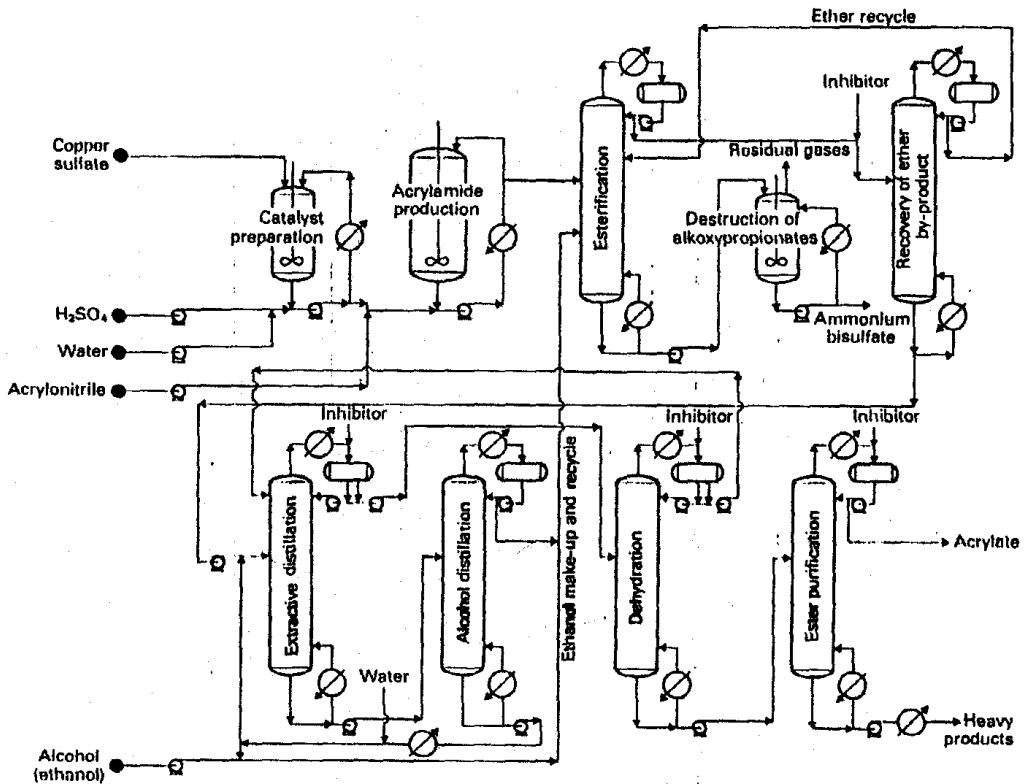


Fig. 11.16. Acrylate production from acrylonitrile.

11.3.2.6 Manufacture of high molecular weight acrylates

These acrylates are usually manufactured in batches, because of the low tonnages required. Moreover, the corresponding alcohols are generally insoluble in water and thus difficult to recover by extraction (*t*-butanol, 2-ethyl hexanol, for example). They are obtained either by direct esterification of acrylic acid, or by transesterification of low molecular weight acrylates (methyl and ethyl acrylates).

Direct esterification takes place in the presence of sulfuric acid or sulfonic toluene, or sulfonic cation exchange resins, at atmospheric pressure and temperatures between 20 and 120°C depending on the ester. Solvents are used to remove the water produced during the reaction. Residual acrylic acid and the catalyst are neutralized, and the acrylate purified by distillation. The total yield of the operation is up to 80 to 90 molar per cent.

Transesterification, used in particular to produce functional esters, is represented by the following reaction:



It takes place at atmospheric pressure, in the presence of catalysts based on strong acids (sulfuric acid) or alkyl titanates (tetraisopropyl titanate) to obtain the higher acrylates, sodium phenoxides, magnesium or thallium alkoxides, alkyltin oxides, etc., to produce functional esters.

The temperature is adjusted to remove the alcohol by-produced by azeotropic distillation as soon as it is formed, with the ester from which it is derived (ethanol/ethyl acrylate azeotrope, for example). A third compound may be used, such as cyclohexane (ethanol/cyclohexane azeotrope). After the catalyst system is separated, the liquid stream from the reactor is fractionated and purified under vacuum in the presence of a polymerization inhibitor (such as phenothiazine).

Certain higher esters (hydroxyethyl and 2-hydroxypropyl acrylates) are also obtained by the reaction of ethylene oxide with acrylic acid in the presence of catalysts based on tertiary amines, quaternary ammonium salts, ion exchange resins, etc.

11.3.3 Methacrylates

Methacrylic acid ($d_4^{20} = 1.015^{(5)}$, mp = 16°C, bp_{1.013} = 163°C) is not generally used as such. It is normally converted immediately to methyl methacrylate ($d_4^{20} = 0.936^{(5)}$, bp_{1.013} = 100°C) which is the most widely used ester, with a steadily growing market, especially in the United States (43 per cent of world capacity), in Western Europe (nearly 31 per cent), and in Japan (about 19 per cent).

Two main industrial methods are employed to manufacture methyl methacrylate:

(a) Processes based on the formation of acetone cyanohydrin as an intermediate.

These are the only processes used in Western Europe and in the United States, and the most widespread worldwide, accounting for more than 95 per cent of installed capacity.

(5) Specific gravity, 68.0:39.2

- (b) Processes involving the production of tertiary butyl alcohol followed by methacrolein. These processes, not widely commercialized today, may supersede conventional technologies in the near future.

The former starts with propylene, and the latter with isobutane or isobutene, whose oxidation by nitrogen oxides and nitric acid in α -hydroxybutyric acid, an intermediate of methacrylic acid production, has already led to industrial developments (*Nissan*) and construction (*Escambia*), now abandoned.

Many research projects are also currently under way to develop new processes starting with ethylene, propylene and isobutene.

11.3.3.1 Manufacture of methyl methacrylate from acetone and hydrogen cyanide

A. Conversion principle

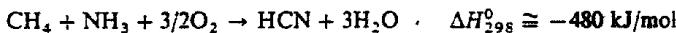
The transformation takes place in four main steps:

- Hydrogen cyanide preparation.
- Condensation of acetone and hydrogen cyanide to acetone cyanohydrin.
- Cyanohydrin transformation to methacrylamide sulfate in acid medium.
- Hydrolysis or esterification of the amide to the acid or ester.

a. Hydrogen cyanide preparation

Hydrogen cyanide is often obtained as a by-product of acrylonitrile manufacture (see Section 11.4). However, its availability by this method is steadily decreasing, in view of the improved yields of techniques for producing acrylonitrile and the faster growth of markets for methyl methacrylate. It is therefore produced by direct synthesis from hydrocarbons, according to three main schemes:

- The Andrusow process; this involves the ammonoxidation of methane:



and hence by a highly exothermic reaction, in the presence of air, between 1100 and 1200°C, with an air/CH₄/NH₃ volume ratio of 5/1/1, and on a catalyst based on platinum (90 per cent) and rhenium (10 per cent weight). The relatively dilute gaseous effluent obtained, which contains only 6 to 8 per cent volume HCN, must be quenched rapidly at 400°C to avoid any secondary reaction. The molar yield reaches about 80 per cent.

- Degussa BMA process (Blausäure Methan Ammoniak): this process carries out the conversion in the absence of oxygen:



This is an endothermic reaction, which takes place in sintered alumina tubes, covered with platinum and raised to between 1200 and 1300°C by external heating. The HCN concentration of the effluent formed is much higher, up to around 20 per cent volume, facilitating its recovery. The yield is also better, up to 85 molar per cent.

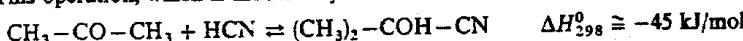
• Degussa Fluohmic process; this is a variant of the above, which employs propane as the raw material:



The conversion takes place in the absence of catalyst, around 1500°C, on a fluidized bed of petroleum coke to achieve complete conversion of the reactants. The molar yields are about 85 to 90 per cent in relation to both propane and ammonia.

b. Condensation of acetone and hydrogen cyanide

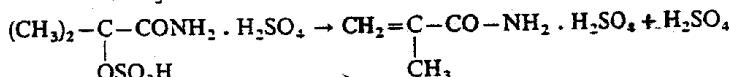
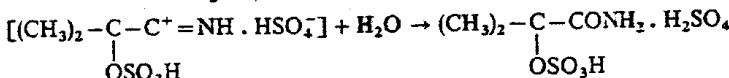
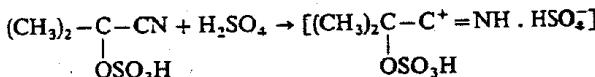
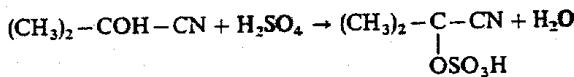
This operation, which is moderately exothermic and balanced:



is favored at low temperature by the presence of alkaline compounds (caustic soda, barium hydroxide, potash, potassium carbonate, calcium phosphate, etc.) deposited on silica. It takes place at atmospheric pressure, at a temperature of about 25 to 40°C, in the liquid phase, with an HCN/acetone molar ratio of about 0.7/1.1. Hydrogen cyanide conversion is virtually complete, and the molar yields are higher than 90 per cent in relation to the two starting reactants.

c. Production of methacrylamide sulfate

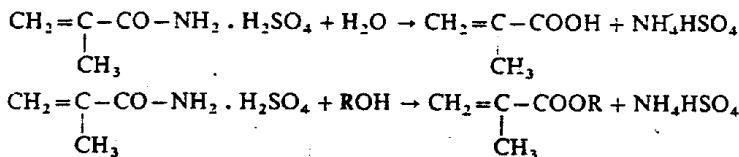
This takes place in the presence of 98 per cent weight sulfuric acid by the following reaction mechanism:



This represents a two-step hydrolysis. In the first phase, it requires anhydrous reactants to avoid the formation of α -hydroxylamide, which is more difficult to convert to methacrylamide sulfate. It takes place in liquid medium, at atmospheric pressure, first at about 80 to 110°C, and then 125 to 145°C to complete the transformation, with residence times of about 1 h, an H_2SO_4 /acetone cyanohydrin molar ratio of 1.5 to 2, and a molar yield of 95 to 97 per cent. The main by-products are carbon monoxide and acetone disulfonic acid. It is necessary to operate in the presence of an inhibitor (phenol, phenothiazine, sulfur, etc.) to prevent the formation of polymers.

d. Hydrolysis or esterification of methacrylamide sulfate

Depending on the reactant employed, water or alcohol (methanol), the following reactions are obtained:



They can be carried out in the following conditions:

- (a) At atmospheric pressure, around 80 to 110°C, in the presence of excess aqueous methanol, with residence times of 2 to 4 h.
- (b) Under pressure ($0.8 \cdot 10^6$ Pa absolute), around 100 to 150°C, with residence times less than 1 h and in excess sulfuric acid (10 molar per cent in relation to methanol), at 0.02 per cent water maximum, in agitated jacketed reactors or reactors equipped with intermediate cooling systems, to remove the heat generated by the reaction and to control the thermal level. The transformation yield is up to 90 molar per cent in relation to the initial acetone cyanohydrin and 80 to 90 molar per cent in relation to methanol. The main by-products formed are dimethyl ether, methyl formate, acetone, α -hydroxyisobutyric acid, α -hydroxymethylisobutyrate and β -methoxymethylisobutyrate. Polymerization inhibitors must also be used.

B. Industrial manufacture (Fig. 11.17)

Originally developed by *ICI*, and then modified and improved by *Du Pont*, *Rohm and Haas*, etc., this type of process has also been commercialized by *Asahi*, *Mitsubishi*, *Montedison*, *Norsolor*, *PCUK (Produits Chimiques Ugine Kuhlmann)*, etc. A typical flowsheet of an industrial installation comprises the following main operations.

a. Hydrogen cyanide production

- Preparation of the air/ammonia mixture, to which methane feed is added by the absorption of gaseous ammonia in cold water, followed by air and steam stripping.
- Reaction of the mixture obtained by circulation through a catalyst gauze based on platinum and rhenium, raised to 1000°C by the passage of an electric current and the maintenance of the thermal level by the heat generated by the conversion.
- Three-stage quench of the effluents with the production of steam during the first two phases:
 - (a) Indirect heat transfer, first by a vertical boiler placed immediately below the catalyst gauze, equipped with aluminum tubes, followed by a reboiler, which lowers the temperature to 300 and then 150°C.
 - (b) Transfer by direct contact with a cold liquid sulfuric acid recycle to lower the temperature to 20°C and simultaneously neutralize the excess ammonia, with the formation of ammonium sulfate, from which the hydrogen cyanide content is recovered by stripping.
- Absorption by cold water of hydrogen cyanide present in the gases leaving the final quench and regeneration by stripping.

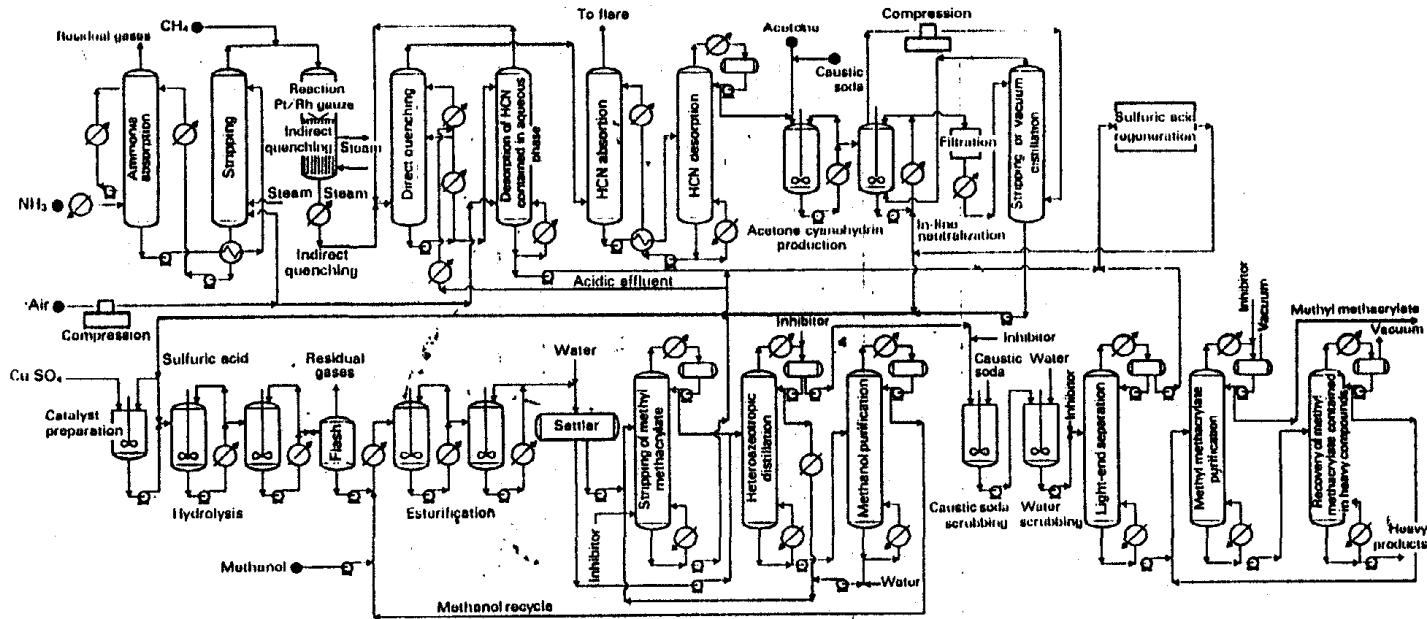


Fig. 11.17. Methyl methacrylate production from acetone and hydrogen cyanide.

b. Acetone cyanohydrin production

- Reaction of hydrogen cyanide, acetone and an alkaline solution (ammonia or caustic soda containing 25 per cent weight, etc.), at atmospheric pressure, at about 30 to 35°C, in a series of agitated reactors cooled by external circulation of the medium through a heat exchanger.
- Neutralization of the effluent with 98 per cent weight sulfuric acid and filtration to remove the ammonium sulfate formed.
- Vacuum distillation, at about 30°C at the top, in two steps with initial separation of light ends (acetone, hydrogen cyanide, etc.) and most of the water, which are then recycled, followed by the thorough removal of water with the production of 98 per cent weight cyanohydrin at the bottom.

c. Hydrolysis and esterification

- Reaction of acetone cyanohydrin with concentrated sulfuric acid forming methacrylamide sulfate, in a series of agitated double-shell reactors featuring external circulation of the medium through a heat exchanger, around 130 to 150°C, at between 0.7 and $0.8 \cdot 10^6$ Pa absolute. Cooling to 60°C and flashing to remove the light products (CO, HCN, acetone, etc.).
- Addition of make-up and recycle aqueous methanol (to prevent the formation of dimethyl ether). Esterification in a series of agitated reactors cooled as described above, after heating of the feed to 100°C and repressurization under 0.6 to $0.7 \cdot 10^6$ Pa absolute. The thermal level must be selected to prevent the crystallization of ammonium bisulfate.

d. Methyl methacrylate separation and purification

- Cooling and settling of the esterification effluent in two phases: the aqueous phase rich in dissolved sulfate is stripped to recover the methacrylate it contains and to add it to the organic fraction, which is fractionated.
- Separation of the water/ester azeotrope by heteroazeotropic distillation ($\text{bp}_{1.013} = 83^\circ\text{C}$, water content 14 per cent weight), in the presence of make-up water and a polymerization inhibitor ($\cong 50$ trays). The aqueous phase obtained by settling is used as reflux. The organic phase, containing 97 per cent weight ester, is purified, after neutralization. The withdrawal, consisting of water and methanol, is redistilled ($\cong 35$ trays), and the alcohol recovered at the top is recycled.
- Purification of methyl methacrylate by distillation in a series of three columns operating under vacuum and in the presence of a polymerization inhibitor. The first ($\cong 25$ trays) removes the light products (dimethyl ether, water, etc.). The second (25 to 30 trays) produces the ester to commercial specifications by removing the heavy products, from which the methacrylate contained is recovered in the last column, and recycled to the previous one.

e. Waste treatment and sulfuric acid regeneration

The different aqueous solutions of bisulfate, ammonium sulfate and sulfuric acid can be utilized as fertilizers after supplementary processing or reconverted to concentrated sulfuric acid. To do this, they are incinerated in the presence of methane and air, at

about 1000°C and $1 \cdot 10^6$ Pa absolute. After the effluent is cooled, the sulfur dioxide contained is first transformed to sulfur trioxide by passage over a vanadium pentoxide-based catalyst, and then to 98 per cent weight sulfuric acid by the addition of steam.

11.3.3.2 Production of methyl methacrylate from tertiary butyl alcohol

Tertiary butyl alcohol currently available in the industry is derived from two main sources:

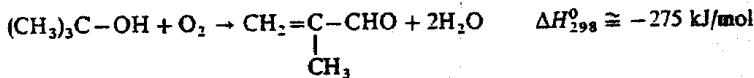
- As a co-product in the manufacture of propylene oxide by the ARCO Chemical (formerly Oxirane) technology for the hydroperoxidation of isobutane (see Section 7.2.4.2).
- It is also obtained by hydration of the isobutene contained in catalytic pyrolysis C₄ cuts, by sulfuric hydration or on ion exchange resins (see Section 9.3.3).

The latter method is used to produce the alcohol employed by *Mitsubishi Rayon* in its Ohtake plant (40,000 t/year) and by *Nippon Shokubai* in its Himeji facility (15,000 t/year) to manufacture methyl methacrylate.

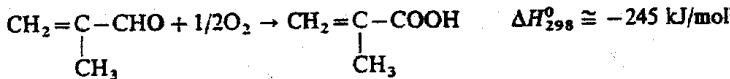
A. Conversion principle

Tertiary butyl alcohol is converted to methyl methacrylate in three steps:

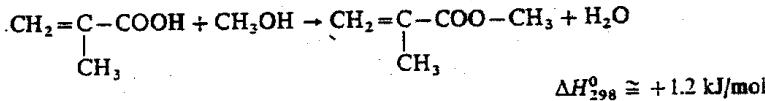
(a) Oxidation of the alcohol to methacrolein:



(b) Oxidation of methacrolein to methacrylic acid:



(c) Esterification of methacrylic acid to methyl methacrylate:



This reaction scheme is comparable to the one that is increasingly employed to manufacture acrylates from propylene (see Section 11.3.1.1):

- The first reaction takes place in the vapor phase, between 330 and 360°C, at low pressure (between 0.3 and $0.4 \cdot 10^6$ Pa absolute), in the presence of air and steam in a t-butanol/air/steam ratio of about 1/10 to 15/6 to 12, on a catalyst based on mixed oxides of molybdenum, cobalt, bismuth, iron, nickel, and additions of derivatives of alkaline metals, antimony, tellurium, phosphorus, tungsten, tin, manganese, etc. With residence times of 2 to 3 s, the molar yield of methacrolein exceeds 85 per cent for virtually total once-through conversion of t-butanol. The main by-products formed are

light compounds (CO , CO_2 , isobutene), acetic and methacrylic acids, and heavy compounds. This reaction was researched and developed in particular by *Halcon, Japan Catalytic Chemical (Nippon Shokubai)*, *Mitsubishi Rayon*, *Nippon Kayaku*, *Sumitomo Chemical*, etc.

- The second transformation also takes place in the vapor phase in industrial plants, preferably between 300 and 350°C, and between 0.1 and $0.5 \cdot 10^6$ Pa absolute, in the presence of air, which may be diluted with nitrogen, and steam, to avoid the flammability range and to facilitate control of the thermal level of the reaction medium. A typical feed composition in these conditions is as follows (per cent volume):

Methacrolein	3 to 6
Steam	20 to 75
Nitrogen	0 to 50
Air	10 to 60

The catalyst systems employed are based on molybdenum and phosphorus. They also contain various additives (oxides of bismuth, antimony, thorium, chromium, copper, zirconium, etc.) and occur in the form of complex phosphomolybdates, or preferably heteropolyacids deposited on an inert support (silicon carbide, α -alumina, diatomaceous earths, titanium dioxide, etc.). This makes them quite different from the catalysts used to produce acrylic acid, which do not offer sufficient activity in this case. With residence times of 2 to 5 s, once-through conversion is better than 90 to 95 per cent, and the molar yield of methacrylic acid is up to 85 to 90 per cent. The main by-products formed are acetic acid, acetone, acrylic acid, CO , CO_2 , etc. The major developments in this area were conducted by *Asahi Glass*, *Daicel, Japan Catalytic Chemical*, *Japanese Geon*, *Mitsubishi Rayon*, *Nippon Kayaku*, *Standard Oil*, *Sumitomo Chemical*, *Toyo Soda*, *Ube*, etc. A number of liquid phase processes, operating at about 30°C, in the presence of a catalyst based on silver or cobalt in alkaline medium, have been developed by *ARCO (Atlantic Richfield Co.)*, *Asahi*, *Sumitomo*, *Union Carbide*, etc.

- Esterification is finally an equilibrium reaction (85 per cent methyl methacrylate), which can be continued to completion by removing one or both of the products obtained as soon as they are formed. It takes place preferably in the liquid phase, in the presence of sulfuric acid or cation exchange resins as a catalyst, with a slight excess of methanol (1.2/1 in mol), at temperatures (110 to 115°C) and pressures (30 to 50 kPa absolute) designed to limit polymerization reactions. The addition of an inhibitor (such as hydroquinone) is also practised. With residence time of about 1 h, once-through conversion is total and the molar yield is close to 99 per cent.

B. Industrial manufacture (Fig. 11.18)

The installation scheme comprises the following main operations:

a. Oxidation of tertiary butyl alcohol to methacrolein

- Transformation of the alcohol, pure or mixed with water, in the azeotrope composition ($\text{bp}_{1.013} = 79.9^\circ\text{C}$, water content 12 per cent weight), previously vaporized, with air and steam added, and then raised to the required temperature in a multi-tube reactor operating at around 330°C and $0.35 \cdot 10^6$ Pa absolute. The thermal level is controlled by removing the heat generated by the reaction by means of the shell-side circulation

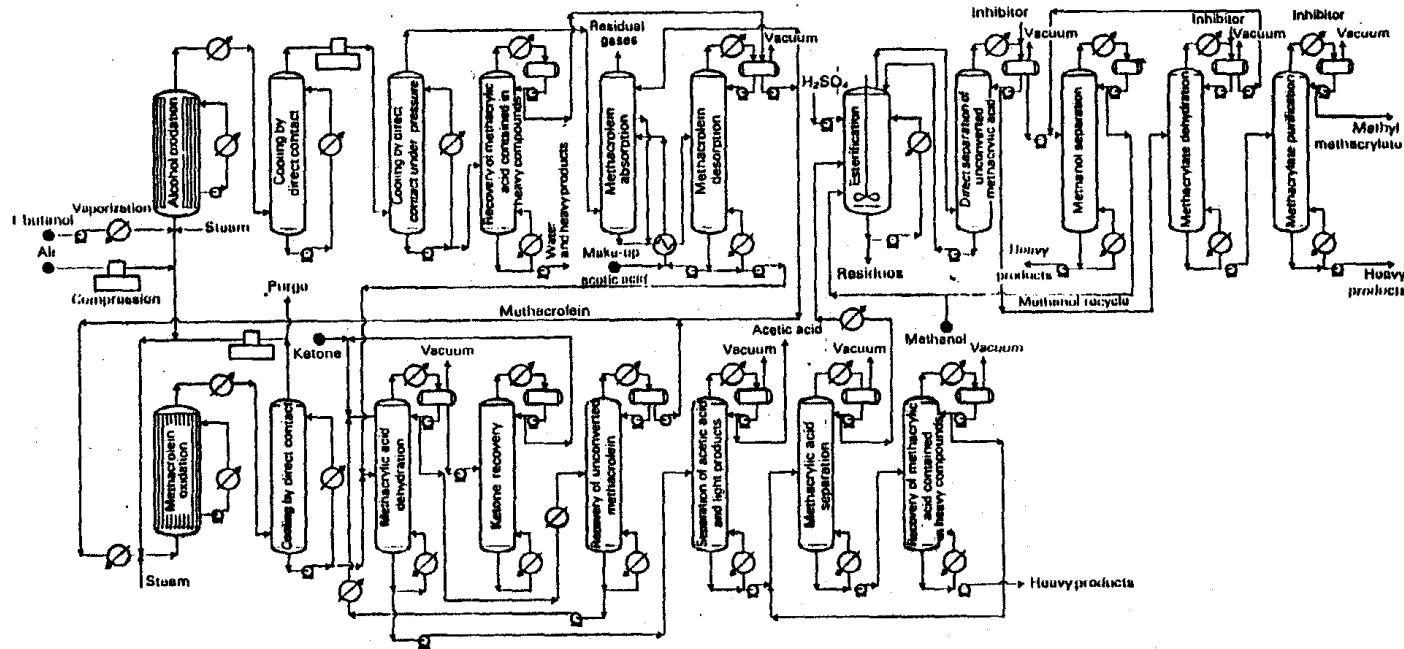


Fig. 11.18. Methyl methacrylate production from tertiary butyl alcohol.

plant fluid and the production of low-pressure steam. The catalyst contained in its must be regenerated periodically by controlled combustion of coke deposits.

Separation and purification of methacrolein. To optimize the energy balance, this operation can take place after the second oxidation, to which the effluent obtained by conversion of the alcohol is therefore sent directly. If not, after cooling to 40°C and partial condensation by indirect and direct heat exchange, the condensates formed are stripped by reboiling to recover the dissolved methacrolein. The methacrolein in the residual vapors is absorbed by scrubbing with acetic acid and water. Regeneration is achieved by stripping, yielding a product in a purity of 98 per cent weight.

b. *Oxidation of methacrolein to methacrylic acid*

- Transformation of make-up and recycle methacrolein, previously vaporized, to which air and steam are added, and then raised to the required temperature. The operation takes place in a multi-tube reactor with shell-side coolant circulation and the production of low-pressure steam. It operates at about 300°C and $0.3 \cdot 10^6$ Pa absolute. The catalyst contained in the tubes must be regenerated periodically by controlled combustion of coke deposits.
- Cooling. The gaseous effluent is cooled to between 40 and 45°C by indirect and direct heat exchange, and the residual gases are scrubbed, purged, and recompressed and recycled.
- Dehydration. The crude methacrylic acid is dehydrated by heteroazeotropic distillation of water in the presence of a solvent (ketone), of which the traces dissolved in the aqueous phase are recovered by stripping. This treatment is also employed to separate and recycle the methacrolein present in the organic phase.
- Purification. The dehydrated methacrylic acid is purified in a series of three vacuum distillation columns, with the separation at the top in succession of acetic acid by-product and light ends (40 to 50 trays), 99.9 per cent weight methacrylic acid (10 to 50 trays) and residual amounts entrained in the heavy compounds.

c. *Esterification of methacrylic acid*

- Transformation of the feed, in the presence of 98 per cent weight sulfuric acid and methanol, around 115 to 120°C, at atmospheric pressure, in an agitated reactor equipped with a jacket or heated by external circulation of the medium through a heat exchanger.
- Separation. Coupling of the reactor with a distillation column operating under vacuum, directly on the effluents leaving in the gas phase, in order to separate unconverted methacrylic acid at the bottom and recycle it immediately, and to obtain two aqueous layers at the top, after cooling and settling. The heavier phase is rich in methanol. The lighter, part of which is used as reflux, contains most of the methacrylate formed. This procedure guarantees the removal of the products from the reaction medium, and helps to achieve complete conversion of the reactants.
- Treatment of the heavy phase by distillation, with separation at the top of the methanol, and of entrained dimethyl ether, methacrylate, etc. These compounds are recycled to the reactor to achieve complete transformation of the methanol, to maintain

a steady-state ether concentration, and a sufficient methacrylate content to guarantee stripping of all the water produced in the form of the azeotrope.

- Treatment of the light phase comprising dehydration and purification of methyl methacrylate in two columns operating under vacuum and in the presence of a polymerization inhibitor. The water ester heteroazeotrope ($\text{bp}_{1.013} = 83^\circ\text{C}$, water content 14 per cent weight) is distilled in the first column. The organic layer obtained by settling is used as reflux, and the aqueous phase is sent to the previous treatment. The second column is used to produce methacrylate to commercial specifications by removing the heavier impurities.

11.3.3.3 Main methods for producing methyl methacrylate under development

Many methods currently in the research or development phase can be grouped together in accordance with the raw material, from which the methyl methacrylate is initially obtained: C_4 olefins, propylene and ethylene.

A. Technologies based on the conversion of C_4 olefins

These can be differentiated by the following main criteria:

- Type of raw material: isobutene, pure or in mixtures.
- The intermediate desired: methacrolein, methacrylonitrile, etc.
- Number of stages.

- Starting with isobutene, the following alternatives are available:

- Isobutene \rightarrow oxidation \rightarrow methacrolein \rightarrow oxidation \rightarrow methacrylic acid \rightarrow esterification \rightarrow methyl methacrylate.

Only the first step differs from the tertiary butyl alcohol conversion scheme. It has given rise to considerable research, particularly by *Asahi, Dow, Japan Catalytic, Kureha, Mitsubishi, Montedison, Nippon Kayaku, Nippon Zeon, Sohio, Toyo Soda, Ube*, etc. It takes place in the vapor phase, between 300 and 400°C, at 0.1 to 0.5 Pa absolute in the presence of a fixed bed of unsupported mixed oxides based on molybdenum, bismuth, tellurium and various additives. To avoid the flammability range, the isobutene and air feed must be diluted with nitrogen and possibly steam. With a residence time of 2 to 3 s, once-through conversion is better than 95 per cent and the molar yield of methacrolein is up to 85 to 90 per cent.

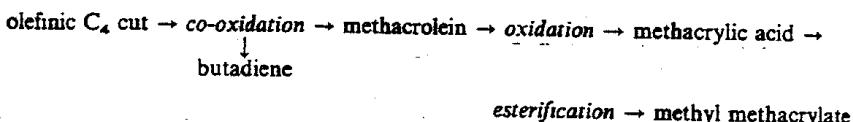
- isobutene \rightarrow ammonoxidation \rightarrow methacrylonitrile \rightarrow sulfuric hydrolysis \rightarrow methacrylamide sulfate \rightarrow esterification \rightarrow methyl methacrylate.

In the first step, this method is comparable to the Sohio process for manufacturing acrylonitrile from propylene (see Section 11.4). The remaining steps are similar to the production of acrylates from acrylonitrile (see Section 11.3.2.5). The operating conditions, catalysts and performance are substantially the same, and the major drawback is the formation of ammonium sulfate as a by-product.

- Starting with olefinic C₄ cuts, the following can be achieved simultaneously:

- Oxidation of isobutene to methacrolein.
- Oxidative dehydrogenation of n-butenes to butadiene.

This is carried out in the presence of mixed oxides based chiefly on molybdenum, bismuth, tellurium, etc., in the vapor phase, around 350 to 450°C, at low pressure, with residence times of 1 to 5 s to enable once-through isobutene conversion higher than 95 per cent, n-butenes conversion of about 80 to 85 per cent, and methacrolein and butadiene molar yields of 75 to 80 per cent. Developed in particular by *Japan Synthetic Rubber, Mitsubishi Rayon, Nippon Kayaku, Nippon Zeon, Ube*, etc., this type of process comprises the succession of the following sequences:



- Various attempts have also been made to reduce the number of steps necessary to produce methyl methacrylate, by passing directly from:

- Isobutene to methacrylic acid (*Asahi, Japan Catalytic, National Distillers, Nippon Kayaku, Nitto*, etc.).
- Methacrolein to methyl methacrylate (*Asahi, Kuraray, Mitsubishi, Mitsui, Nippon Kayaku, SIR (Societa Italiana Resine), Sohio, Sumitomo*, etc.).
- Isobutene to methyl methacrylate (*Mitsubishi*, etc.).

B. Technologies based on propylene conversion

The following two main methods are available:

- Dehydrogenation of isobutyric acid to methacrylic acid, which is then esterified to methyl methacrylate. The isobutyric acid derives from two possible sources:

- Oxidation of isobutyraldehyde, a by-product of Oxo synthesis on propylene (see Section 9.3.1.2).
- Carbonylation of propylene in the presence of water and a catalyst based on rhodium carbonyl and an iodine derivative.

Dehydrogenation itself takes place in the vapor phase, around 400 to 450°C, with catalysts consisting of mixed oxides of molybdenum, phosphorus, vanadium, iron, etc. It has been developed chiefly by *Eastman, Hitachi, Mitsubishi*, etc.

- Dehydrogenation to methyl methacrylate of the isobutyrate produced by the carbonylation of propylene in the presence of methanol and a complex of rhodium, cobalt or palladium. The isobutyrate is converted with catalysts based on molybdenum, tungsten, vanadium, phosphomolybdic acids and possibly heteropolyacids. It has been developed chiefly by *Asahi, BASF, Eastman, Mitsubishi, Mobil, Toray*, etc.

A variant consists in first oxidizing the isobutyrate to α -hydroxymethylisobutyrate, which is then dehydrated to methyl methacrylate.

C. Technologies based on ethylene conversion

These primarily concern the routes involving the use of formaldehyde in transformations of the Cannizzaro reaction type, in the presence of catalysts based on potash or alkaline, earth alkali metals, etc., and passing through the following intermediates:

- (a) Propionaldehyde, obtained by Oxo synthesis on ethylene, to give methacrolein, oxidized to methacrylic acid, which is itself esterified to methyl methacrylate.
- (b) Propionic acid, produced either by the carbonylation of ethylene in the presence of water, or by the oxidation of propionaldehyde, to yield methacrylic acid, which is esterified to methyl methacrylate.
- (c) Methyl propionate, produced by the esterification of propionic acid or the carbonylation of ethylene in the presence of methanol and a complex of rhodium, at about 180°C, at $5 \cdot 10^6$ Pa absolute, to yield methyl methacrylate directly.

A variant consists in replacing the formaldehyde by methylal ($\text{CH}_3 - \text{O} - \text{CH}_2 - \text{O} - \text{CH}_3$). This type of process has been developed by *Air Reduction, BASF, Du Pont, Monsanto, Rohm and Haas*, etc.

Another method associated with the utilization of ethylene and developed by *BASF* involves the following steps:

- (a) Acetic acid conversion to allyl acetate.
- (b) Hydroformylation of allyl acetate to normal and iso acetoxybutyraldehydes, in the presence of rhodium carbonyl, at 30 to 100°C and between 20 and $30 \cdot 10^6$ Pa absolute.
- (c) Oxidation of acetoxybutyraldehydes in the presence of the remaining rhodium, around 30 to 50°C, and between 0.1 and $0.5 \cdot 10^6$ Pa absolute, to the corresponding acids.
- (d) Deacetoxylation of acetoxybutyric acids to acetic acid and butyrolactone for the normal isomer, and to acetic and methacrylic acids for the branched isomer, around 300 to 400°C on alumina, titanium dioxide, silica, activated charcoal, etc., fluidized or fixed beds.

11.3.4 Economic data

Table 11.9 gives technico-economic data on the main methods for manufacturing methacrylic acid, acrylates and methyl methacrylate.

11.3.5 Uses and producers

Table 11.10 lists the average specifications of the main acrylates, methyl methacrylate and the corresponding acids.

Tables 11.11 a, 11.11 b, 11.11 c and 11.11 d give various data on the applications, production, capacities and consumption of acrylic derivatives in Western Europe, the United States and Japan.

**PRODUCTION OF ACRYLIC DERIVATIVES. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/YEAR**

Acrylic compound	Acrylic acid		Methyl acrylate	Ethyl acrylate	Methyl methacrylate	
	From ethylene	From propylene	Esterification	Esterification	From acetone and hydrogen cyanide	From t-butyl alcohol
Process	BASF	BASF-Sohio	—	—	Asahi-Dupont Rohm and Haas	Mitsubishi Nippon Shokubai
Battery limits investments (10 ⁶ US\$) ..	31.5	87	18	18	75	64
Consumption per ton of product						
Raw materials						
Acetylene (t)	0.42	—	—	—	—	—
Propylene (t).....	—	0.72	—	—	—	—
Methanol (t)	—	—	0.40	—	0.36	0.37
Ethanol (t)	—	—	—	0.52	—	—
t-butanol (t)	—	—	—	—	—	0.95
Acetone (t)	—	—	—	—	0.65	—
Acrylic acid (t)	—	—	0.78	0.78	—	—
Hydrogen cyanide (t)	—	—	—	—	0.30	—
Sulfuric acid (t)	—	—	—	—	1.60	0.01
Oxygen (t)	—	0.50	—	—	—	—
Carbon monoxide (Nm ³)	420	—	—	—	—	—
By-products						
Acetic acid (t)	—	0.05	—	—	—	—
Ammonium bisulfate (t)	—	—	—	—	1.15	—
Utilities						
Steam (t)	9	3	6	6	3	6
Electricity (kWh)	100	580	30	30	400	900
Fuel (10 ⁶ kJ)	—	—	—	—	10	5
Cooling water (m ³)	650	250	200	200	300	400
Process water (m ³)	—	—	15	15	10	5
Nitrogen (Nm ³)	—	—	10	10	25	—
Chemicals and catalysts (US\$)	38	70	21	21	18	35
Labor (Operators per shift)	6	5	2	2	7	8

TABLE II.10
AVERAGE COMMERCIAL SPECIFICATIONS OF ACRYLATES

Acrylic derivative	Acrylic acid	Methacrylic acid	Methyl acrylate	Ethyl acrylate	<i>n</i> -butyl acrylate	2-ethylhexyl acrylate	Methyl methacrylate
Purity (% Wt) min.....	98.0	98.5	98.5	99.0	99.0	99.0	99.5
$d_{20}^{20(1)}$	1.052	1.014 ⁽²⁾	0.950	0.922	0.900	0.886	0.941 ⁽²⁾
Acidity (ppm) max. (expressed as acrylic acid)....	—	—	90	100	800	400	50
Water (ppm) max.....	5,000	5,000	1,500	1,500	1,500	1,500	500
Inhibitor (ppm) max.....	5	1,000	10	200	80	150	30
Color (Pt/Co) max.....	50	25	10	20	30	20	10

(1) d_{25}^{25} , specific gravity, 77.0/77.0.(2) To ± 0.02 , specific gravity, 68.0/68.0.

TABLE II.11 a
ACRYLIC ACID PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acrylic esters.....	91	93	93
Miscellaneous ⁽¹⁾	9	7	7
Total	100	100	100
Sources (% product)			
Acetylene.....	45	—	—
Acrylonitrile.....	55	—	18
Propylene.....	—	100	82
Total	100	100	100
Production (10^3 t/year).....	170	330	100
Capacity (10^3 t/year).....	285	405	110
Consumption (10^3 t/year).....	150	320	100

(1) Acrylic solution polymers, acrylic and vinyl polymer emulsions, water-soluble resins (acrylamide/acrylic acid copolymers, polyacrylic acid and salts).

(2) The worldwide production capacity of acrylic acid was about $1.0 \cdot 10^6$ t/year in 1984 and $1.1 \cdot 10^6$ t/year in 1986, with the following distribution:

United States.....	0.42	Western Europe.....	0.31	Middle East.....	—
Canada.....	—	Eastern Europe.....	>0.10	Japan.....	0.12
Latin America.....	0.04	Africa.....	—	Asia and Far East...	>0.06

TABLE 11.11 b
PRODUCTION AND CONSUMPTION OF ACRYLIC ESTERS IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acrylic fibers	6	5	14
Adhesives	17	6	20
Surface coatings	36	40	35
Textiles	17	23	16
Paper	14	5	
Polishes		4	
Leather	10	2	
Miscellaneous ⁽¹⁾		15	
Total	100	100	100
Sources (% product)			
Acetylene	45	—	—
Acrylonitrile	—	—	14
Propylene	55	100	86
Total	100	100	100
Production (10^3 t/year)	245	415	115
Capacity (10^3 t/year) ⁽²⁾	380	530	160
Consumption (10^3 t/year)	230	335	105

(1) Barrier resins, ethylene/ethyl acrylate copolymers, fluorinated alkyl acrylates, impact modifiers, inks, methyl acrylate/methyl methacrylate resins, specialty and functional acrylates (1,4-butanediol diacrylate, trimethylolpropane acrylate, hydroxylalkyl acrylates,...)

(2) The worldwide production capacity of acrylic esters was about $1.2 \cdot 10^6$ t/year in 1984 and $1.3 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.55	Western Europe	0.42	Middle East	—
Canada	—	Eastern Europe	> 0.15	Japan	0.16
Latin America	0.05	Africa	—	Asia and Far East	> 0.09

TABLE 11.11 c
DEMAND DISTRIBUTION OF THE MAIN ACRYLIC ESTERS IN 1984
(% Wt)

Geographic areas	Western Europe	United States	Japan
Methyl acrylate	14	4	23
Ethyl acrylate	24	36	14
Butyl acrylate	38	46	31
2-ethylhexyl acrylate	16	9	29
Other acrylates	8	5	3
Total	100	100	100

TABLE 11.11d
METHYL METHACRYLATE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acrylic sheet	38	34	31
Emulsion polymers	5	11	21
Molding and extrusion powders	20	19	27
Surface coating resins	26	24	—
Miscellaneous ⁽¹⁾	11	12	21
Total	100	100	100
Sources (% product)			
Acetone/HCN	100	100	79
ter-butanol	—	—	21
Total	100	100	100
Production (10 ³ t/year)	230	405	220
Capacity (10 ³ t/year) ⁽²⁾	420	505	260
Consumption (10 ³ t/year)	280	375	185

(1) Impact modifiers, polyester modification (unsaturated polyester resins), processing aids, transesterification (decyl, 2-ethylhexyl, stearyl methacrylates).

(2) The worldwide production capacity of methyl methacrylate was around $1.2 \cdot 10^6$ t/year in 1984 and $1.4 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.60	Western Europe	0.43	Middle East	—
Canada	—	Eastern Europe	0.2 ^(a)	Japan	0.26
Latin America	0.03	Africa	—	Asia and Far East	0.04

(a) Not available.

11.4 ACRYLONITRILE

Discovered in 1893 by the Frenchman Charles Moreau, acrylonitrile ($d_4^{20} = 0.806$ ⁽⁶⁾, mp = -83.5°C , bp_{1.013} = 77.3°C) remained a laboratory curiosity until the end of the First World War. Its industrial importance emerged around 1930, when it was used in Germany and the United States to manufacture nitrile rubber, Buna N, a copolymer of butadiene and acrylonitrile, displaying high resistance to hydrocarbons. Since then, its applications have expanded considerably, including textile fibers, synthetic resins, elastomers, and intermediates of organic syntheses.

Nearly all the acrylonitrile produced worldwide is obtained by the ammonoxidation of propylene. Furthermore, nearly 90 per cent of installed production capacities employ the Sohio process. This company has developed a whole series of increasingly better-performing catalysts, with the first commercial achievement dating from 1960. The other technologies of this type offering an industrial character are those of *Chemie Linz OSW (Österreichische Stickstoff Werke)*, *Montedison/UOP (Universal Oil Products)*, *SNAM (Societa Nazionale Metanodotti)*, *Ugine/Distillers (PCUK/Distillers)*.

(6) Specific gravity, 68.0/39.2.

The earlier methods were the following:

- (a) Addition of hydrogen cyanide to ethylene oxide to form cyanohydrin, which is then dehydrated to acrylonitrile. Developed by *IG Farben*, this process was adopted by *American Cyanamid* and *Union Carbide*, and then abandoned in 1965.
- (b) Reaction of hydrogen cyanide with acetylene, developed by *Bayer*, used by *American Cyanamid*, *Du Pont*, *Monsanto* until 1970.
- (c) Production of lactonitrile from acetaldehyde and hydrogen cyanide, and its dehydration to acrylonitrile. Developed and industrialized by *Hoechst* in Greisheim (Knapsack-Greisheim) until 1959, it is still partly used by the Japanese company *Nusashino* to manufacture lactic acid by lactonitrile hydrolysis.
- (d) Ammonoxidation of propylene by nitrogen oxides, commercialized by *Du Pont* in Beaumont, Texas, until 1966.

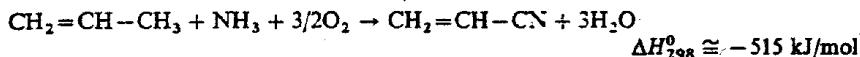
Many developments are currently under way to employ ethylene, propane and butane directly.

11.4.1 Acrylonitrile manufacture by ammonoxidation of propylene

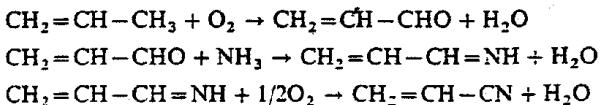
Although a large number of its basic patents already lie in the public domain, the process commercialized by *Sohio*, concerning the ammonoxidation of propylene, has acquired a virtual monopoly in view of the technological know-how accumulated in the past decade.

11.4.1.1 Transformation principle

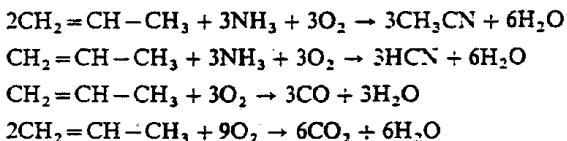
The formation of acrylonitrile by ammonoxidation occurs according to the following highly exothermic reaction:



It now appears clear that this overall result can be explained by the production of acrolein as the main intermediate. In these conditions, the reaction scheme is as follows:



This transformation is also characterized by the importance assumed by degradation side reactions of propylene and of its oxygen and nitrogen derivatives, which lead simultaneously to the formation of hydrogen cyanide, acetonitrile, nitrogen, carbon monoxide and carbon dioxide:



Since these reactions are themselves highly exothermic, it is found in practice that the total exothermicity of acrylonitrile manufacture is higher than indicated by theory, and is as high as 650 to 670 kJ/mol.

A. Catalysts

To offset the lower yield resulting from the development of side reactions, many catalyst formulations have been suggested, and their performance has steadily improved with time. They are all using mixed oxides based on antimony, arsenic, bismuth, cobalt, tin, iron, molybdenum, nickel, phosphorus, rare earths, tellurium, uranium, vanadium, etc., with or without a support.

The most significant development was achieved by *Sohio*, who initially employed bismuth phosphomolybdate. This system was replaced in 1967 by a mixture based on oxides of antimony and uranium (catalyst 21). In 1972, *Sohio* then returned to an iron and bismuth phosphomolybdate (catalyst 41⁽⁷⁾) doped by additions of cobalt, nickel and potassium, and achieving acrylonitrile productivity gains of 10 to 35 per cent. A fourth generation of catalysts (type 49) finally emerged in 1978, achieving a slight improvement in yield, but offering better mechanical properties.

Cooperation between *Distillers* and *PCUK*, followed by *Border Chemicals*, was originally based on the development of a two-step process. In the first step, propylene was converted to acrolein on a catalyst based on selenium and copper oxides, and, in the second step, ammonia reacted in the presence of a system including MoO_3 and various other compounds. A single-step technology was subsequently developed, involving the use of molybdenum oxide promoted by caustic soda, or cobalt molybdate and tellurium oxide, followed by the use of systems of antimony and tin oxides. The best results are now obtained with formulations based on cobalt, iron and molybdenum.

While *SNAM* developed mixtures based on the use of bismuth and vanadium compounds, *Montedison*, whose exclusive operating license was acquired in 1975 by *UOP*, preferred a supported catalyst based on oxides of cerium, molybdenum and tellurium on silica. *OSW* employs a mixture of metallic bismuth and molybdenum deposited on a support.

The latest developments in catalysts for manufacturing acrylonitrile are those of the Japanese-firm *Nitto Chemical*, which commercialized a system in 1974 based on doped antimony and iron, called NS 733A or catalyst 13, offering higher productivity in comparison with *Sohio* catalyst 41, as well as lower production of acetonitrile and hydrogen cyanide by-products.

These formulations, which operate in the vapor phase, are preferably used in a fluidized bed, to facilitate the removal of the heat generated by the reaction, the homogenization of the thermal level within the reaction medium, better temperature control and hence superior catalyst performance (*Sohio*, *Montedison/UOP*, *Nitto*, etc.). However, this arrangement implies improved mechanical properties. Fixed beds have also been used (*PCUK/Distillers/Border*, *SNAM*, *Chemie-Linz*, etc.), the main problem being the need to withstand a thermal gradient, and possibly the existence of hot points causing the

(7) *Sohio's* catalyst 41 formulation is as follows:

$\text{Co}_{4.5} \text{Fe}_{Ni}_{1.5} \text{Bi}_{\text{P}}_{0.5} \text{K}_{0.6} \text{Mo}_{12} \text{O}_{35}$	82.5 per cent weight
SiO_2	17.5 per cent weight

accelerated destruction of the catalyst due to the migration of active phases and to attrition. Apparent residence times range from 2 to 15 s, and catalyst life is generally between one and three years, and possibly more with the latest formulations.

B. Operating conditions

As a rule, the ammonoxidation of propylene takes place in the presence of a slight excess of ammonia and oxygen in comparison with stoichiometry. The purity of the reactants employed is generally high (over 90 per cent weight for propylene, and 99.5 per cent weight for ammonia). With certain catalyst systems, especially the first-generation systems, the addition of steam raises selectivity and limits the conversion of ammonia to nitrogen. However, the current trend, due to the improvement in catalyst performance and the advances in metallurgy, is to eliminate this water hold-up to achieve better optimization of the energy balance of the operation. Table 11.12 lists a number of typical molar feed compositions depending on catalyst type.

Experience shows that the acrylonitrile yield increases with the $\text{NH}_3/\text{propylene}$ ratio. In practice, however, stoichiometry is approached as closely as possible (ratio of 1), and, in certain cases, operations are even conducted at sub-stoichiometric values (≈ 0.8). This is because the reaction is normally incomplete, and the ammonia remaining in the reactor exit gases, independent of the initial excess, gives rise to side reactions. These can be avoided by rapidly neutralizing it by sulfuric acid. Thus increasing the $\text{NH}_3/\text{propylene}$ ratio results in needless losses of raw materials, with repercussions at the economic level. From this standpoint, research projects under way are directed both for the development of better-performing catalysts and the development of ammonia recovery techniques, which allow for its recycling while maintaining high acrylonitrile selectivity.

The reaction temperature usually ranges between 400 and 500°C and pressure remains below $0.3 \cdot 10^6 \text{ Pa absolute}$. The acrylonitrile/acetonitrile molar ratio rises rapidly above 400°C, and reaches a peak around 470 to 480°C.

C. Performance

Once-through conversion of propylene is virtually complete, that of ammonia is higher in a fluidized bed (over 95 per cent) than in a fixed bed (≈ 85 per cent). Selectivity, and consequently the acrylonitrile transformation yield, is very sensitive to the type of catalyst and to the operating conditions, especially the residence time, which must remain above 1 s. The yield may be as high as 72 to 75 molar per cent with the latest catalyst systems operating in a fluidized bed, and nearly 78 molar per cent with those operating in a fixed bed.

Table 11.13 offers some indications about the typical effluent compositions leaving the propylene ammonoxidation reactor according to the technology implemented. It also reveals the high proportion of by-products, whose utilization after separation and purification can influence the economics of the operation considerably. Thus the acetonitrile, which could be used as a butadiene extraction solvent, is usually burned. Another possibility is to convert it to acrylonitrile by the following reaction:



This reaction takes place in the presence of a supported potassium bromide-based catalyst. Hydrogen cyanide serves for the synthesis of methacrylic acid, methionine, etc. In many cases, however, it is also incinerated, minimizing the risks of pollution and accidents.

11.4.1.2 Industrial manufacture

With the Sohio technology, fluidized catalyst bed processes represent the most widespread industrial method. Lying far behind in the number of units installed, the PCUK/Distillers fixed bed technique is nevertheless the most widely used of competing processes.

TABLE 11.12
TYPICAL MOLAR COMPOSITION OF REACTOR FEED FOR THE PRODUCTION
OF ACRYLONITRILE BY PROPYLENE AMMONIATION

Catalyst	Component			
	Propylene	Ammonia	Air	Steam
Sohio	1	1.5 to 2	10 to 20	2 to 4
Sohio	1	1.05 to 1.2	10 to 15	—
PCUK/Distillers	1	1.1 to 1.2	12 to 15	—

TABLE 11.13
ACRYLONITRILE PRODUCTION BY PROPYLENE AMMONIATION.
TYPICAL COMPOSITIONS OF REACTOR EFFLUENT (% VOL)

Catalyst processing	Fluidized bed		Fixed bed
Catalyst	Sohio 41	Nitto 13	PCUK/ Distillers
Effluent composition			
Acrylonitrile	5.2	5.3	4.3
Hydrogen cyanide	1.8	1.1	1.0
Acetonitrile	0.7	0.1	0.3
Carbon monoxide	1.0	0.8	0.5
Carbon dioxide	1.6	2.9	1.2
Higher nitriles	—	—	—
Heavy products	ε	ε	—
Propane	0.8	0.8	0.6
Propylene	0.5	0.2	0.3
Water	26.3	25.2	33.6
Ammonia	0.2	1.0	1.1
Oxygen	2.2	1.8	4.0
Nitrogen	59.7	60.8	53.1
Total	100.0	100.0	100.0

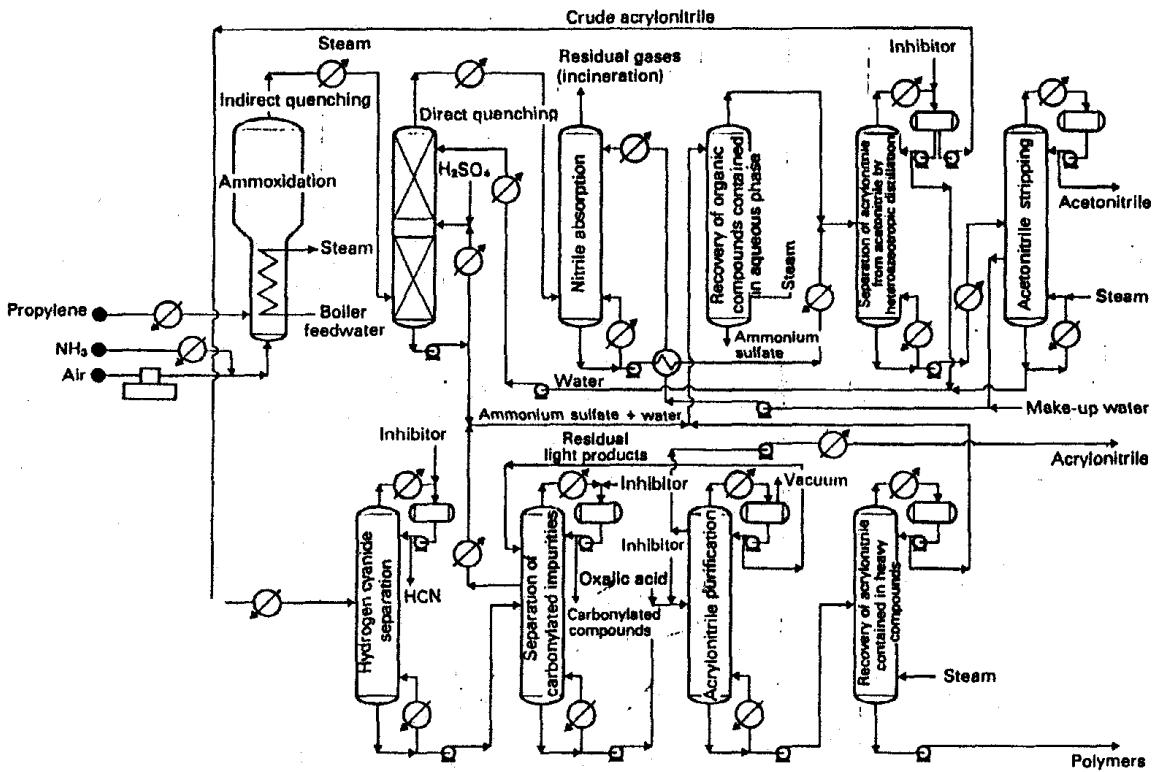


Fig. 11.19. Acrylonitrile production by fluidized bed ammonoxidation of propylene. Sohio process.

A. Propylene ammonoxidation in fluidized bed, Sohio process

The flowsheet of this type of installation (Fig. 11.19) comprises the following main operations:

- The reaction itself: this takes place in a specific vessel (Fig. 11.20) at the base of which a mixture of air compressed to between 0.15 and $0.3 \cdot 10^6$ Pa absolute and fertilizer grade ammonia is introduced, previously vaporized and preheated to between 150 and 200°C by passage through heat exchangers. This feed first crosses a distribution plate and then reaches the catalyst bed, which it fluidizes. Chemical grade propylene

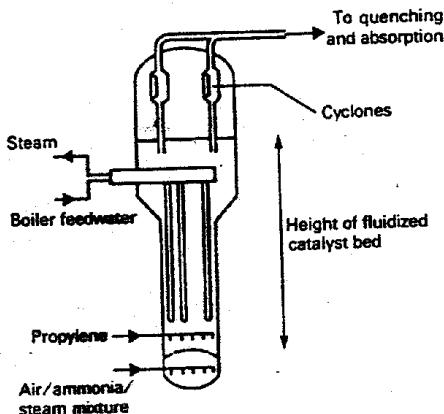


Fig. 11.20. Schematic diagram of Sohio reactor for acrylonitrile production by fluidized bed ammonoxidation of propylene.

(> 95 per cent weight) is introduced separately above the previous distributor, after first having been vaporized and preheated to around 200°C. The fluidization height is 7 to 8 m. A set of immersion tubes with internal boiler feedwater circulation is placed within the catalyst bed. This serves to remove the heat generated by the reaction and to control the temperature at between 420 and 480°C, while producing high-pressure steam (over $3 \cdot 10^6$ Pa absolute). Cyclone separators are installed in the upper part of the reactor to retain catalyst particles entrained in the gaseous effluents.

- Quenching of the products obtained: to prevent any side reactions in the effluents, especially the addition of hydrogen cyanide to acrylonitrile and the formation of polymers which cause a drop in yield, the gases leaving the top of the reactor are rapidly cooled. They are first sent to a quench boiler for the production of low-pressure steam, and then to a direct contact cooling tower, which lowers their temperature to about 80 to 85°C. This operation takes place in the lower part of the tower by means of a solution of sulfuric acid or acidified ammonium sulfate, designed to neutralize the ammonia present. Water scrubbing in the upper section removes the residual acidity. This treatment is accompanied by the production of a side stream of ammonium sulfate solution, which is then stripped of the organic compounds it contains.

• Product recovery: after additional cooling to between 40 and 45°C by indirect heat exchange, the neutralized gases are sent to an absorber operating in the presence of cooled water (5°C), to recover the maximum of hydrogen cyanide, acetonitrile, acrylonitrile and the heavier components. The residual gaseous effluents, which still have very low contents of certain nitriles and hydrocarbons, are incinerated. Since acetonitrile and acrylonitrile have comparable boiling points ($bp_{1.013} = 81.6$ and 77.3°C respectively), and also form azeotropes with comparable characteristics with water, their separation is relatively difficult, requiring about 70 to 80 trays. The heteroazeotrope obtained at the top, after settling, yields an aqueous phase used as reflux, and an organic phase rich in acrylonitrile and hydrogen cyanide, which is sent to the purification step. The aqueous acetonitrile recovered at the bottom is enriched to over 97 per cent weight by azeotropic distillation (60 trays). The residual water is used as an absorption liquid after cooling to 5°C.

• Acrylonitrile purification: this operation comprises a series of distillations for the following in succession:

- Separation of hydrogen cyanide (40 to 50 trays).
- Removal of carbonylated impurities (acetone, acetaldehyde, propionaldehyde, acrolein, etc., 50 to 60 trays).
- Vacuum purification of acrylonitrile (25 to 30 trays).

The presence of cyanohydrin, which is liable to decompose into HCN and carbonylated compounds, and to lower the purity of the final product, makes it necessary to operate in the presence of a stabilizer (oxalic acid), in addition to a polymerization inhibitor added at various stages of the treatment scheme for ammonoxidation effluents. Acrylonitrile to specifications is obtained in a side stream. Residual hydrogen cyanide is separated at the top and recycled to the previous column. The polymers withdrawn at the bottom are stripped to recover the acrylonitrile they contain and thus to improve the overall conversion yield.

B. Fixed bed propylene ammonoxidation, PCUK/Distillers process

The flowsheet (Fig. 11.21) of plants operating with a fixed bed displays the following main characteristics:

- Reaction: it takes place on a feed preheated to around 220°C of ammonia, propylene and compressed air ($0.3 \cdot 10^6$ Pa absolute) in controlled proportions. It takes place in a multi-tube reactor (catalyst tube dimensions: inside diameter 25 to 30 mm, height 3 to 3.5 m), with shell-side circulation of a bath of molten salt intended to remove the heat generated by the reaction, and which is then cooled to produce high-pressure steam.
- Cooling: the gases leaving the ammonoxidation reactor are quenched at about 380 to 400°C , first in a boiler designed to produce low-pressure steam, and then by direct contact in a tower operating in the presence of sulfuric acid at the bottom zone to neutralize the residual ammonia, and water in the top section. The ammonium sulfate withdrawn can be treated subsequently to extract the organic compounds which it contains.
- Separation: transformation product recovery is also similar to that of the Sohio process, with cooling to about 40°C , partial condensation, absorption of nitriles and

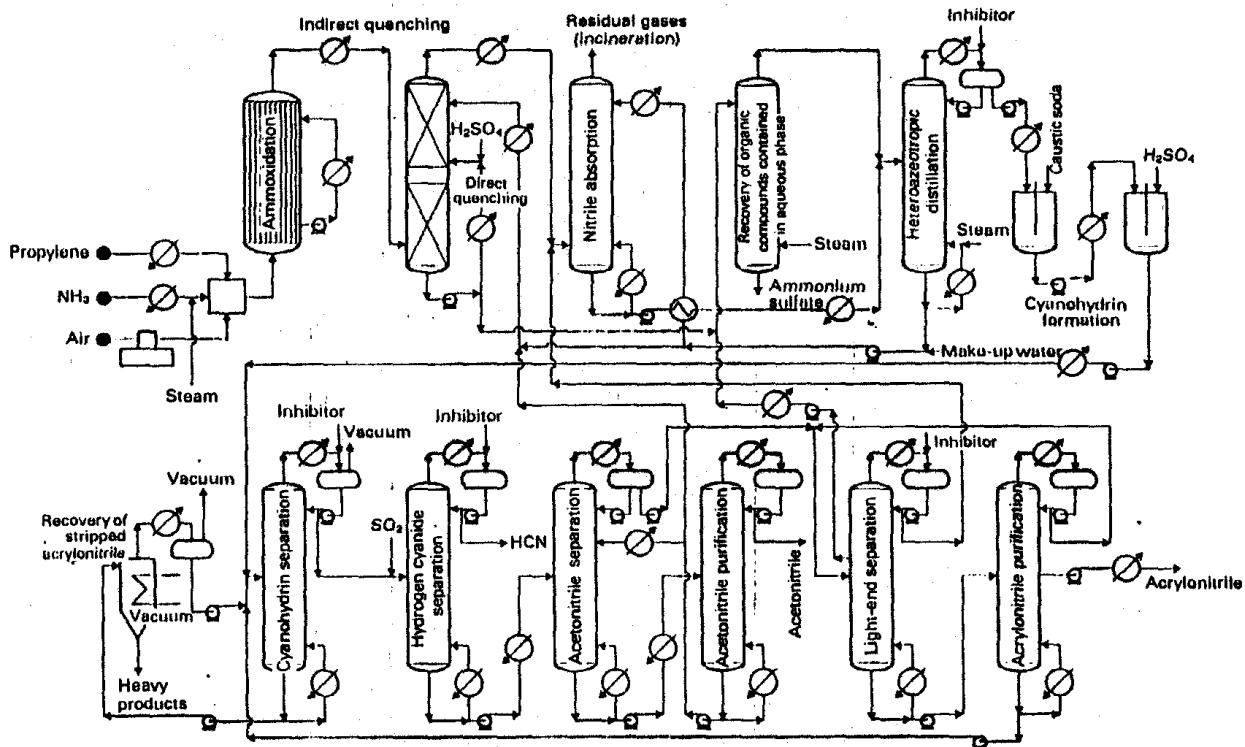


Fig. 11.21. Acrylonitrile production by fixed bed ammonoxidation of propylene. PCUK/Distillers process.

heavier compounds by cooled water (5°C), and incineration of the residual gases. Heteroazeotropic distillation (20 to 30 trays) then eliminates a large part of the water, both in the withdrawal, which is then used as a quench and absorption fluid, and in the distillate, after settling of an aqueous phase employed as reflux, and of an organic fraction, which is sent to the next fractionation step.

- **Purification:** this step features the second innovation of the process which, to eliminate the by-product acrolein, favors the formation of cyanohydrin by means of the hydrogen cyanide which is also present. This operation takes place at low temperature (20°C) in agitated reactors, either continuously in the presence of a copper-based catalyst, or semi-continuously with a reaction phase in basic medium (caustic soda addition), followed by a neutralization period (sulfuric acid addition). The cyanohydrin obtained is then removed by vacuum distillation. The withdrawal may be sent to a thin layer evaporator to recover entrained acrylonitrile. These treatments must be conducted in the presence of a polymerization inhibitor and at a temperature below 55°C to prevent the re-decomposition of cyanohydrin.

Subsequent operations on the distillate are more conventional. Distillation is used to separate the following in succession:

- (a) Hydrogen cyanide (40 to 45 trays).
- (b) Acetonitrile, in two columns, whose operation is based on the separation of heteroazeotropes between water and, on the one hand, acrylonitrile at the top of the first column (45 to 50 trays), and, on the other, acetonitrile at the top of the second (60 to 65 trays), and the water withdrawn is recycled to the first distillation.
- (c) Light compounds and residual water at atmospheric pressure (50 to 60 trays).
- (d) Heavy compounds under vacuum (25 to 30 trays), with an impure acrylonitrile distillate recycled to the light-ends separation column, and a side stream of acrylonitrile meeting commercial specifications.

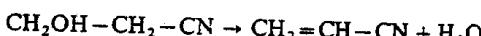
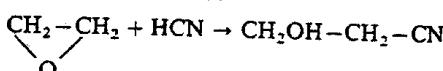
11.4.2 Other industrial methods for manufacturing acrylonitrile

11.4.2.1 Early processes

The conditions in which these conversions take place will now be reviewed briefly.

A. Passage through ethylene cyanohydrin

The following reactions are involved:

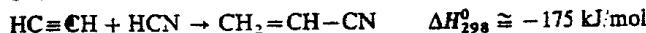


The preparation of cyanohydrin was described in connection with the synthesis of acrylates (see Section 11.3.2.2). As for dehydration, this can be conducted in the liquid phase, around 200°C, in the presence of a soluble catalyst based on magnesium formate

or carbonate, or in the vapor phase between 250 and 350°C, by passage over alumina. The molar yield is 90 per cent.

B. Addition of hydrogen cyanide to acetylene

This highly exothermic reaction:



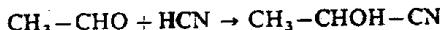
has been conducted industrially in the liquid phase, in the presence of a catalyst consisting of cuprous chloride and ammonium chloride in solution in hydrochloric acid. A large excess of acetylene is used (6 to 15 mol. mol HCN) at a pressure slightly above $0.1 \cdot 10^6 \text{ Pa}$ absolute and a temperature of 80 to 90°C. The molar yield is up to 90 per cent in relation to hydrogen cyanide, and 75 to 80 per cent in relation to acetylene. The main by-products are acetaldehyde, vinylacetylene, divinylacetylene, vinyl chloride, cyanobutene, lactonitrile, methyl vinyl ketone, etc.

The same reaction can be conducted in the vapor phase (Goodrich) around 500 to 600°C, on charcoal impregnated with caustic soda and cyanides.

C. Passage through lactonitrile

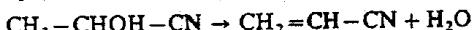
The raw material is acetaldehyde, converted in two steps to acrylonitrile:

- (a) In the first step, lactonitrile is formed by the addition of hydrogen cyanide to acetaldehyde:



This reaction, which is highly exothermic and very fast, takes place between 10 and 20°C, at pH between 7 and 7.5, with a molar yield of 97 to 98 per cent.

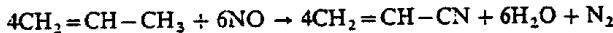
- (b) In the second step, the lactonitrile is dehydrated to acrylonitrile:



To prevent redecomposition into acetaldehyde and hydrogen cyanide, the reaction takes place with a large excess of phosphoric acid (three times by volume) by spraying at 600 to 700°C in a reactor in which the lactonitrile is placed in contact with a hot, oxygen-free inert gas, during an interval shorter than 3 s. The total molar yields are about 90 per cent in relation to acetaldehyde and 92 per cent in relation to hydrogen cyanide.

D. Nitric oxide with propylene

This involves the following conversion:

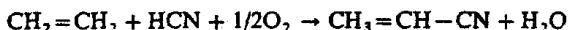


It takes place at atmospheric pressure, between 450 and 550°C, in the presence of a silver oxide based catalyst deposited on silica or of earth alkali metal oxides, thallium and lead, and with excess propylene. An inert (nitrogen, steam, etc.) is used as diluent, in order to absorb the heat generated during the conversion, whose molar yield is 70 per cent in relation to propylene.

11.4.2.2 Processes under development

These processes are designed to convert the hydrocarbons directly, particularly ethylene and propylene, by the following main methods:

- Action of HCN at high temperature (between 750 and 1000°C), in the absence of catalyst, to achieve previous *in situ* dehydrogenation.
- Action of HCN in the presence of oxygen; *Asahi* and *Du Pont* have developed a process for vapor phase ethylene conversion, between 330 and 360°C, on nickel- or palladium-based catalysts deposited on alumina (possibly acidified by the addition of hydrochloric acid) and doped by elements such as vanadium, cesium, etc:



The molar yields are in the neighborhood of 90 per cent.

- Ammonoxidation of paraffins: *Monsanto* and *Power Gas ICI* have proposed processes employing propane instead of propylene:



They operate around 480 to 520°C, in the presence of a catalyst based on antimony, tungsten, uranium, vanadium, etc.

TABLE 11.14
ACRYLONITRILE PRODUCTION. ECONOMIC DATA
(France conditions mid-1986)
PRODUCTION CAPACITY 100,000 t/YEAR

Process	Fluidized bed	Fixed bed
Typical technology	Sohio	PCUK/Distillers
Battery limits investments (10^6 US\$)	89	96
Consumption per ton of acrylonitrile:		
Raw materials		
Propylene (t)	1.18	1.10
Ammonia (t)	0.50	0.52
By-products		
Hydrogen cyanide (kg)	170	125
Acetonitrile (kg)	120	50
Utilities		
Steam (t)	1.0	0.5
Electricity (kWb)	270	250
Cooling water (m^3)	400	500
Process water (m^3)	5	5
Chemicals and catalysts (US\$)		
Sulfuric acid (100%) (t)	0.05	0.30
Caustic soda (100%) (t)	—	0.02
Miscellaneous (US\$)	45	30
Labor (Operators per shift)	6	6

TABLE 11.15
AVERAGE COMMERCIAL SPECIFICATIONS OF ACRYLONITRILE
AND ITS BY-PRODUCTS

Product		Acrylonitrile	Acetonitrile	Hydrogen cyanide
Purity (% Wt) min.	99.0	99.0	98.0	—
Distillation range at 101.3 kPa absolute (°C)	74.5-78.5	80.5-82.5	—	—
pH	6.0-7.5	—	—	—
Water (% Wt) max.	0.5	0.2	0.5	—
Ammonia (ppm) max.	—	1	—	—
Acetone (ppm) max.	300	—	—	—
Acrolein (ppm) max.	10	—	—	—
Aldehydes (expressed as acetaldehyde) (ppm) max.	100	—	—	—
Hydrogen cyanide (ppm) max.	5	5	—	—
Acidity (expressed as acetic acid) (ppm) max.	20	50	—	—
Acetonitrile (ppm) max.	500	—	—	—
Acrylonitrile (ppm) max.	—	500	2,000	—
Methyl vinyl ketone (ppm) max.	300	—	—	—
Peroxides (expressed as H ₂ O ₂) (ppm) max.	0.5	—	—	—
Divinyl acetylene (ppm) max.	5	—	—	—
Non-volatile residue (ppm) max.	100	—	—	—
Iron (ppm) max.	0.1	0.5	—	—
Copper (ppm) max.	5	0.5	—	—
Color (Pt/Co) max.	5	5	—	—

TABLE 11.16
ACRYLONITRILE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
ABS/SAN resins ⁽¹⁾	12	20	21
Acrylic fibers	72	50	60
Adiponitrile	—	15	—
Nitrile rubber	3	4	4
Acrylamide	13	5	15
Miscellaneous ⁽²⁾		6	
Total	100	100	100
Production (10 ³ t/year)	1,040	1,005	525
Capacity (10 ³ t/year)	1,195	1,020	590
Consumption (10 ³ t/year)	1,090	630	610

(1) ABS: acrylonitrile-butadiene-styrene; SAN: styrene-acrylonitrile.

(2) Barrier resins, carbon fibers, fatty amines, high molecular weight polyether-polyols, high-nitrile copolymer resins, starch/acrylonitrile copolymers.

(3) The worldwide production capacity of acrylonitrile was about $3.7 \cdot 10^6$ t/year in 1984 and 1986. The distribution in 1986 was the following:

United States	1.02	Western Europe	1.20	Middle East	0.07
Canada	—	Eastern Europe	0.42	Japan	0.59
Latin America	0.15	Africa	—	Asia and Far East	0.30

11.4.3 Economic data

Table 11.14 gives technico-economic data concerning the two principal processes for manufacturing acrylonitrile currently industrialized, and which involve the ammonoxidation of propylene in a fluidized bed or a fixed catalyst bed.

11.4.4 Uses and producers

Table 11.15 lists the average commercial specifications of acrylonitrile and of the by-products formed in propylene ammonoxidation (acetonitrile and hydrogen cyanide).

Table 11.16 lists the main applications of acrylonitrile in Western Europe, the United States and Japan, together with the production, capacity and consumption figures in these three geographic areas in 1984.

Chapter 12

MONOMERS FOR POLYAMIDE SYNTHESIS

Polyamides are synthetic polymers characterized by the presence in their macromolecular chain of recurrent amide groups —CO—NH—, separated by segments that are usually aliphatic $-(CH_2)_n-$ or aromatic in certain cases. These polymers, which were first synthesized by Carothers in 1933, have experienced considerable development, both for artificial textile fibers and plastics, dating from the introduction of nylon-6,6 by *Du Pont* in 1939. Since then, other polyamides have been synthesized. They are usually designated by the word nylon followed by one or two figures, depending on whether they are produced by the polymerization of a single monomer or of two different monomers, with each figure indicating the carbon numbers of the component monomer or monomers.

Nylons can be manufactured by three main methods:

- Polycondensation of an ω -amino acid (nylon-11 from ω -aminoundecanoic acid).
- Polyaddition, with the cycle opening of a lactam (nylon-6 from caprolactam).
- Polycondensation of an ω diacid with an ω diamine (nylon-6,6 from adipic acid and hexamethylenediamine).

Table 12.1 shows the main nylons currently commercialized and the monomers from which they are obtained.

Other polyamides, not as important industrially as the above, can also be synthesized:

- Nylon-4, obtained by anionic polymerization of butyrolactam, is very hygroscopic and resembles cotton.
- Polyamide PCAM 12, obtained by polycondensation of *p*-diaminocyclohexylmethane (PCAM) and dodecanedioic acid, is commercialized by *Du Pont* under the name Qiana. Its fibers resemble silk.
- Polyamides with aromatic rings between the amide groups (aramids) are characterized by excellent heat stability. They can be obtained from an aromatic diacid (terephthalic or isophthalic acid) and an aromatic diamine (para- or metaphenylene diamine).

These plastics and fibers, which are primarily employed by the rubber industry, are commercialized by *Du Pont* (Kevlar, Nomex) and *Goodyear* (Flexten).

TABLE 12.1
DIFFERENT TYPES OF NYLON

	Monomer	
	Name	Formula
Nylon-6	Caprolactam	$(\text{CH}_2)_5 \begin{array}{c} \text{C=O} \\ \\ \text{NH} \end{array}$
Nylon-6,6	Adipic acid Hexamethylene diamine	$\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$
Nylon-6,10	Sebacic acid Hexamethylene diamine	$\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$ $\text{H}_2\text{N}-(\text{CH}_2)_{10}-\text{NH}_2$
Nylon-11	11-aminoundecanoic acid	$\text{HOOC}-(\text{CH}_2)_{10}-\text{NH}_2$
Nylon-12	Laurolactam	$(\text{CH}_2)_{11} \begin{array}{c} \text{C=O} \\ \\ \text{NH} \end{array}$

12.1 MANUFACTURE OF NYLON-6,6, ADIPIC ACID AND HEXAMETHYLENE DIAMINE

Nylon-6,6 is produced by the polycondensation of adipic acid with hexamethylene diamine:

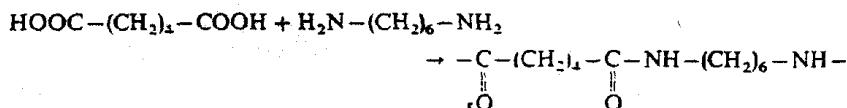


Figure 12.1 summarizes the main methods for obtaining the two polymers:

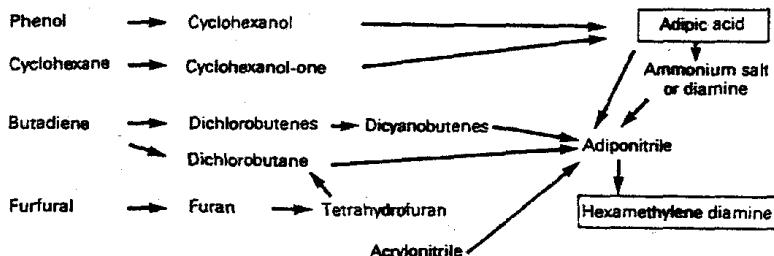


Fig. 12.1. Main methods for the production of nylon 6,6 monomers.

Those initially selected by *Du Pont* started with:

- (a) Phenol for adipic acid.
- (b) Furfural for hexamethylenediamine.

The first conversion has been virtually abandoned today due to the very high cost of phenol. The second, which starts with cheap biomass wastes, was abandoned many years ago due to the very low yields obtained in relation to the starting biomass raw material (23 t of cornstovers are required to manufacture 1 t of tetrahydrofuran intermediate).

Figure 12.1 also shows the importance of adiponitrile in the synthesis of hexamethylene diamine. Cyclohexane is also an essential intermediate for the synthesis of nylon-6 and nylon-6,6. We shall therefore examine the manufacture of the following four products:

- (a) Cyclohexane.
- (b) Adipic acid.
- (c) Adiponitrile.
- (d) Hexamethylene diamine.

12.1.1 Cyclohexane

Cyclohexane ($d_4^{20} = 0.779^{(1)}$, mp = 6.5°C, bp_{1.013} = 81.4°C) can be extracted from certain appropriate naphtha cuts which contain 5 to 15 per cent weight cyclohexane, but simple distillation cannot achieve enrichment higher than 85 per cent weight. The purity level required for the uses of cyclohexane, especially for its oxidation, are much higher. This purity can be obtained by extractive distillation with phenol (Humble process) or with phenoxyethanol (URBK) by which purities higher than 99 per cent can be obtained.

In the United States, *Phillips* has achieved this result by combining distillation with the isomerization of methylcyclopentane to cyclohexane. *Phillips* is the only world producer employing extraction, and the process supplies 13 per cent of the cyclohexane produced in the United States. These processes are not practised in Western Europe or Japan, which prefer the benzene hydrogenation technique.

12.1.1.1 Benzene hydrogenation

A. Conversion principle

The conversion is highly exothermic and occurs with a contraction in volume, according to the following reaction:



Hence it is favored by low temperature and high hydrogen partial pressure. Whatever the value of the latter, the temperature must not exceed 235°C, in order to meet current

(i) Specific gravity, 68.0 39.2

specifications for cyclohexane (less than 100 ppm benzene). The reaction can take place in the liquid and vapor phases, and requires the use of a catalyst. Nickel and platinum are the most widely used, but palladium, copper and rhodium, as well as sulfides of molybdenum, tungsten and nickel, can also be employed. If noble metals are used, the sulfur content of the feed must be less than 1 ppm.

The reaction rate remains constant up to high conversion rates (zero order in relation to benzene). Two side reactions must be avoided because they lower the cyclohexane purity. These are conversion to methylcyclopentane and hydrocracking. The isomerization equilibrium of cyclohexane to methylcyclopentane corresponds to a conversion of 68 per cent at 200°C, reaching 83 per cent at 300°C. This makes it necessary to select a catalyst that does not favor this reaction. With nickel-based systems, the reaction appears only above 250°C. Moreover, the hydrogen must not contain impurities liable to poison the active phases introduced.

B. Industrial manufacture

Industrial processes differ in the following characteristics :

- (a) Operating conditions, according to whether the reaction takes place in the liquid or vapor phase.
- (b) Catalyst type.
- (c) The method used to offset the rise in temperature due to the exothermicity of the reaction. In a fixed bed, this problem can be solved in two ways:
 - by installing several adiabatic reactors in series, and lowering the temperature between each reactor, by direct quench, or by cooling in heat exchangers; however, this solution requires considerable equipment and is cumbersome,
 - by using a multi-tube reactor with circulation of a heat transfer fluid on the shell side; however, the need to fill each catalyst tube uniformly to guarantee uniform pressure drops, flow rates and unit conversions, as well as the necessarily large number of these tubes, make this solution costly in terms of capital expenditure and problematic in operation.

If the catalyst is in suspension, the heat can be removed by the circulation of the medium outside the reactor, through a heat exchanger.

a. Liquid phase processes

UOP (Universal Oil Products) Hydrar process (currently HB Unibon) (Fig. 12.2)

This was the world's first commercial benzene hydrogenation process on the industrial scale. It uses a fixed bed of platinum-based catalyst promoted by a lithium salt, which can tolerate sulfur contents up to 300 ppm in the benzene, and whose LHSV in relation to liquid benzene is about 1.5.

In this process, the hydrogen generally undergoes pretreatment: caustic soda scrubbing to remove H₂S and CO₂, methanation to remove CO. The benzene feed and a cyclohexane recycle, mixed with fresh or recycled hydrogen after compression to the required pressure, are preheated, and then introduced into a series of two or three reactors, whose temperatures are staged between 200 and 300°C, and which operate

under about $3 \cdot 10^6$ Pa absolute. Once-through conversion of benzene is practically complete.

The reactor effluent, cooled by heat exchange with the feed, is first flashed. After purging to avoid the accumulation of inert, the gases are recycled. Part of the liquid is also returned as a diluent to facilitate temperature control. The remainder undergoes a renewed flashing to remove hydrocarbons. The recycled gases must have a minimum hydrogen content of about 30 per cent volume. The hydrogen/hydrocarbon molar ratio at the reactor inlet is about 2:1.

Houdry process

This process comprises three reactors in series, operating in fixed beds between 140 to 190 at the inlet and 220 to 250°C at the outlet. The first treats the bulk of the feed and a cyclohexane recycle, and the second the remainder of the feed, the effluent from the first reactor, and a cyclohexane recycle. The third reactor, which contains about half of the catalyst required for the reaction, completes the hydrogenation on the effluent from the second reactor.

Sinclair/Engelhard process

In this process, called HA 84, hydrogenation takes place in a single reactor operating in a fixed bed. Heat is removed *in situ* by means of a tube bundle with the production of steam. Cyclohexane recycle is unnecessary. However, it appears that a high hydrogen flow rate is required to prevent a runaway reaction.

These three processes use noble metal catalysts.

IFP (Institut Français du Pétrole) process (Fig. 12.3)

The reaction takes place nearly entirely in the liquid phase, in a unit operating at 200°C and $4 \cdot 10^6$ Pa absolute, in the presence of Raney nickel kept in suspension by agitation by means of external circulation. The hydrogenated product leaves the reactor in the vapor phase, thus making it easier to remove part of the heat. The remainder of the heat generated is recovered in an exchanger placed on an external circuit, and employed to produce low-pressure steam.

A finishing reactor treats the unconverted gaseous effluent and ensures production regularity and quality, in the event that the liquid phase catalyst is deactivated due to the presence of sulfur in the feed. The yield is practically stoichiometric. The purity of the final product depends on that of the benzene feed. If its melting point is 5.4°C, the cyclohexane obtained is in a purity of 99.8 per cent + (melting point 6.2°C).

In recent years, IFP has developed a non-pyrophoric nickel, currently employed in the new plants. This eliminates the need for the *in situ* catalyst fabrication facility.

Processing using nickel in a fixed bed

- The Arosat process, developed by Lummus, uses simultaneous liquid and gaseous recycles. Low-pressure steam is produced by appropriate heat exchange in a reaction system.
- The BP (British Petroleum) process performs hydrogenation in two steps. The effluent from the first reactor contains 95 per cent weight cyclohexane. The reaction temperature is controlled by liquid and vapor recycles. Since the sensible heat and the heat of vaporization of the recycled cyclohexane are used simultaneously, the recirculation ratio

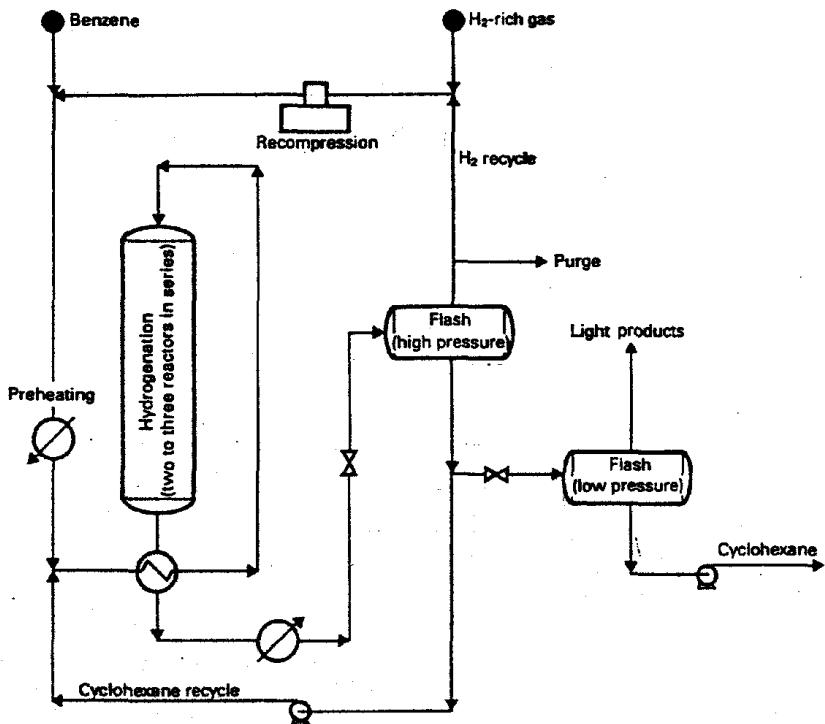


Fig. 12.2. Cyclohexane production. UOP process (HB-Unibon).

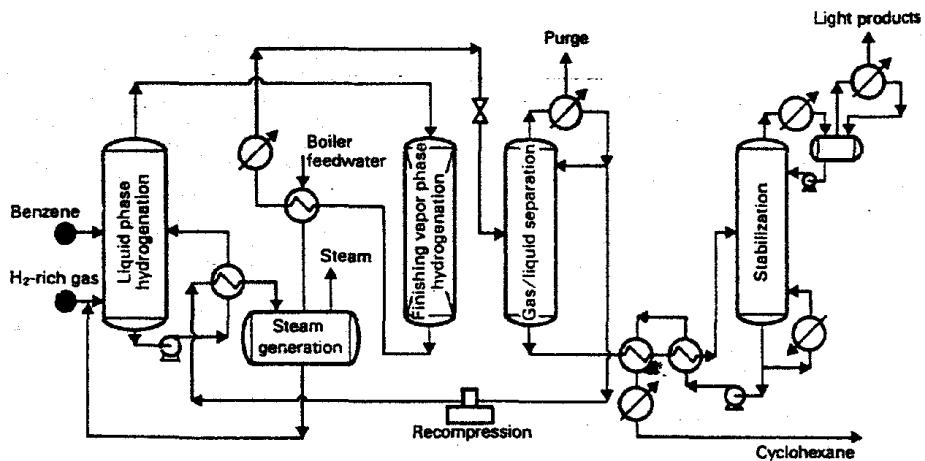


Fig. 12.3. Cyclohexane production. IFP process.

TABLE 12.2
CYCLOHEXANE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/year)

Process	Liquid phase	Vapor phase
Typical technology	IFP	Toray
Battery limits investments (10 ⁶ US\$)	5.7	7.1
Consumption per ton of cyclohexane		
Raw materials		
Benzene (t)	0.93	0.93
Hydrogen (Nm ³)	850	990 ⁽¹⁾
By-product		
Combustible gas (Nm ³)	—	140
Utilities		
MP steam (t)	0.08	0.60
LP steam (t)	(—0.95)	1—0.95)
Electricity (kWh)	11	30
Cooling water (m ³)	3.5	8
Boiler feedwater (m ³)	0.95	0.95
Chemicals and catalysts (US\$)	1	1
Labor (Operators per shift)	1	1

(1) 90% vol.

TABLE 12.3
AVERAGE COMMERCIAL SPECIFICATIONS OF CYCLOHEXANE

Characteristics	Values
Purity (% Wt) min.	99.5
Melting point (°C)	5.6
Distillation range (5 to 95%) (°C) max.	1.5
Benzene (ppm) max.	300
Aliphatic hydrocarbons (ppm) max.	5,000
Sulfur (ppm) max.	5
Non-volatile residues (ppm) max.	125

TABLE 12.4
CYCLOHEXANE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Adipic acid	45	65	10
Caprolactam	36	31	35
Solvent and miscellaneous ⁽¹⁾	19	4	5
Total	100	100	100
Production (10 ³ t/year)	845	963	490
Capacity (10 ³ t/year) ⁽²⁾	995	1,125	530
Consumption (10 ³ t/year)	930	915	490

(1) Solvent (cellulose esters, essential oils, fats and oils, isopropanol, LLDPE, paints, rubber...), chemicals (cyclohexanone, cyclohexyl amine, cyclohexyl esters as dicyclohexyl phthalate, cyclohexyl mercaptan, herbicide, hexamethylene diamine...).

(2) The worldwide production capacity of cyclohexane was around 3.95 · 10⁶ t/year in 1984 and 3.85 · 10⁶ t/year in 1986, with the following distribution:

United States	0.2	Western Europe	1.02	Middle East	0.03
Canada	—	Eastern Europe	0.69	Japan	0.61
Latin America	0.22	Africa	—	Asia and Far East	0.26

can be significantly lowered, but the partial pressure of hydrogen is accordingly reduced. This means that a second hydrogenation reactor is necessary to complete the reaction.

Other processes employing the same principles have been developed with specific technologies (*Haines, Mitsubishi, Société Chimique des Charbonnages*).

b. Vapor phase processes

Bexane process developed by Stamicarbon (DSM : Nederlandse Staats Mijnen)

This process uses a multi-tube reactor containing a supported platinum-based catalyst. Heat is removed by a coolant which vaporizes the benzene feed, previously dehydrated by azeotropic distillation, and also produces steam at $1 \cdot 10^6$ Pa absolute.

The reaction takes place at about $3 \cdot 10^6$ Pa absolute, at an initial temperature of about 370°C, lowered to 220°C at the outlet. Conversion is practically complete. A finishing reactor is provided to guarantee total hydrogenation in the presence of nickel.

Hytoray process developed by Toyo Rayon (Toray)

The catalyst employed, called T-61, is undoubtedly based on a noble metal.

12.1.1.2 Economic data

Table 12.2 shows the economic performance of two typical processes for manufacturing cyclohexane in the liquid and vapor phases.

12.1.1.3 Uses and producers

Table 12.3 gives the average commercial specifications of cyclohexane. Nearly all the cyclohexane produced worldwide is employed for the synthesis of adipic acid and caprolactam. A small amount is used as a solvent, as shown by Table 12.4. This table also gives the production, capacity and consumption figures in 1984 for Western Europe, the United States and Japan.

12.1.2 Adipic acid

Adipic acid ($d_4^{15} = 1.360^{(2)}$, mp = 135°C) is manufactured industrially from cyclohexane for about 95 per cent of total production, or from phenol.

12.1.2.1. Adipic acid production from phenol

In the first step, phenol is hydrogenated in the molten state to cyclohexanol, in the presence of a nickel catalyst. The operation takes place at around 150°C and $0.3 \cdot 10^6$ Pa absolute. Once-through conversion of phenol is up to 99.5 per cent. The second step consists in oxidizing the cyclohexanol to adipic acid by nitric acid, in the presence of a

(2) Specific gravity, 68.0/39.2.

vanadium and copper-based catalyst. This operation is identical to the one performed in the second cyclohexane oxidation step (see Section 12.1.2.2, paragr. B.a).

The molar yield of adipic acid from phenol is 85 to 90 per cent of theoretical yield. This process is employed in the United States by *Allied* and *Monsanto*.

12.1.2.2 Adipic acid production from cyclohexane

This operation takes place in two steps.

A. Cyclohexane oxidation

This takes place in the liquid phase, around 145 to 175°C, between 0.8 and $1 \cdot 10^6$ Pa absolute, in the presence of a soluble cobalt salt (naphthenate or octoate), as shown in Section 10.1.6.1 concerning phenol synthesis. Once-through conversion is 4 to 6 per cent, and the total yield of a cyclohexanol/cyclohexanone mixture, adipic acid and its esters is about 80 molar per cent (Stamicarbon process).

Oxidation in the presence of boric acid (Scientific Design and IFP processes) serves to raise the once-through conversion to 10 per cent, increase the yield of the Ol/One mixture to 90 per cent, with an Ol/One molar ratio to between 9 and 10/1 instead of 1/1. Although many by-products obtained by the conventional method are precursors of adipic acid, the adoption of a first step offering high selectivity of the Ol/One mixture ultimately achieves a higher adipic acid yield.

B. Oxidation of the first-step products to adipic acid

This takes place with two types of oxidant.

a. Nitric acid

The mixture obtained after initial oxidation is treated with an excess of 60 per cent weight nitric acid (nitric acid to Ol/One mixture ratio 5/1) in the presence of 0.2 per cent weight of a catalyst consisting of ammonium metavanadate and copper scraps. The reaction is highly exothermic. It is conducted in two reactors in series, in which the reaction medium is maintained at between 60 and 80°C in the first and 100°C in the second, by external circulation and cooling. Residence time in these two units is approximately 5 and 7 min respectively. If a very pure Ol/One mixture or cyclohexanol is employed, the molar yield of adipic acid reaches 92 to 96 per cent. The gases must be separated to remove the nitrogen and N_2O and to recycle the $NO + NO_2$.

The adipic acid is recovered by crystallization between 30 and 70°C. The mother liquor is concentrated under vacuum, and then recycled to nitric oxidation. A fraction of this liquor is purged and treated to remove succinic and glutaric acids, the main by-products of the reaction. The crude adipic acid is purified by recrystallization, centrifuging and drying. This process is proposed in particular by *Scientific Design*. Figure 12.4 is the flow sheet of an industrial installation operating on this technique.

b. Air

The second oxidation step can be carried out by air, around 70 to 80°C, under $0.7 \cdot 10^6$ Pa absolute, in the presence of copper acetate and manganese as catalyst. As in the case of nitric oxidation, the adipic acid is purified by crystallization. This process

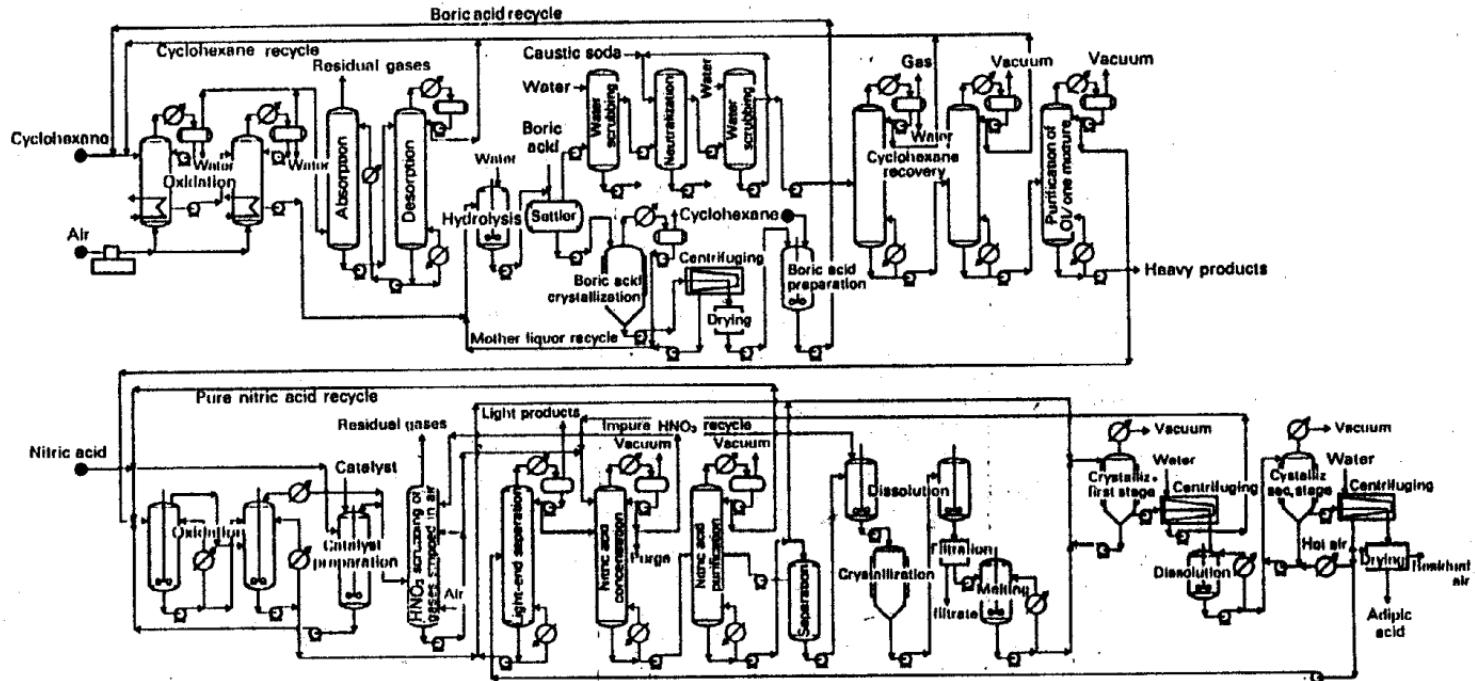


Fig. 12.4. Adipic acid production by two-stage oxidation of cyclohexane with air (boric acid) and nitric acid. Scientific Design process.

offers the advantage over the nitric oxidation process of raising fewer corrosion problems, but the adipic acid yield is not as high.

12.1.2.3 Other industrial processes under development

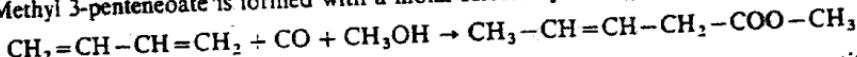
Various other methods have been proposed for the manufacture of adipic acid.

A. Direct air oxidation of cyclohexane in solution in acetic acid (proposed by Asahi)

This technique uses cobalt acetate as the oxidation catalyst, and operates around 90 to 100°C. Molar selectivity of adipic acid is up to 70 to 75 per cent, for once-through conversions of 50 to 75 per cent. Although this process allows an adipic acid yield comparable to that of the methods discussed above, it has not yet witnessed the industrial development that had been anticipated. This is because of the high capital expenditure involved, connected particularly with the recovery and recycling of acetic acid, the regeneration of the catalyst, and the cooling systems required due to the high exothermicity of the reaction.

B. Carbonylation of butadiene (BASF process)

This process takes place in two steps. In the first, butadiene reacts with carbon monoxide and methanol at 120°C, and $60 \cdot 10^6$ Pa absolute. The catalyst employed is dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, in the presence of a heterocyclic nitrogenous base. Methyl 3-pentenoate is formed with a molar selectivity of 98 per cent:

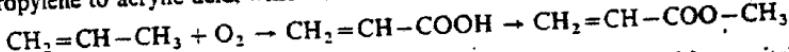


In the second step, the olefinic ester is sent to another reactor with a new quantity of carbon monoxide and methanol. The operation takes place at high temperature, 185°C, but at lower pressure ($3 \cdot 10^6$ Pa absolute). Methyl adipate is formed with a molar yield of 75 per cent. Methyl glutarate and methyl ethyl succinate are also formed. After purification by distillation, the methyl adipate is hydrolysed to adipic acid.

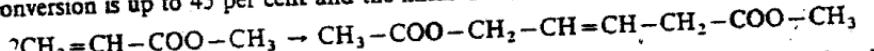
Despite the large investments connected with the high pressures employed in the first step, this process appears to be comparable economically to conventional methods.

C. Dimerization of acrylates

Like the foregoing technique, this one may offer the advantage of not producing the adipic acid from benzene, but from olefins. The methyl acrylate results from the oxidation of propylene to acrylic acid, which is then esterified by methanol:



The acrylate is dimerized in the presence of palladium chloride and benzonitrile as catalyst, operating at 80°C, under nitrogen. For a residence time of 35 min, once-through conversion is up to 45 per cent and the linear dimer selectivity is 92 molar per cent:



The ester formed must then be purified by fractionation, hydrogenated and hydrolysed to adipic acid.

The economic advantage of this process in comparison with conventional methods depends on the price ratio of the raw materials initially converted, i.e. of propylene and benzene.

12.1.2.4 Economic data

Table 12.5 gives some economic data concerning the different industrial methods available for producing adipic acid.

TABLE 12.5
ADIPIC ACID PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/year

Process	Phenol hydrogenation/nitric oxidation	Cyclohexane oxidation	
		Air oxidation (cobalt)/nitric oxidation	Air oxidation (boric acid)/nitric oxidation
Typical technology	Allied/Monsanto	Stamicarbon	Scientific Design
Battery limits investments (10 US\$)	50	60	75
Consumption per ton of adipic acid			
Raw materials			
Cyclohexane (t)	—	0.75	0.73
Phenol (t)	0.71	—	—
Chemicals			
Hydrogen (kg)	70	—	—
Nitric acid (t)	0.82	0.87	0.80
Boric acid (kg)	—	—	95
Caustic soda (kg)	—	65	—
Miscellaneous and catalysts (US\$)	3.5	25	9
Utilities			
Steam (t)	4.5	10	14
Electricity (kWh)	200	400	390
Fuel (10^6 kJ)	—	1.2	0.5
Cooling water (m^3)	100	620	580
Process water (m^3)	2	10	10
Nitrogen (Nm^3)	—	1.5	—
Labor (Operators per shift)	8	12	14

12.1.2.5 Uses and producers

Table 12.6 gives the average commercial specifications of adipic acid employed in polyamides.

TABLE 12.6
AVERAGE COMMERCIAL SPECIFICATIONS OF ADIPIC ACID

Characteristics	Values
Purity (%) min.	99.7
Melting point (°C)	152
Residue (ppm) max.	12
Iron (ppm) max.	2

Table 12.7 lists the main uses of this monomer in 1984, in Western Europe, the United States and Japan, together with the production, capacities and consumption in these three geographic areas.

TABLE 12.7
ADIPIC ACID PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Nylon 6,6	66	89	54
Fibers	58	77	36
Resins	8	12	18
Plasticizers	5	3	16
Polyurethane resins	6	5	—
Unsaturated polyester resins	23	1	17
Miscellaneous ⁽¹⁾		2	13
Total	100	100	100
Sources (% product)			
Butadiene	6	—	—
Cyclohexane	90	98	99
Phenol	4	2	1
Total	100	100	100
Production (10 ³ t/year)	610	630	60
Capacity (10 ³ t/year) ⁽²⁾	795	765	80
Consumption (10 ³ t/year)	565	610	90

(1) Adipic acid/hexamethylene diamine salts (for Western Europe), food additives, leather, polyamide/epichlorohydrin resins, synthetic lubricants, textiles...

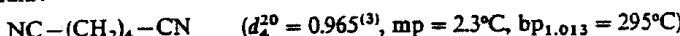
(2) The worldwide production capacity of adipic acid was about $1.8 \cdot 10^6$ t/year in 1984 and 1986, with the following distribution:

United States	0.77	Western Europe	0.80	Middle East	—
Canada	0.12	Eastern Europe	—(a)	Japan	0.08
Latin America	0.05	Africa	—	Asia and Far East	—

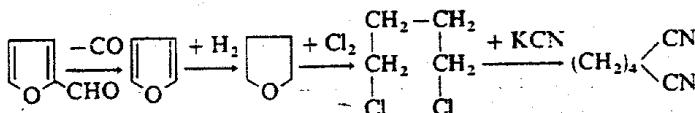
(a) A 80.000 t/year plant will be built at Kursk in the USSR in the near future.

12.1.3 Adiponitrile

Adiponitrile, which is wholly used to produce hexamethylenediamine, has the following formula:



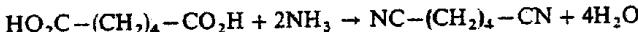
Adiponitrile was formerly manufactured by *Du Pont* from furfural, by the following reaction mechanism:



This method has been abandoned, and three industrial methods are available to manufacture adiponitrile today, starting with adipic acid, butadiene or acrylonitrile.

12.1.3.1 Adiponitrile from adipic acid

This process is no longer used in the United States since the Monsanto plant was shut down in 1980, but is still employed in a number of other countries. It consists in causing ammonia to react with adipic acid in the presence of a phosphoric acid based catalyst, so as to accelerate the following reaction:



Ammonium adipate and adipamide are formed as intermediates, which are dehydrated to adiponitrile by means of the catalyst.

In the earlier vapor phase process, a mixture consisting of ammonia and adipic acid in a volumetric ratio of 20/1 was sent between 300 and 350°C to a catalyst bed based on phosphoric acid and boron. The thermal decomposition which occurred upon the vaporization of adipic acid limited the dinitrile molar selectivity to 80 per cent. The new liquid phase process, developed by *ICI (Imperial Chemical Industries)* and *Monsanto*, operates in the molten acid between 200 and 300°C, in the presence of phosphoric acid. The selectivity to adiponitrile, purified by distillation and recrystallization, is 90 molar per cent.

12.1.3.2 Adiponitrile from butadiene

Two methods are available, the indirect method, in which dichlorobutenes are the intermediates, and the direct hydrocyanation method.

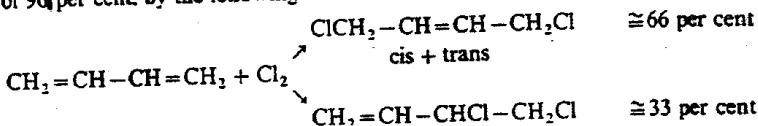
A. Indirect method

Du Pont has employed this method since 1950. It comprises three steps, butadiene

(3) Specific gravity, 68.0 39.2

chlorination, cyanation of the dichlorobutenes obtained, and hydrogenation of the dicyanobutenes:

- (a) Butadiene chlorination. Butadiene is chlorinated in the vapor phase, without catalyst, between 125 and 230°C, with excess butadiene in relation to chlorine. A mixture of three dichlorinated derivatives are obtained with a molar selectivity of 96 per cent, by the following reaction:



Polychlorinated by-products are also formed, as well as chlorinated dimers (chlorinated vinylcyclohexene) and butadiene oligomers. After the removal of these secondary derivatives, the mixture of the three dichlorobutene isomers is sent to the cyanation stage.

- (b) Cyanation of the dichlorobutenes. The reaction takes place in the liquid phase around 80°C, in the presence of a catalyst consisting of a complex copper cyanide. Hydrogen cyanide or an alkaline cyanide is used for the purpose. The presence of 3,4-dichloro-1-butene is not disturbing, because, by an allyl rearrangement, it leads after cyanation to 1,4-dicyano-2-butene cis and trans. Molar selectivity is about 95 per cent.
- (c) Dicyanobutenes hydrogenation. In the third step, the mixture of the two cis and trans dicyanobutenes is hydrogenated in the vapor phase, at 300°C, on a palladium catalyst. The molar selectivity of adiponitrile in this final reaction phase is 95 to 97 per cent.

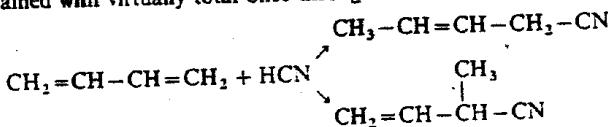
This process presents the major drawback of employing very large amounts of chlorine, which does not form part of the final product composition, explaining the interest in direct hydrocyanation techniques.

B. Direct method

This process is in operation in Du Pont's plant in Orange, Texas, since 1971. A second plant was started up in France in 1977 by Rhône-Poulenc and Du Pont (Fig. 12.5).

Operations take place in two stages:

- In the first, a previously dried mixture of butadiene and hydrochloric acid is sent to the reactor with hydrogen cyanide entrained by nitrogen. The butadiene/HCN/N₂/HCl molar ratio is 1/1/1/0.1. Residence time remains less than one hour, at between 210 and 220°C, in the presence of copper chromite and magnesium as catalyst. A mixture of 3- and 4-pentene nitriles (88 per cent) and branched 3-methyl 1- and 2-butene nitriles (12 per cent) is obtained with virtually total once-through conversion:



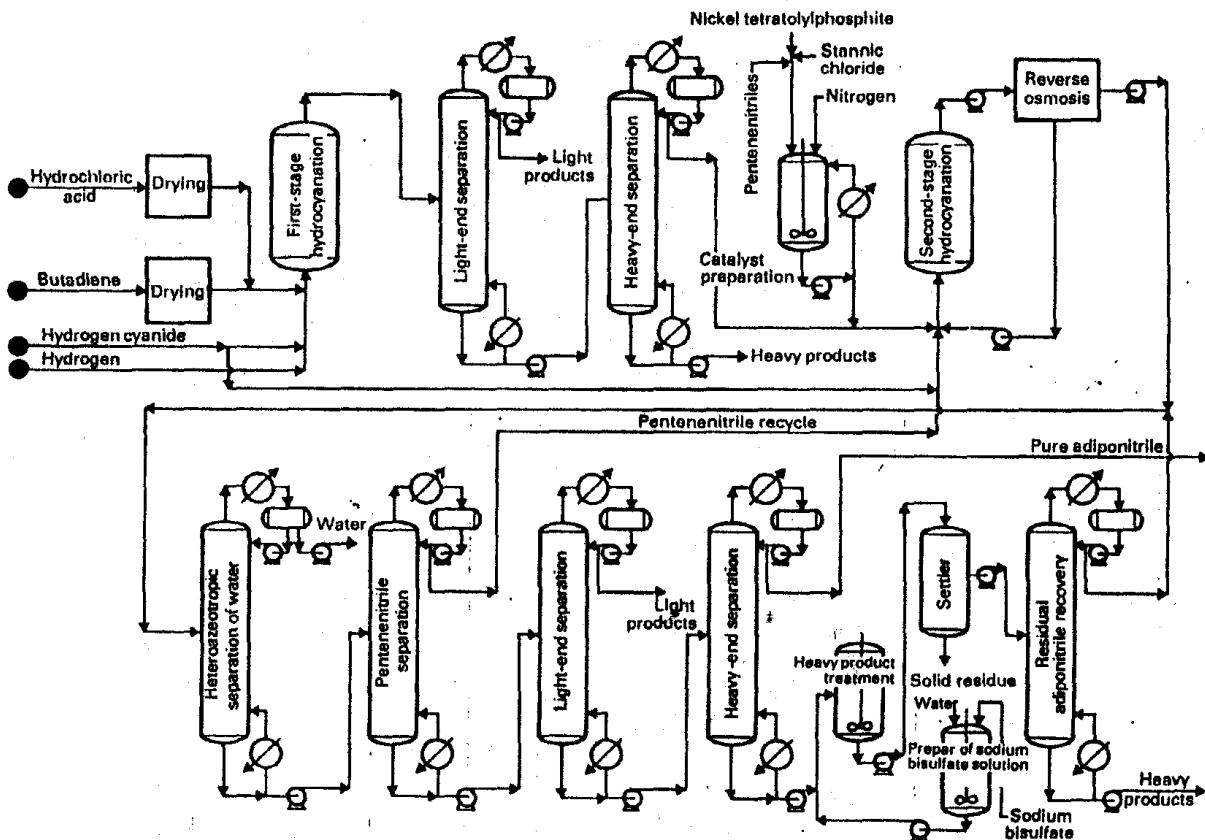


Fig. 12.5. Adiponitrile production by butadiene hydrocyanation. Du Pont process.

The reactor effluent is subjected to two successive distillations (about 30 trays each) to separate the linear isomers from the branched compounds and various other products, including HCN, HCl, etc.

- In the second step, the linear pentene nitriles are treated again with HCN in the presence of a catalyst, which is prepared in an auxiliary reactor, by causing a solution of nickel tetratolylphosphite to react in a mixture of *m*- and *p*-tritolylphosphites with a solution of SnCl₂ in tetrahydrofuran. The catalyst is prepared under nitrogen in the presence of 3- and 4-pentene nitriles. The reaction products are separated from the catalyst to be recycled by reverse osmosis through a suitable membrane.

The adiponitrile is purified in a series of distillation columns (20 to 35 trays), but, in the final distillation step, a non-negligible fraction of the adiponitrile falls to the bottom of the column with the heavy products and tars. This stream is treated with sodium hydrogen sulfate in a 10 per cent weight solution, with residence time of about 30 min. The settled organic phase is fractionated and recycled. Adiponitrile is obtained with a molar yield of 90 per cent for a once-through conversion of 98 per cent.

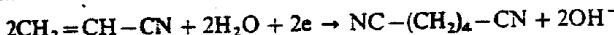
12.1.3.3 Adiponitrile from acrylonitrile

This involves the dimerization of acrylonitrile with hydrogenation. This technique was developed by an electrochemical method in the 1960s by *Monsanto* and commercialized as the EHD (Electro Hydro Dimerization) process. Other companies, manufacturers of nylon-6,6, have proposed a number of variants, including *Asahi*, *Du Pont*, *Halcon*, *ICI* and *UCB* (*Union Chimique Belge*).

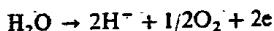
A. Transformation

Transformation takes place in an electrolytic cell in which the following reactions take place:

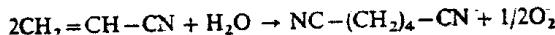
- At the cathode:



- At the anode:

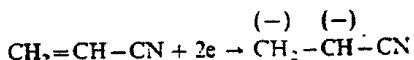


- Overall reaction:

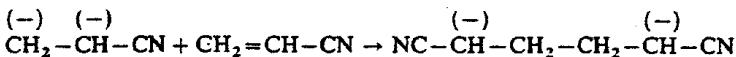


Operations are conducted with a once-through conversion of 50 per cent and adiponitrile molar selectivity approaches 92 per cent. Side reactions consist essentially of the hydrogenation of acrylonitrile to propionitrile and the polymerization of acrylonitrile, to which must be added the production of acrylamides, acrylates, hydroxypropionitrile and oxydipropionitrile.

The mechanism generally assumed for hydroisomerization appears to consist in the prior formation of a di-anion by the transfer of two electrons:



followed by dimerization by coupling with another acrylonitrile molecule:



The dimer di-anion appears to be neutralized by protons produced by the electrolysis of water:



B. Industrial manufacture

Figure 12.6 shows a scheme of a plant based on the Monsanto process. The electrolyser (Fig. 12.7), in the form of a filter press, comprises a sequence of polypropylene compartments, with a lead/silver alloy anode on one side and a lead cathode on the other. The cells are also equipped with polypropylene frames, placed between the electrodes, and supporting a fiberglass membrane impregnated with sulfonated polystyrene. The anolyte, consisting of a dilute sulfuric acid solution, flows in the anode compartment, at a pressure slightly above that prevailing in the cathode compartment, to guarantee diffusion of the water across the membrane, rather than the passage of the catholyte in the reverse direction. The catholyte consists of a mixture of acrylonitrile, adiponitrile, an aromatic quaternary ammonium sulfonate and water.

The two electrolytes are cooled by indirect heat exchange outside the electrolyser, in which they flow rapidly, to avoid a temperature rise of more than 3°C, and to limit the concentration of adiponitrile at the cathode surface. The cells, grouped in batteries of twelve, have a capacity of 3020 kW each. They are supplied with 440 V power, at 33 A/dm². Each cell can produce 70 kg of adiponitrile per hour.

The oxygen formed is removed in the anolyte surge tank. A small fraction of the liquid flowing in the cathode part is continuously withdrawn. It is sent to the separation and purification section of the electrolyte products.

In a first extractor the adiponitrile is isolated by means of concentrated acrylonitrile. The aqueous phase collected at the base essentially contains the quaternary ammonium salt. The residual amounts in this raffinate are recovered in a second extraction device by means of a 7.4 per cent weight solution of acrylonitrile in water. The extract obtained is first fractionated to recover the solvent and purify it in two successive distillation columns, and then to produce adiponitrile to specifications in a separation train operating under vacuum and consisting of three distillation columns in series and an evaporator. The molar yield of the operation is up to nearly 90 per cent in relation to acrylonitrile.

The variants developed by other companies from the original Monsanto process essentially involve the elimination of the membrane between the anode and cathode compartments of the cell, the acrylonitrile concentration in the electrolyte, and the use of a specific conducting salt, tetraalkylammonium tosylate, which serves to increase the electric conductivity and to protect the cathode. The hydrophobic alkyl groups of this salt prevent the water from reaching this electrode, where it would be electrolysed with the formation of hydrogen. Thus the side hydrogenation of acrylonitrile to propionitrile is avoided. As for the membrane, it has been eliminated completely in the latest technological developments proposed by *Asahi*, *BASF* and *UCB*. It is replaced in this case by

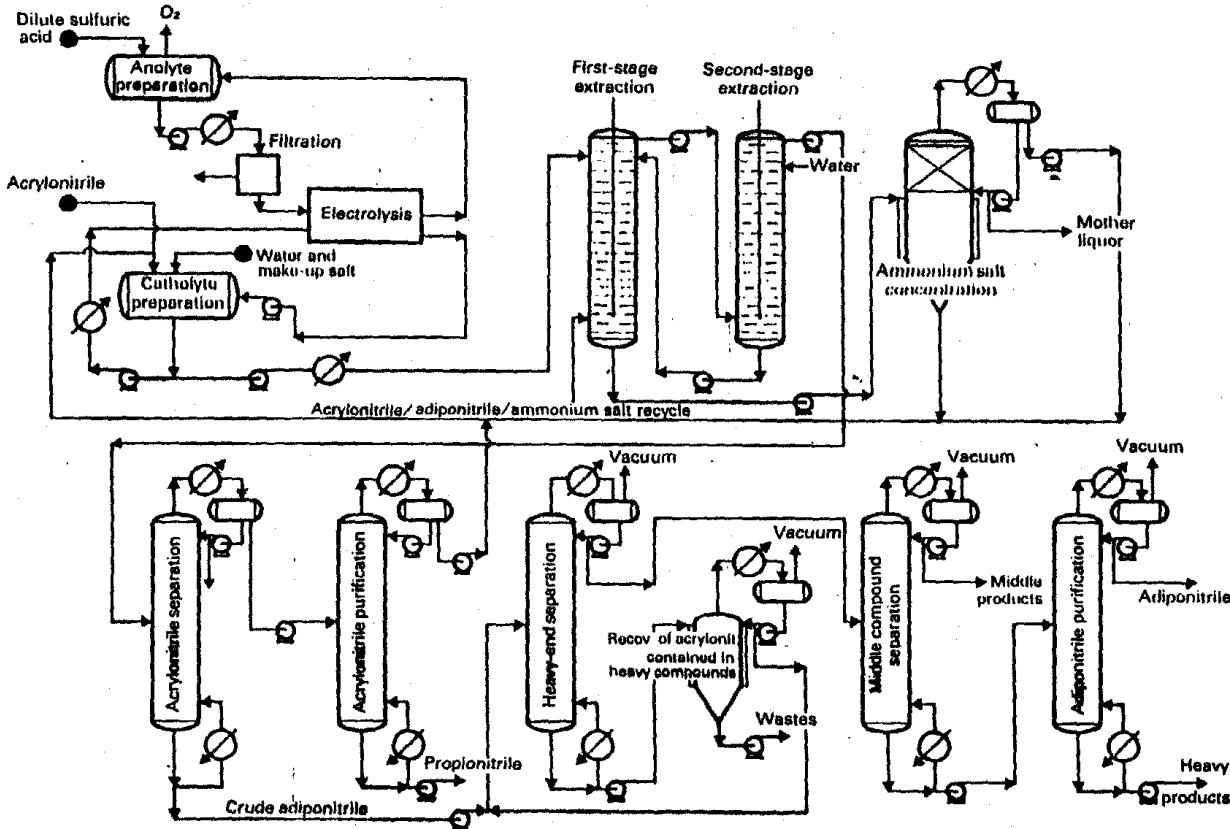


Fig. 12.6. Adiponitrile production by electrodimerization of acrylonitrile. Monsanto process.

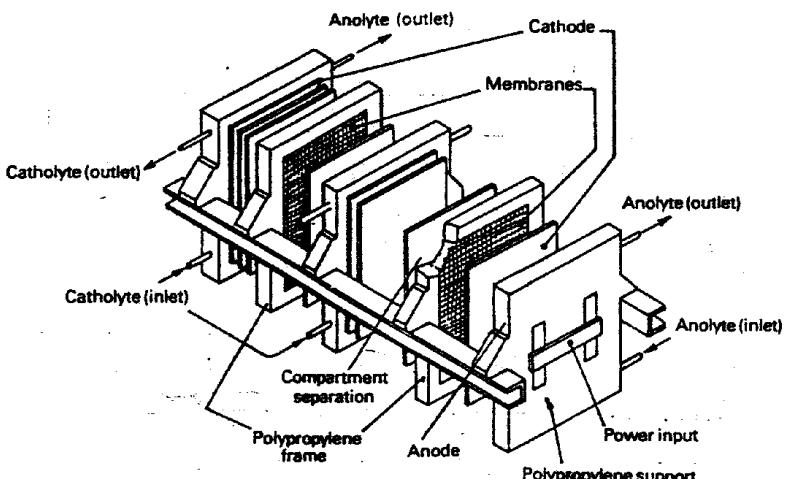


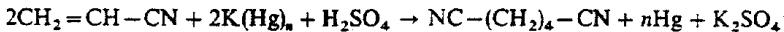
Fig. 12.7. Adiponitrile production by electrodimerization of acrylonitrile. Monsanto process. Schematic view of electrolytic cell.

a finely divided emulsion created by turbulent flow in the electrolyser. The aqueous fraction of the emulsion contains the conducting salt and a little acrylonitrile. The organic part is a mixture of acrylonitrile and adiponitrile. The easy passage of the acrylonitrile from the emulsified organic phase to the aqueous layer offsets its low concentration in the latter. The use of different electrodes has also been proposed among various other improvements.

C. Other acrylonitrile dimerization processes

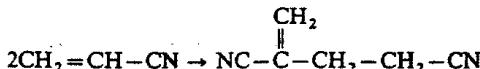
The high consumption of electricity in electrochemical processes stimulated research on purely chemical dimerization methods:

- The process proposed by UCB, as well as ICI and Mitsui Toatsu, consists in using alkaline amalgams as reducing agents in a solvent such as formamide:



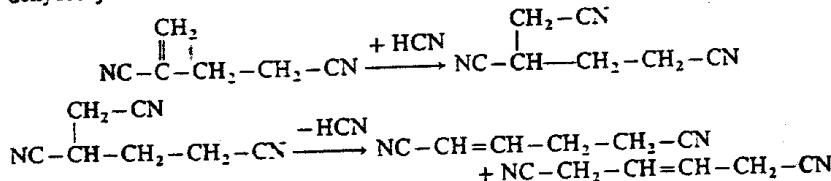
However, since the amalgam is obtained by the electrolysis of the corresponding salts, this method is only economically viable if the dimerization unit is integrated with an electrolysis installation (for the production of chlorine, for example). Furthermore, the co-product alkaline salt (especially K_2SO_4) has to be commercialized.

- The Halcon process performs chemical dimerization in two steps. In the first, acrylonitrile is dimerized to methylene glutaronitrile (branched dimer):



This takes place in the liquid phase, at 30°C, in the presence of *p*-toluenesulfonic acid and triethylamine as catalyst.

In the second step, the branched dimer is isomerized in the presence of 0.5 molar per cent of lithium cyanide. This operation consists of a series of hydrocyanations and dehydrocyanations:



1,4-dicyano 1- and 2-butenes are obtained with a molar yield of 83 per cent, for a once-through conversion of 73 per cent. The dicyanobutenes are then hydrogenated to adiponitrile, or directly to hexamethylenediamine on Raney nickel.

- In the ICI process, chemical dimerization yields linear dimers in a single step. The catalyst is a phosphinite or phosphonite, $\text{R}_2-\text{P}(\text{OR})$ or $\text{R}-\text{P}(\text{OR})_2$, employed in the presence of an anhydrous proton donor (usually an alcohol) between 30 and 100°C. The yield of linear dimers (1,4-dicyano 1- and 2-butenes) exceeds 95 molar per cent. They are then hydrogenated as above.

12.1.4 Hexamethylene diamine (HMDA)

Hexamethylene diamine ($\text{mp} = 42^\circ\text{C}$, $\text{bp}_{1.013} = 204^\circ\text{C}$) is obtained by the catalytic hydrogenation of adiponitrile or through 1,6-hexanediol as an intermediate.

12.1.4.1 Adiponitrile hydrogenation processes

The early technique, patented by *Du Pont* in 1942, required high pressures. Hence, with a catalyst based on cobalt and copper, the operation took place at 60 to $65 \cdot 10^6$ Pa absolute, and between 100 and 135°C . With iron catalysts, the pressure was lowered to $30 \cdot 10^6$ Pa absolute, while the temperature remained the same or slightly higher (100 to 180°C). The HMDA molar selectivity approached 90 to 95 per cent in these conditions.

More recently, *Rhône-Poulenc* (Fig. 12.8) developed a low-pressure process making it possible to operate at $3 \cdot 10^6$ Pa absolute and 75°C , in the liquid phase, thanks to the use of nickel catalysts in suspension in a caustic soda solution. HMDA molar selectivity is as high as 99 per cent. Since the catalyst loses its activity with time, it must be regenerated frequently by water scrubbing and recycle. The reactor is a vertical vessel with agitation by a stream of hydrogen. It features the possibility of producing HMDA at the top, entraining some catalyst, so that a high concentration can be maintained in the active phase in the reaction medium. The impurities mainly result from the formation of a diimine by partial hydrogenation of dinitrile, by the following reaction:



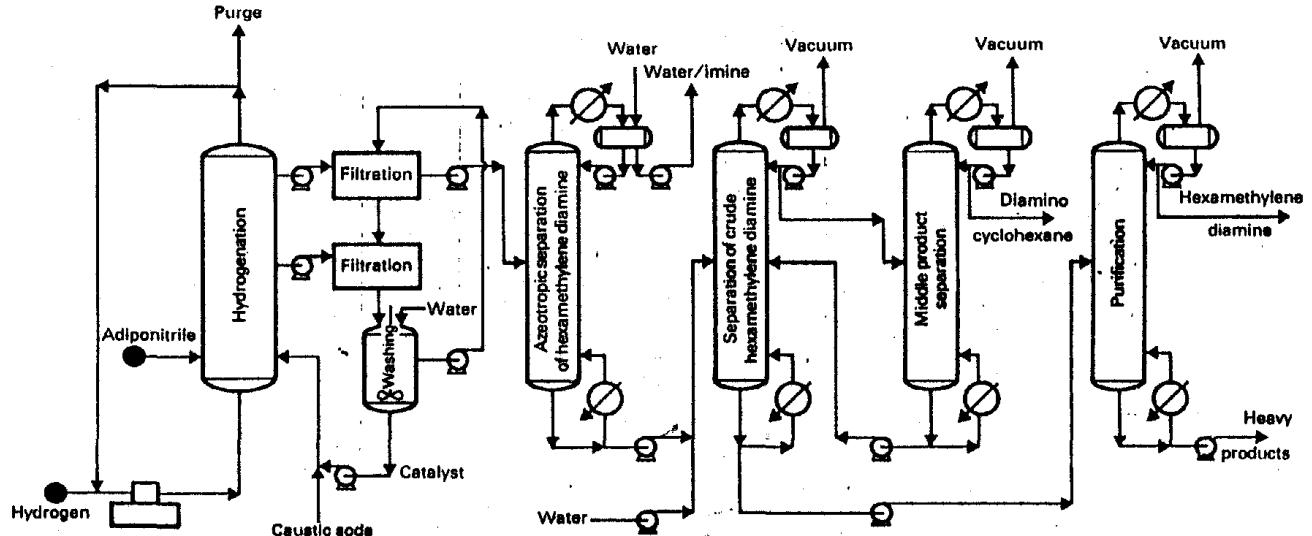


Fig. 12.8. Hexamethylene diamine production by adiponitrile hydrogenation. Rhône-Poulenc process:

This diimine can react with the amine formed and, after the removal of ammonia, yield an azomethine, which can be hydrogenated to form a secondary amine. The first stage of HMDA purification thus consists in removing the hexamethylene diimine by heteroazeotropic distillation in the presence of water. Phase separation occurs after condensation. The aqueous phase is used as reflux, and the organic fraction is removed. The withdrawal is sent to a fractionation train operating under vacuum. The crude HMDA is recovered at the top of the first column, combined with 1,2-diaminocyclohexane, water, and different compounds with similar boiling points. The bottoms consist of residual HMDA, heavy products, tars and adiponitrile. The distillate is sent to a second column, where diaminocyclohexane, water and medium products are removed at the top, and HMDA recovered at the bottom and recycled to the first column.

The initial withdrawal is retreated in a final distillation column. HMDA to commercial specifications is obtained at the top at 112°C and 5 kPa absolute. Since it melts at 41°C, it is stored at 93°C and then used for the manufacture of nylon-6,6.

12.1.4.2 Processes with 1,6-hexanediol as intermediate

In a 40,000 t/year plant in the United States, Celanese employed a method for synthesizing hexamethylene diamine starting, like the others, with cyclohexane, but using 1,6-hexanediol, HOCH₂—(CH₂)₄—CH₂OH, as an intermediate. In this process, the cyclohexane is first oxidized at 150°C and 3.3 · 10⁶ Pa absolute to a mixture of adipic acid and ω -hydroxycaproic acid. These acids are esterified by reaction with a fraction of the hexanediol previously produced.

In a second step, the esters are hydrogenolysed to 1,6-hexanediol, which is then purified. A third step consists in aminating the diol at 200°C and 23 · 10⁶ Pa absolute by means of ammonia, and in the presence of Raney nickel as catalyst. Hexamethylene-diamine is obtained with a molar yield approaching 90 per cent, and the main by-products are hexamethylene imine and 6-aminohexanol.

12.1.4.3 Economic data

Table 12.8 gives economic data concerning the manufacture of HMDA from adipic acid, butadiene and acrylonitrile.

12.1.4.4 Uses and producers

Table 12.9 gives the average commercial specifications of HMDA. Nearly all the HMDA consumed in Western Europe (95 per cent) is used to manufacture nylon-6,6. The remainder finds various applications, the most important being the production of hexamethylene diisocyanate, which is used to manufacture certain polyurethane foams and nylon-6,6.

HMDA production capacities and consumption in Western Europe, the United States and Japan in 1984 are given in Table 12.10, together with the main uses in these three geographic areas.

TABLE 12.8
 HEXAMETHYLENE DIAMINE PRODUCTION. ECONOMIC DATA
 (France conditions, mid-1986)
 PRODUCTION CAPACITY 50,000 t/year

Process.....	Action of ammonia on adipic acid	Butadiene hydrocyanation	Acrylonitrile electro-dimerization
Typical technology	Monsanto	Du Pont	Monsanto
Battery limits investments (10^6 US\$)	40	50	60
Consumption per ton of hexamethylene diamine:			
Raw materials			
Butadiene (t)	—	0.63*	—
Adipic acid (t)	1.43	—	—
Acrylonitrile (t)	—	—	1.05
Chemicals			
Hydrogen (kg)	70	70	70
Ammonia (t)	0.58	—	—
Hydrogen cyanide (t)	—	0.60	—
Miscellaneous and catalysts (USS)	—	160	105
Utilities			
Steam (t)	3.5	9	12
Electricity (kWh)	1,200	1,100	6,000
Fuel (10^6 kJ)	22	26	8
Cooling water (m^3)	300	760	700
Labor (Operators per shift)	6	8	8

TABLE 12.9
 AVERAGE COMMERCIAL SPECIFICATIONS OF HEXAMETHYLENE DIAMINE

Characteristics	Values
Purity (%) (anhydrous) min.	99.9
$d_{25}^{25(1)}$	0.889 to 0.900
Color (Pt Co) max.	10
1,2-diamino cyclohexane (ppm) max.	250

(1) Specific gravity, 77.0/77.0.

TABLE 12.10
HEXAMETHYLENE DIAMINE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Nylon 6.6	89	98	99
Fibers	73	87	90
Resins	16	11	9
Miscellaneous ⁽¹⁾	11	2	1
Total	100	100	100
Sources (% product)			
Acrylonitrile	23	34	95
Adipic acid	52	—	—
Butadiene	25	66	—
Miscellaneous ⁽²⁾	—	—	5
Total	100	100	100
Production (10 ³ t/year)	250	410	30
Capacity (10 ³ t/year) ⁽³⁾	410	540	50
Consumption (10 ³ t/year)	240	420	30

(1) Hexamethylene diisocyanate, nylon 6.10 (fibers and resins), rubber accelerators,...

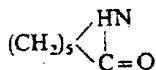
(2) Waste caprolactam.

(3) The worldwide production capacity of hexamethylene diamine was about $1.07 \cdot 10^6$ t/year in 1984 and $1.11 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.54	Western Europe	0.41	Middle East	—
Canada	0.04	Eastern Europe	—	Japan	0.05
Latin America	0.05	Africa	—	Asia and Far East	0.02

12.2 MANUFACTURE OF NYLON-6. CAPROLACTAM

The monomer of nylon-6 is caprolactam ($d_4^{27} = 1.02$ ⁽⁴⁾, mp = 69.3°C , bp_{1.7 kPa, substrate} = 140°C), the lactam of aminocaproic acid:



The first industrial production of caprolactam dates from 1938, when BASF started manufacturing perlon (BASF nylon-6). The starting material was phenol. Other processes have been developed since then, using the same intermediate, but also cyclohexane and toluene.

Figure 12.9 shows the different industrial methods for producing caprolactam.

Although many units based on phenol are still in operation, new plants use cyclohexane as the raw material. In 1987, 68 per cent of worldwide caprolactam production capacity

(4) Specific gravity, 170.6/39.2.

employed cyclohexane, 25 per cent phenol and only 5 per cent toluene (miscellaneous = 2 per cent in Eastern Europe).

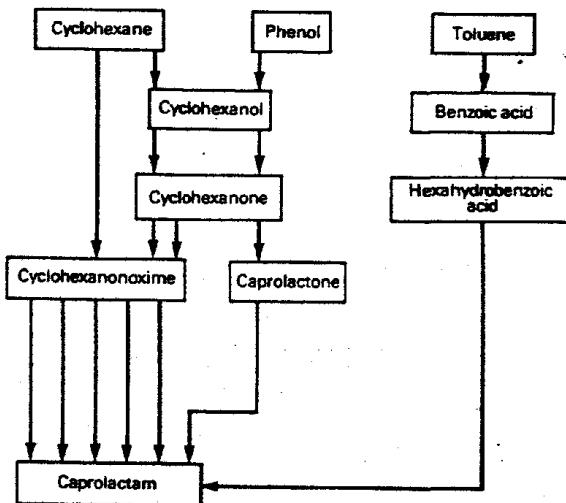


Fig. 12.9. Different methods for producing caprolactam.

12.2.1 Processes for producing caprolactam from phenol and cyclohexane

All the processes except one (Toray NPC process) examined further involve cyclohexanone as an intermediate, which is then converted to the oxide and then to the lactam.

12.2.1.1 Production of cyclohexanone

A. Processes using phenol

Earlier processes operated in two steps. In the first, phenol was hydrogenated to cyclohexanol on a nickel catalyst, and the alcohol formed was then dehydrogenated to cyclohexanone.

The process currently used by *Inventa* and *Allied Chemical* is a single-step liquid phase process (Fig. 12.10). Phenol is first placed in contact at 180°C, in two reactors in series and in the presence of caustic soda, with a sequestering agent (EDTA: Ethylene-Diamine Tetra Acetic acid) to remove the metallic impurities that are detrimental to the hydrogenation catalyst. It is then sent to a first distillation column (15 trays), where a fraction corresponding to the requisite quality is collected at the top. A large share remains in the withdrawal. This stream is sent to a second column (20 trays) operating

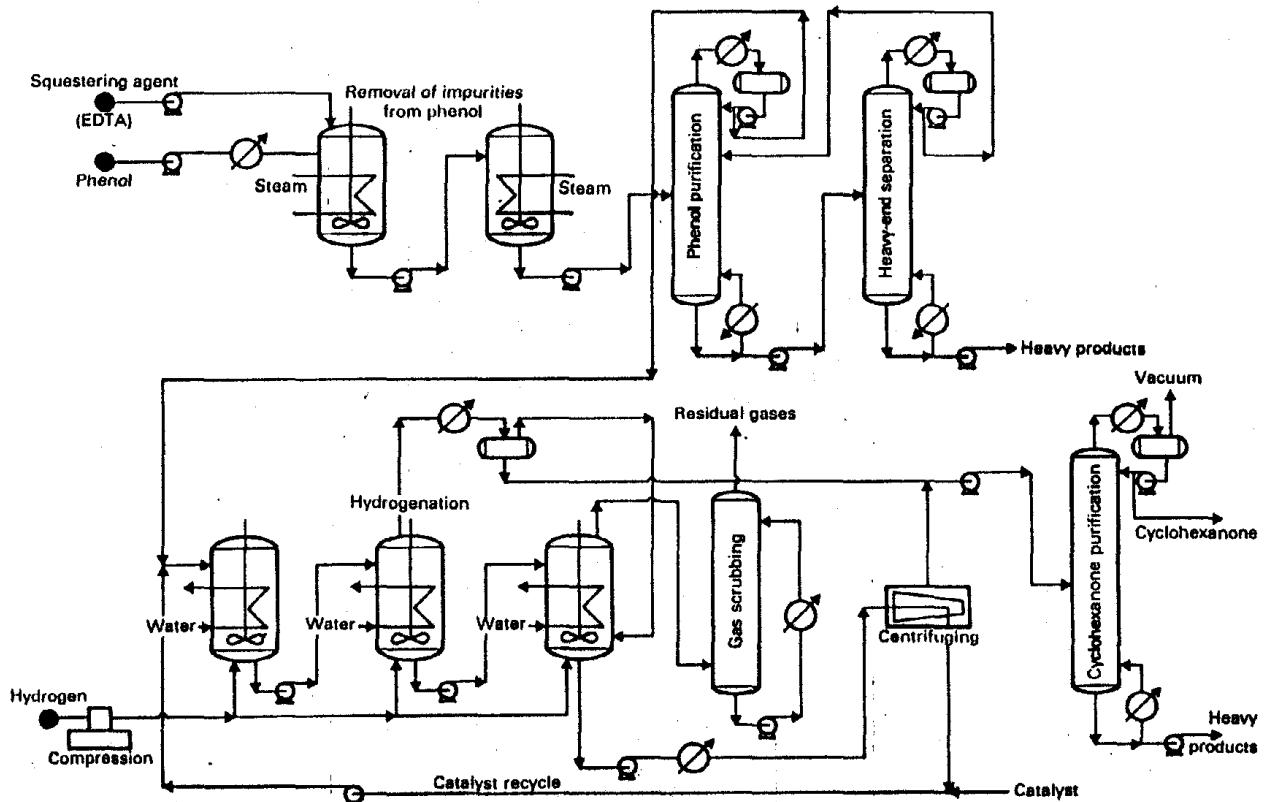


Fig. 12.10. Cyclohexanone production from phenol. Inventa/Allied processes.

under vacuum. The distillate is recycled to the initial distillation, and the bottom, which contains 30 ppm of free or combined phenol, is removed.

The purified phenol is hydrogenated at 175°C, in a series of three reactors operating at $1.3 \cdot 10^6$ Pa absolute. The catalyst, used at the level of 0.5 per cent weight of the feed, is 5 per cent weight palladium deposited on coal. 95 per cent volume hydrogen is employed, in a 20 per cent excess in relation to stoichiometry. The heat generated by the transformation is removed by internal circulation of cooling water, to limit the temperature at the outlet of the last reactor to 200°C. The hydrogenated effluent is cooled to 90°C and centrifuged to recover the catalyst, which is then recycled. Molar selectivity is 97 per cent for cyclohexanone and 2.5 per cent for cyclohexanol. The cyclohexanone is then purified by distillation (35 trays).

B. Processes using cyclohexane

These processes involve two stages. Cyclohexane is first oxidized to a cyclohexanol/cyclohexanone mixture (see Section 9.1.6.1 and Section 12.1.2.2), which is then dehydrogenated (Fig. 12.11). This OI/One mixture is first fractionated in a series of three distillation columns operating under vacuum, of which the first two (20 trays each) separate the

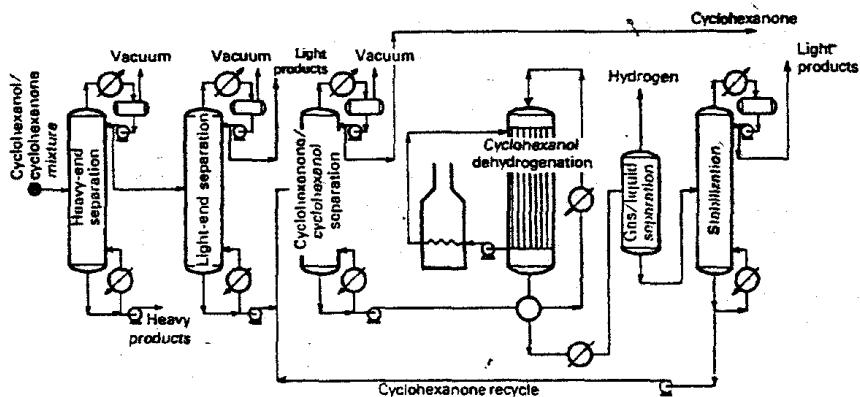


Fig. 12.11. Cyclohexanone production from cyclohexane. Dehydrogenation of cyclohexanol/cyclohexanone mixture.

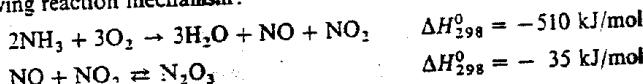
light and heavy compounds. Cyclohexanone is collected at the top of the last column (40 trays). The withdrawal, consisting essentially of cyclohexanol, is vaporized and superheated, and then sent to the dehydrogenation reactor. The endothermic reaction takes place around 400°C, in the presence of a zinc catalyst and at atmospheric pressure, with heating provided by the circulation of a molten salt. 84 per cent cyclohexanone and 1 per cent of light compounds are formed. Unconverted cyclohexanol and the cyclohexanone produced are recycled to the fractionation column of the OI/One mixture, after separation of the hydrogen produced and removal of the light compounds.

12.2.1.2 Hydroxylamine preparation

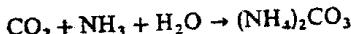
The production of cyclohexanone oxime implies the prior manufacture of hydroxylamine.

A. Conventional processes

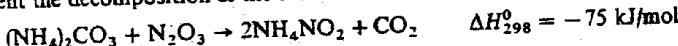
In conventional processes (*Stamicarbon* and *Inventa*), hydroxylamine sulfate is prepared by the Raschig technique. The first reaction is the catalytic combustion of ammonia in air at 850°C, in the presence of a platinum foam catalyst. The heat generated by the reaction is recovered in a boiler which produces steam. Nitrogen oxides are formed by the following reaction mechanism:



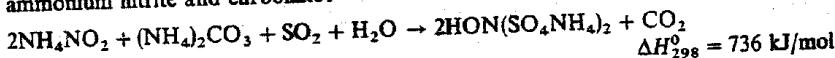
A solution of ammonium carbonate is also prepared by the reaction of CO₂ with ammonia:



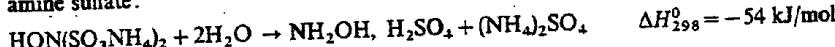
The reaction of ammonium carbonate with nitrous oxide, with temperature control to prevent the decomposition of the nitrite formed, yields ammonium nitrite:



Hydroxylamine disulfonate is then prepared by the action of SO₂ on a mixture of ammonium nitrite and carbonate:



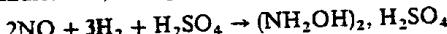
Finally, hydrolysis of the hydroxylamine disulfonate at 95°C yields hydroxylamine sulfate, with the co-production of ammonium sulfate at the rate of 805 kg/t of hydroxylamine sulfate:



The co-production of such a large amount of ammonium sulfate, which is often difficult to utilize economically, has led to research on new processes to synthesize hydroxylamine.

B. New industrial developments

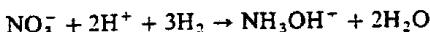
- In the BASF process, nitric oxide is produced by the oxygen oxidation of ammonia in the presence of steam. The nitric oxide thus obtained is then reduced by hydrogen, in the presence of sulfuric acid, on a palladium catalyst:



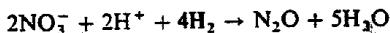
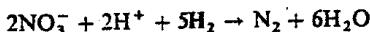
- The technology proposed by *Inventa* is similar in principle to that of *BASF*, but it differs in practice in the type of material used in the unit (plastic instead of stainless steel), and in the choice of the catalyst (platinum instead of palladium).

These two processes, which do not co-produce ammonium sulfate, nevertheless present the drawback of requiring costly catalyst recovery. They also fail to eliminate the co-production of ammonium sulfate entirely with the production of caprolactam, as shown below.

- The HPO (hydroxylamine phosphate oxime) process, developed by *DSM* and licensed by *Stamicarbon*, totally eliminates the production of ammonium sulfate, both in the production of hydroxylamine itself, and in the oxime production stage. It consists of the catalytic hydrogenation of the nitrate ions resulting from the oxidation of ammonia to hydroxylamine ions in a solution buffered by phosphates. The nitrate reduction reaction is as follows:



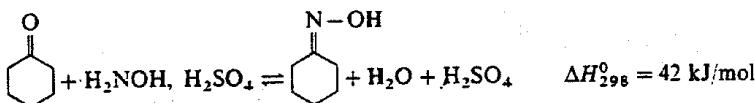
The reaction is exothermic. The catalyst employed is palladium on coal. It operates between 20 and 60°C, with a hydrogen partial pressure of $1 \cdot 10^6$ Pa absolute. Molar selectivity of hydroxylamine in relation to ammonia is 58 per cent, and the main side reactions are the following:



12.2.1.3 Cyclohexanone oximation

Figure 12.12 shows a conventional industrial flow sheet for the manufacture of crude caprolactam from cyclohexanone.

The oximation reaction is written:



This can be carried out in several (4) agitated reactors in series or in a column with several injection levels. In the former case, hydroxylamine sulfate reacts with an approximately equal-weight mixture of cyclohexanone and oxime in the primary reactor. The sulfuric acid is then neutralized by ammonia. The liquid oxime rises above the solution of ammonium sulfate and hydroxylamine sulfate. In the secondary reactor, this solution reacts with the fresh cyclohexanone feed. This is followed by a second neutralization by ammonia, in order to obtain the initial effluent (50:50) of cyclohexanone and oxime fed to the primary reactor.

In the case of the DSM/HPO process, the buffer mixture containing the phosphate and oxime reacts with cyclohexanone in the presence of toluene, which extracts the oxime as it is formed. The oxime is recovered from its solution in toluene by distillation, and the buffer mixture is recycled to hydroxylamine production.

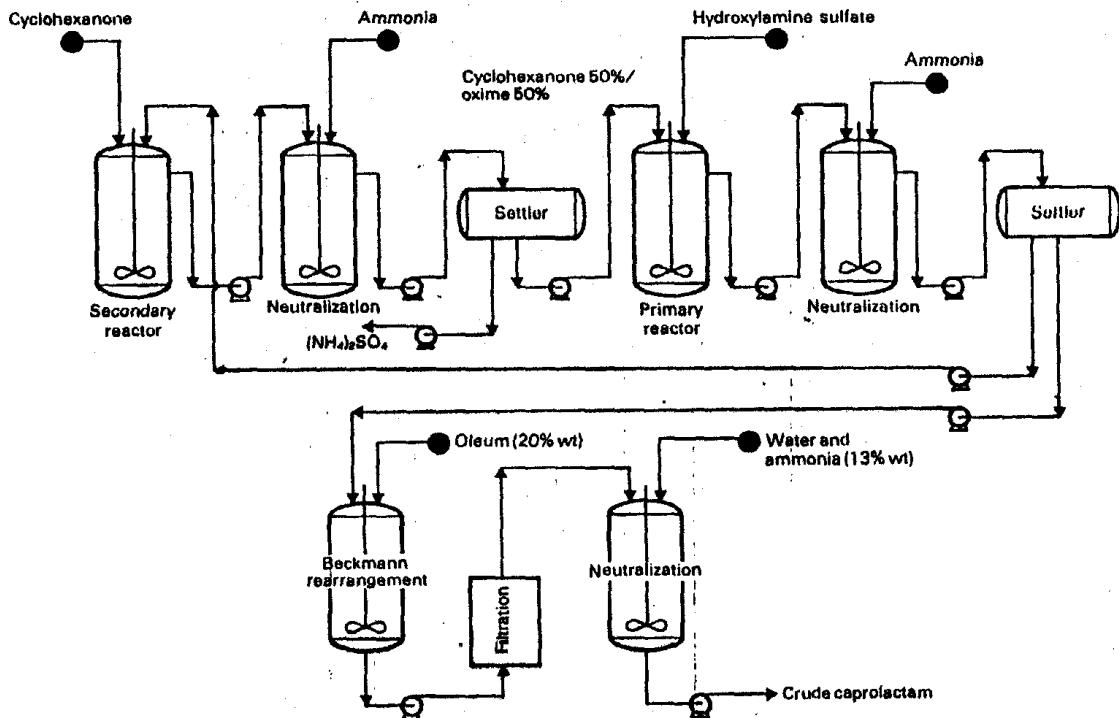
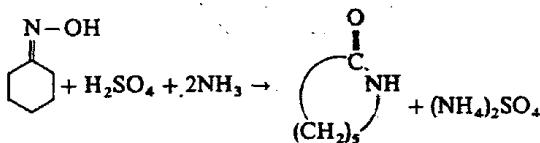


Fig. 12.12. Caprolactam production from cyclohexanone. Conventional process.

12.2.1.4 Beckmann rearrangement (Fig. 12.13)

The arrangement of the oxime to caprolactam is carried out by oleum, which is then neutralized by ammonia with the production of ammonium sulfate, by the following reaction:



The heat of reaction ($\Delta H_{198}^0 = -184 \text{ kJ/mol}$) is removed by external circulation of the reaction medium through an exchanger, thus maintaining the temperature between 75 and 80°C. The mixture of caprolactam and sulfuric acid obtained is first neutralized by a 13 per cent weight ammonia solution. The recycle of a large fraction of the ammonium sulfate solution prevents an excessive temperature rise, which would cause decomposition of the lactam. After cooling, this mixture is settled. The phase containing the crude product is centrifuged, and then added to a recycle fraction from the final purification stage, before being rid of the light compounds by stripping. The prepurified lactam and the aqueous phase, consisting essentially of ammonium sulfate, are sent with a solvent (toluene) to a series of extractors where they are brought into countercurrent contact between the caprolactam-rich solution and the $(\text{NH}_4)_2\text{SO}_4$ -rich solution. Ammonium sulfate is collected at the bottom of the first extractor, and then purified by ion exchange and crystallized, centrifuged and dried. The lactam leaving at the top of the final evaporator is settled. The lower layer is recycled to extraction, and the upper fraction distilled after the addition of water, to facilitate solvent recovery by the formation of a heteroazeotrope. The water is separated from the solvent, which is recycled, by condensation and settling. The caprolactam withdrawn is sent to the purification section. This involves passage into a column of cation exchange resins, which are regenerated by a 4 per cent weight sulfuric acid solution, and the effluent obtained is concentrated in a series of thin layer evaporators. The compound is stored in the liquid state.

12.2.1.5 Co-production of ammonium sulfate

- In conventional processes, hydroxylamine preparation, oximation and the Beckmann rearrangement produce a total of up to 4.4 t of ammonium sulfate per ton of caprolactam. The molar yield of lactam is around 70 per cent of theory in relation to cyclohexane, and 91 per cent in relation to phenol. With the BASF technology, only 2.6 t of ammonium sulfate is produced per ton of caprolactam, and the molar yield in relation to cyclohexane is 70 per cent of theory. The use of the HPO process reduces the production of ammonium sulfate to 1.8 t per ton of caprolactam, and the molar yield is 61 per cent in relation to cyclohexane, and 93 per cent in relation to phenol.

- Stamicarbon* attempted to eliminate the co-production of ammonium sulfate completely in a variant of the HPO process, in which, during the effluent neutralization and the Beckmann rearrangement, ammonium bisulfate is formed instead of the neutral sulfate (bisulfate process). The sulfate is then pyrolysed to yield SO_2 , nitrogen and water. The

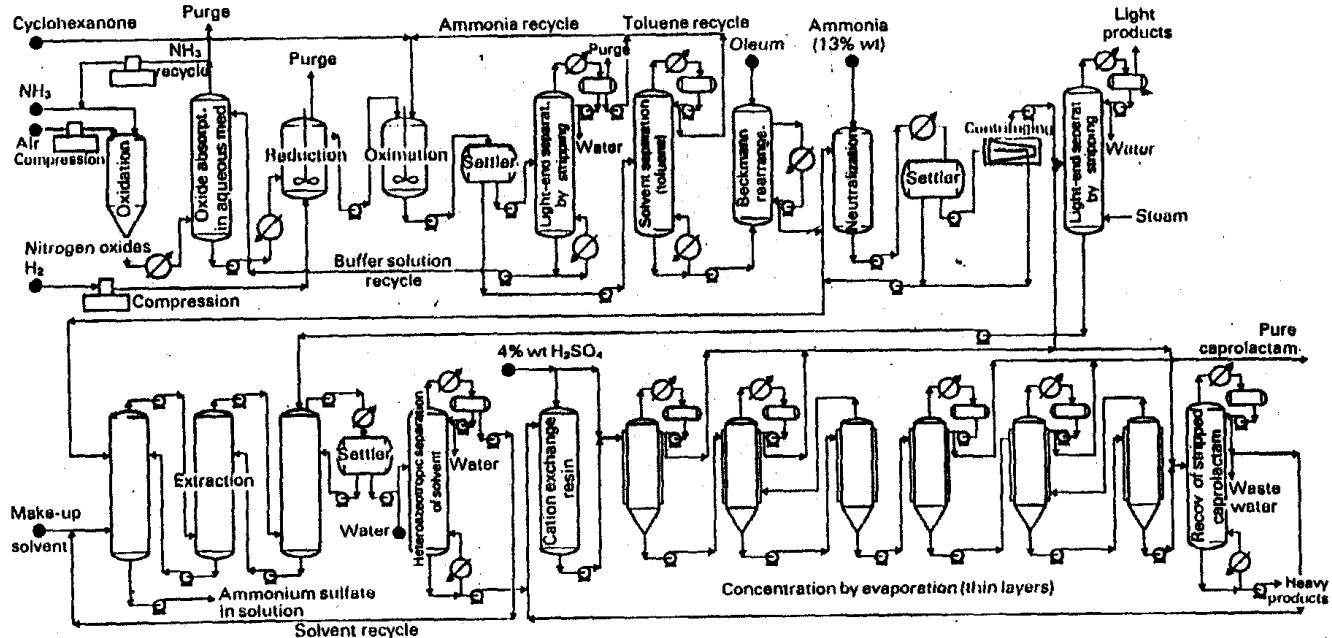


Fig. 12.13. Caprolactam production from cyclohexanone. General scheme.

SO_2 is employed to regenerate the sulfuric acid. This process does not appear to be economical owing to the energy costs it entails, and because of ammonia losses. It has not yet reached the industrial stage.

- *Allied Chemical* recently proposed a simplified technique, producing caprolactam from cyclohexanone, ammonia and oxygen in a single step, in the vapor phase, on a silica- or alumina-based catalyst. However, the drawback of this process resides in the fact that only half of the oxime is converted *in situ* to caprolactam. This makes it necessary to resort to the Beckmann rearrangement. For a 50 per cent conversion of cyclohexanone, the molar selectivity of oxime and caprolactam is 68 per cent. Although this method considerably reduces the production of ammonium sulfate, the yields are still too low for it to appear to be more economical than the foregoing routes.

- *Bayer* recently described a variant in which the Beckmann rearrangement occurs by the passage of cyclohexanone oxime vapors on a fluid catalyst bed, consisting of boric acid on coal. The molar yield of the conversion is claimed to be 98 per cent. By combining the DSM technique for manufacturing hydroxylamine and this catalytic oxime rearrangement process, the co-production of ammonium sulfate is totally eliminated. However, no industrial development has yet been announced since the filing of the first patents in 1978.

12.2.1.6 Direct oxime synthesis by cyclohexane photonitroization

The Toray cyclohexane photonitroization process (PNC) achieves the direct transformation of cyclohexane to oxime hydrochloride by a photochemical method, in the presence of nitrosyl chloride (NOCl) by the following overall reaction:

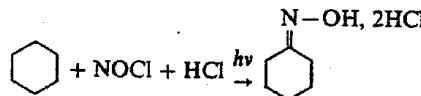
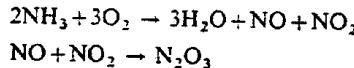
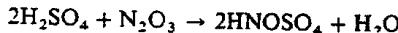


Figure 12.14 shows a flow sheet of this technique.

- Nitrosyl chloride is produced from ammonia and hydrochloric acid in the following way: the ammonia is catalytically oxidized by air at high temperature and yields nitrous oxide N_2O_3 :



The action of sulfuric acid at atmospheric pressure yields a solution of nitrosyl sulfuric acid in sulfuric acid.



Hydrochloric acid displaces sulfuric acid at 75°C to produce nitrosyl chloride:



Unconverted nitrosyl sulfuric acid is recycled. The gaseous mixture of NOCl and HCl is introduced into liquid cyclohexane.

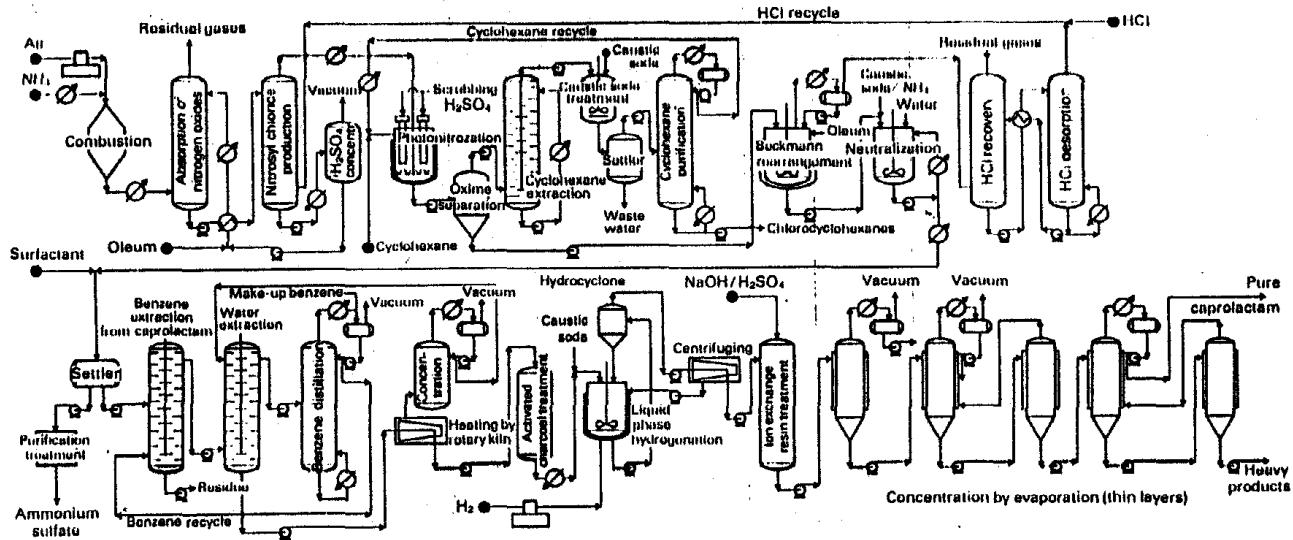
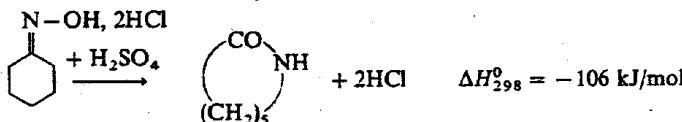


Fig. 12.14. Caprolactam production by cyclohexane photonitration. Toray PNC process.

• Photonitroization takes place in a reactor with mercury vapor lamps, designed to supply the light energy required to activate the reaction. Cyclohexanone oxime hydrochloride, which is very slightly soluble in cyclohexane, is separated in the form of an oily layer. Small amounts of chlorocyclohexane appear simultaneously, which can be utilized after being isolated from the unconverted cyclohexane.

• After separation, the oxime hydrochloride is subjected to the Beckmann rearrangement in the presence of oleum:



Since the heat of reaction is lower than in the rearrangement of the pure oxime ($\Delta H_{298}^0 = -187 \text{ kJ/mol}$), temperature control is easier. The lactam yield in relation to the oxime is greater than 90 per cent weight.

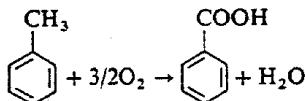
The hydrogen chloride gas evolved is absorbed in dilute hydrochloric acid, and then sent to the production of nitrosyl chloride. The solution of lactam in sulfuric acid is neutralized by ammonia. Two phases are formed: the upper layer is the crude caprolactam which is purified⁽⁵⁾, and the bottom layer is an aqueous solution of ammonium sulfate. The molar yield of caprolactam is 81 per cent of theory in relation to cyclohexane. Co-production of ammonium sulfate is 1.7 kg/kg of product.

The photonitroization reaction has a very low quantum yield (≈ 0.7). However, if 60 kW lamps doped with thallium iodide are used to produce an intense light emission at 535 nm (nanometers), while reducing the intensity of the other mercury bands, 24 kg/h of oxime can be produced per lamp, or about 180 t/year. The only industrial development of this process is that of Toray in Nagoya. The high consumption of electricity restricts it to areas where this type of energy is available cheaply.

12.2.2 SNIA Viscosa process for manufacturing caprolactam from toluene

This method, starting with toluene, involves the following three steps (Fig. 12.15).

12.2.2.1 Oxidation of toluene to benzoic acid



(5) To meet commercial specifications (permanganate number and volatile base content in particular), the crude caprolactam must undergo a rather complex purification. This operation includes the following treatment: extraction by benzene and water, passage over activated charcoal and ion exchange resins, selective hydrogenation in the presence of caustic soda, etc.

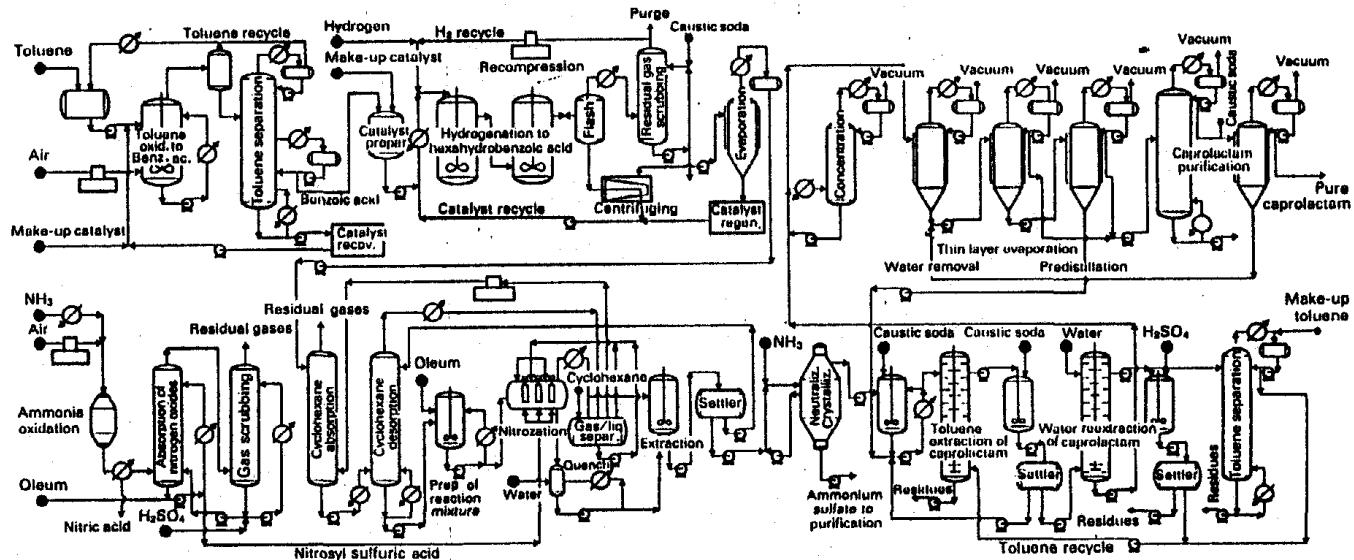
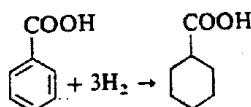


Fig. 12.15. Caprolactam production from toluene. SNIA/Viscosa process.

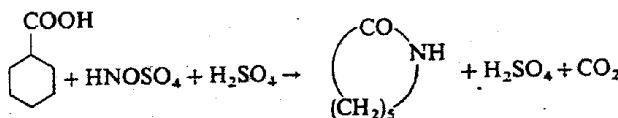
This transformation is identical to the one that occurs in the manufacture of phenol by the Dow process (see Section 10.1.5). The toluene is air-oxidized in the presence of a soluble cobalt salt, at a temperature between 160 and 170°C, at between 0.8 to $1 \cdot 10^6$ Pa absolute. Once-through conversion is limited to between 20 and 40 per cent. Benzoic acid selectivity is about 93 molar per cent.

12.2.2.2 Hydrogenation of benzoic acid to hexahydrobenzoic acid (or carboxylic cyclohexane)



This takes place at 170°C and between 1 to $1.5 \cdot 10^6$ Pa absolute, in the presence of a palladium catalyst, in a series of agitated reactors. Unconverted hydrogen is recycled after scrubbing with caustic soda and water. The catalyst system in suspension in the effluent is recovered by centrifuging and hexahydrobenzoic acid evaporation before regeneration and recycle.

12.2.2.3 Conversion of hexahydrobenzoic acid to caprolactam



Caprolactam is obtained at atmospheric pressure, in the presence of a solvent (cyclohexane) in a multistage reactor. Hexahydrobenzoic acid and oleum, previously mixed at 35°C, are introduced into the reactor. Nitrosyl sulfuric acid (prepared by the absorption of NO – NO₂ in oleum) is injected at each stage in predetermined quantities. Once-through conversion of hexahydrobenzoic acid is limited to 50 per cent. The temperature is kept at 80°C by the evaporation of cyclohexane. The reactor effluent is then diluted with water at low temperature. The cyclohexane evaporated is recondensed and used to extract unconverted hexahydrobenzoic acid and allow its recycle, while the caprolactam formed goes into the aqueous solution. This phase is neutralized by ammonia. Ammonium sulfate, formed at the rate of 4.2 t/t of product, is recovered by centrifuging. The lactam is extracted with the toluene, reextracted with water and dehydrated. The final yield of the operation is 72 per cent weight in relation to toluene.

12.2.2.4 Technological improvements

Three plants based on this process are currently in operation worldwide, two in Italy at Torviscosa, and the third in the USSR. *SNIA Viscosa (Società Nazionale Industria Applicazioni)* has proposed two successive modifications to its process:

- (a) In the first, the caprolactam acid solution is not neutralized by ammonia, and the caprolactam is extracted from it by means of a solvent consisting of an alkyl

- phenol. This avoids the co-production of ammonium sulfate. The aqueous solution remaining is thermally decomposed to produce SO_2 , which is recycled.
- (b) In the second, hexahydrobenzoic acid, instead of being lactamized in a single stage by oleum and nitrosyl sulfuric acid, is first thermally cracked at 600°C to pentamethylene ketene, and this product is treated by the nitrosyl sulfuric acid/oleum mixture. Subsequent neutralization of the caprolactam formed yields only 2 t of ammonium sulfate per ton of lactam.

Neither of these two process improvements appears to have advanced to industrial development.

12.2.3 Other industrial processes for manufacturing caprolactam

Among the many technologies developed to manufacture caprolactam are the following:

- The Du Pont process, in which cyclohexanone oxime is obtained by the nitration of cyclohexane, followed by catalytic hydrogenation of the nitrocyclohexane obtained. A plant of this type, started up by *Du Pont* in 1963, was shut down in 1967.
- The Union Carbide process starting with cyclohexane, which is first converted to cyclohexanone, which is in turn oxidized to caprolactone. This compound is then converted to caprolactam by the action of ammonia, at 400°C , under $17 \cdot 10^6 \text{ Pa}$ absolute pressure. Cyclohexanone is oxidized around 50°C , at normal pressure, by means of peracetic acid, in the presence of acetaldehyde, which is oxidized to acetic acid. The plant built by *Union Carbide* was shut down shortly after its construction. Variants have been proposed by *Degussa*, *Toa Gosei* and *Ugine Kuhlmann* without industrial success.
- The Techni-Chem. process starting with cyclohexanone, and involving four steps:
 - (a) Formation of cyclohexenyl acetate by the action of ketene on cyclohexanone and nitration to 2-nitrocyclohexanone, with the production of acetic acid that is recycled to ketene formation,
 - (b) Hydrolysis of 2-nitrocyclohexanone to 6-nitrocaproic acid,
 - (c) Reduction of 6-nitrocaproic acid to 6-aminocaproic acid,
 - (d) Production of lactam by thermal cyclization of the amino acid.
- The BP process, in which cyclohexanone is oxidized by hydrogen peroxide to form a peroxide intermediate which reacts with ammonia to yield 1,1'-peroxydicyclohexylamine. This compound decomposes into caprolactam and cyclohexanone, which is recycled.
- The Kanebo process, consisting in the catalytic rearrangement of o-acetyl cyclohexanone oxime to N-acetyl caprolactam and caprolactam, at 150°C , in the presence of a silica/alumina catalyst. In a second step, the acetyl caprolactam reacts with cyclohexanone oxime, which it converts to an o-acetyl derivative by liberating lactam. The rearrangement is carried out without forming a co-product.
- The Teijin process, in which cyclohexane is oxidized to a mixture of adipic and 6-hydroxycaproic acids, after which the adipic acid is hydrogenated to 6-hydroxycaproic

CAPROLACTAM PRODUCTION. ECONOMIC DATA (France conditions, mid-1986)
PRODUCTION CAPACITY 80,000 t/year

Process.....	Conventional cyclohexane single-step	Conventional hydroxylamine sulfate by Raschig method	Passage through hydroxylamine phosphate	NO production by NH ₃ oxidation then reduction	Photonitration	Passage through hexahydrobenzoic acid
Typical technology.....	Allied-Inventa	DSM-Inventa	DSM (HPO)	BASF	Toyo Rayon	SNIA Viscosa
Raw material	Phenol	Cyclohexane	Cyclohexane	Cyclohexane	Cyclohexane	Toluene
Battery limits investments (10 US\$) .	98	110	114	124	121	123
Consumption per ton of caprolactam						
Raw materials						
Toluene (t).....	—	—	—	—	—	1.03
Cyclohexane (t).....	—	1.08	1.02	1.06	0.92	—
Phenol (t).....	0.92	—	—	—	—	—
Chemicals						
Hydrogen (kg).....	50	1	95	45	—	70
Oxygen (t).....	—	—	—	0.55	—	—
Sulfur (t)	0.68	0.70	—	—	—	—
Ammonia (t)	1.47	1.60	0.80	0.95	0.67	1.35
Oleum and sulfuric acid (t)	1.36	1.35	1.35	2.10	1.35	3.45
Caustic soda (t).....	—	0.20	0.20	0.20	0.05	0.15
Hydrochloric acid (kg).....	—	—	—	—	45	—
Miscellaneous and catalysts (US\$)	45	25	20	40	140	35
By-products						
Hydrogen (kg).....	—	15	40	10	—	—
Ammonium sulfate (t)	4.4	4.5	1.8	2.6	1.8	4.2
Dilute nitric acid (as 100%) (kg).....	50	20	—	40	—	15
Utilities						
Steam (t)	9	20	13	15	15	10
Electricity (kWh)	300	1,700	500	1,100	4,100	1,500
Fuel (10 ⁶ kJ)	0.1	2.0	0.8	0.8	0.5	10
Cooling water (m ³).....	1,200	1,100	1,700	1,800	1,000	600
Process water (m ³)	10	15	5	10	5	10
Nitrogen (Nm ³)	60	5	60	80	10	40
Labor (Operators per shift)	27	28	28	24	26	30

TABLE 12.12
AVERAGE COMMERCIAL SPECIFICATIONS OF CAPROLACTAM

Characteristics	Values
Solidification point (°C) (dry basis) min.	69
Minimum transmission of 65% Wt aqueous solution at 410 nm (%)	92
Maximum permanganate number	7
Moisture content (%) max.	0.10
Iron (ppm Fe) max.	0.5
Volatile bases (ppm NH ₃) max.	5
Combustion residue (ppm) max.	10
Cyclohexanone oxime (ppm) max.	10
Free alkalinity (meq/kg)	0 to 0.04

TABLE 12.13
CAPROLACTAM PRODUCTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Nylon 6	99	98	100
Fibers	62	86	75
Plastics and films	37	12	25
Miscellaneous ⁽¹⁾	1	2	—
Total	100	100	100
Sources (% product)			
Cyclohexane	51	59	100
Phenol	38	41	—
Toluene	11	—	—
Total	100	100	100
Production (10 ³ t/year)	670	465	435
Capacity (10 ³ t/year) ⁽²⁾	850	550	440
Consumption (10 ³ t/year)	420	440	360

(1) Additives, nylon RIM (reaction injection molding), plasticizers, stabilizers.

(2) The worldwide production capacity of caprolactam was around $2.9 \cdot 10^6$ t/year in 1984 and more than $3.0 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.49	Western Europe	0.85	Middle East	0.03
Canada	—	Eastern Europe	>0.80	Japan	0.44
Latin America	0.08	Africa	—	Asia and Far East	0.35

acid. The hydroxycaproic acid is then cyclized to lactone, which is converted to caprolactam.

These last four processes have not yet been commercialized

12.2.4 Economic data

The main economic data available on processes for manufacturing caprolactam are summarized in the comparative Table 12.11.

12.2.5 Uses and producers

Table 12.12 gives the average commercial specifications of caprolactam. It is devoted essentially to the manufacture of nylon-6, used largely in the form of fibers and also to produce plastics and films. Table 12.13 shows the distribution of caprolactam uses in Western Europe, the United States and Japan, as well as the production, capacities and consumption in these three geographic areas in 1984.

12.3 MANUFACTURE OF NYLON-11 11-AMINOUNDECANOIC ACID

A monomer of nylon-11, commercialized by *ATO Chem*, under the name of *Rilsan*, 11-aminoundecanoic acid is prepared from castor oil. Hence its manufacture does not strictly form part of the field of petrochemicals. It is nevertheless discussed here to provide an example of synthesis from biomass, and for technico-economic comparisons with nylon-12, which has comparable properties, and whose monomer is of petrochemical origin.

Castor oil is essentially produced in Brazil and India. It contains about 89 per cent weight of ricinoleic acid, combined in the form of a triglyceride. The remainder of the oil consists of triglycerides, palmitic, stearic, oleic and linoleic acids, etc.

12.3.1 Successive stages in the manufacture of 11-aminoundecanoic acid

These steps are illustrated by Fig. 12.16. Figure 12.17 gives a flow sheet of the unit.

12.3.1.1 Transesterification of crude castor oil

In the first stage, the crude castor oil is transesterified, in the presence of excess methanol and traces of sodium methylate acting as a catalyst. This takes place at 80°C

in an agitated and jacketed reactor. The reactor is fed continuously to maintain the methanol/ester molar ratio at 3:1. At the end of the reaction, the methyl ricinoleate formed is separated from the glycerol phase by settling.

The glycerol, which represents 9 per cent weight of the oil treated, is recovered. The methyl ester is washed with water to remove the final traces of glycerin. The transesterification yield is practically quantitative for a residence time of about one hour.

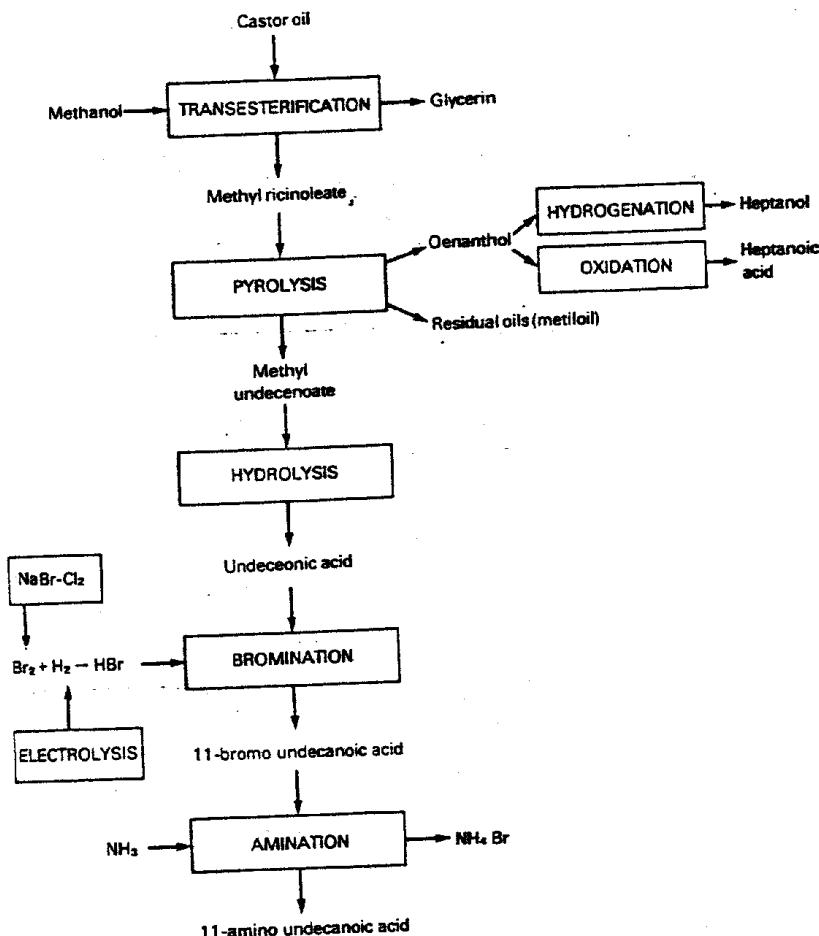


Fig. 12.16. Main steps in the manufacture of 11-aminoundecanoic acid.

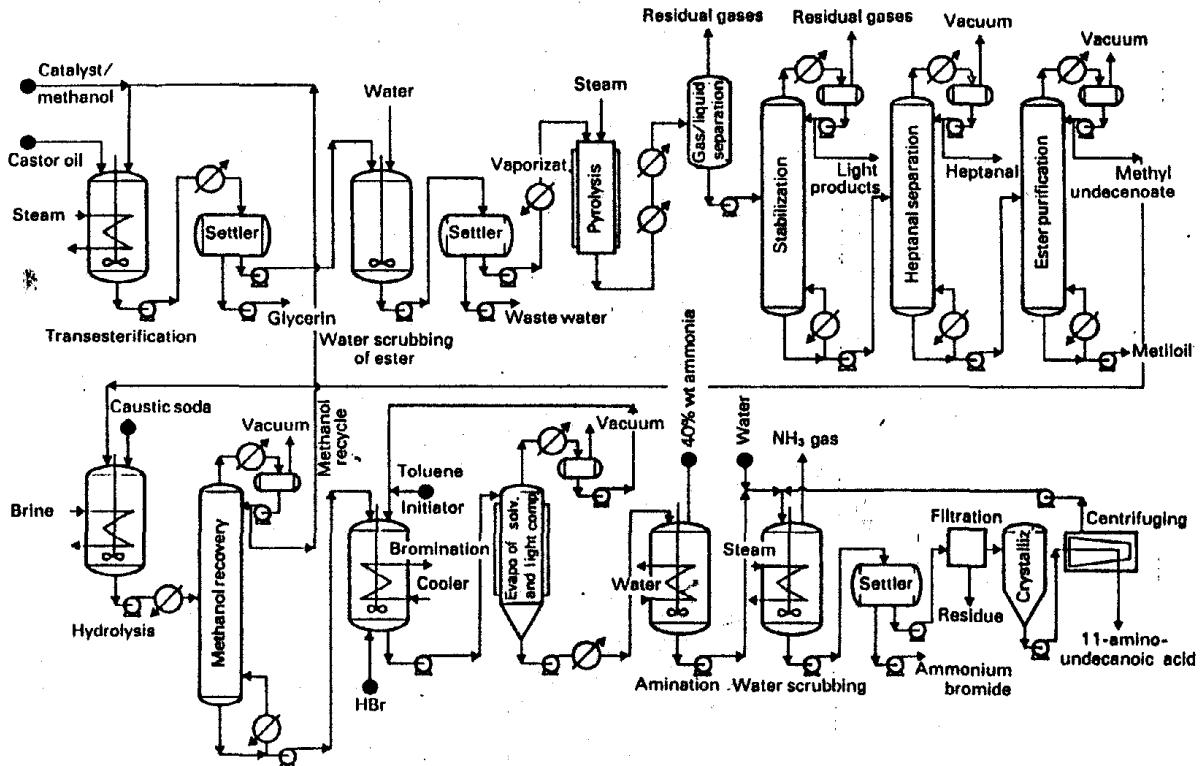
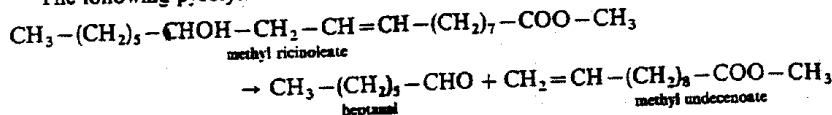


Fig. 12.17. Production of 11-aminoundecanoic acid. ATO process.

12.3.1.2 Pyrolysis of methyl ester

In the pyrolysis stage, the ester, vaporized at 250°C, is mixed with steam at 600°C, in a weight ratio of 1/1. It resides for about 10 s in a furnace, where the temperature lies between 400 and 575°C.

The following pyrolysis reaction takes place:



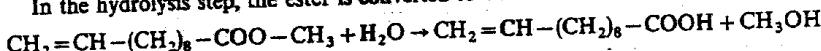
Methyl undecenoate and heptanal (or oenanthol) are formed, as well as light gases and a residue called metiloil, which is a mixture consisting essentially of methyl esters (linoleate, oleate, ricinoleate, stearate, palmitate, etc.) and a few per cent of free fatty acids, saturated and unsaturated, from C₁₄ to C₁₈. Most of the gaseous effluent leaving the furnace is condensed in a series of heat exchangers, where the temperature is lowered to 120°C. Water is separated by settling.

The products formed are fractionated in three successive distillation columns. The first is a stabilization column which removes the dissolved gases at the top. In the second, operating under vacuum, heptanal is collected between 130 and 135°C, at 0.7 kPa absolute. The third column, also operating under vacuum, separates the methyl undecenoate collected at the top and metiloil at the bottom.

Heptaldehyde can be hydrogenated to heptanol or oxidized to heptanoic acid, which can be marketed. The ester cracking yield is up to 75 molar per cent of methyl undecenoate.

12.3.1.3 Hydrolysis of methyl undecenoate

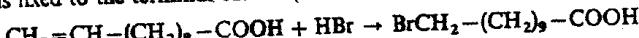
In the hydrolysis step, the ester is converted to undecenoic acid:



The operation takes place around 25°C, in the presence of caustic soda. This reaction is slightly exothermic ($\Delta H_{298}^0 = -15 \text{ kJ/mol}$), and a jacketed reactor is therefore employed, equipped with a coil through which brine circulates. The hydrolysis yield is practically quantitative for a residence time of 30 min. The methanol is recycled and the acid sent to the bromination step.

12.3.1.4 Bromination of undecenoic acid

Bromination is intended to add hydrobromic acid to undecenoic acid, so that the bromine is fixed to the terminal carbon (anti-Markownikoff addition):



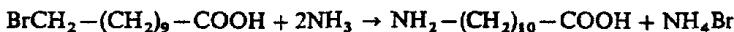
To do this, the conversion takes place in the presence of a solvent (toluene), with a free radical initiator (benzoyl peroxide). Gaseous hydrogen bromide is introduced into the solution. The reaction is fast and highly exothermic. The reactor is cooled by the

passage of a coolant fluid in a double shell, to keep the temperature at 0°C. 11-bromo-undecanoic acid is obtained with a molar yield of 95 per cent. Some 10-bromoundecanoic acid is also formed.

The effluent obtained is not distilled. It is heated under vacuum to evaporate the toluene and the unreacted hydrogen bromide, which are recycled.

12.3.1.5 Amination of 11-bromoundecanoic acid

The bromoacid is sent to the amination step:



This operation takes place at 30°C, in the presence of a large excess of an aqueous solution of 40 per cent ammonia. When the conversion is complete, the mixture formed is sent to a reactor where water is added to it. It is raised to boiling to remove excess ammonia. To produce 100 kg of amino acid in this step, about 3 m³ of reaction volume is required.

The amino acid yield in relation to the bromoacid is 94 molar per cent. The effluent obtained contains about 10 per cent weight of impurities. The hot product, rid of the excess ammonia, is filtered, cooled, crystallized and collected by centrifuging. The only world producer is *ATO Chem.*

12.3.2 Economic data

These are given in Table 12.14.

TABLE 12.14
PRODUCTION OF 11-AMINO UNDECANOIC ACID. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 5,000 t/year

Battery limits investments (10 ⁶ US\$)	15
Consumption per ton of product	
Raw material	
Castor oil (t)	3.50
By-products	
Heptaldehyde (t)	0.85
Glycerol (t)	0.10
Chemicals	
Methanol (kg)	10
Hydrobromic acid (kg)	40
Ammonia (kg)	10
Caustic soda (kg)	100
Utilities	
Steam (t)	4
Electricity (kWh)	250
Cooling water (m ³)	20
Labor (Operators per shift)	12

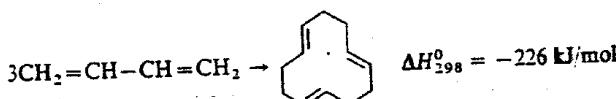
12.4 MANUFACTURE OF NYLON-12. LAUROLACTAM

The properties of nylon-11 and nylon-12 are closely comparable, but nylon-12 is the laurolactam polymer of petrochemical origin. The first step is the trimerization of butadiene to 1,5,9-cyclododecatriene in the presence of Ziegler type catalysts, the second consists of hydrogenation to cyclododecane, and the final step is conversion to lactam, by methods similar to those examined for the production of caprolactam.

12.4.1 Butadiene cyclotrimerization (Fig. 12.18)

Butadiene, pure or in a mixture with other components of the steam-cracked C₄ cut, is diluted in a hydrocarbon solvent (benzene or cyclohexane) and reacts in the trimerization reactor, in the presence of a catalyst previously obtained by the action of TiCl₄ on chlorodiethylaluminum.

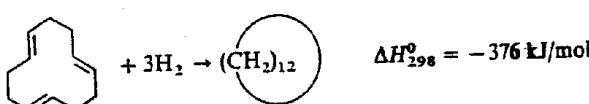
The reaction is highly exothermic:



It yields trans-trans-trans cyclododecatriene (CDT) and also cis-trans-trans CDT. The by-products formed are vinyl cyclohexene, cyclooctadiene (dimers of butadiene) and polybutadiene. The molar trimer yield is 77 per cent for a conversion of 90 per cent. The trimerization effluent is sent to a catalyst deactivation reactor. An alcohol is employed, usually methanol, to deactivate and extract the catalyst. The catalyst residues are removed, and the methanol recycled. The product, rid of the catalyst, is introduced into a column to recover unconverted C₄. Starting with pure butadiene, it is recycled after purging of the light products, or, if not, all the C₄ compounds are removed. Three distillation columns, operating under vacuum (3 to 5 kPa absolute, 15 to 25 trays each) are then used to isolate, in succession, the solvent, which is recycled, the light and heavy compounds, which are used as fuels, and finally the CDT, which leaves at the head of the final separation stage in a purity of over 99.6 per cent weight.

12.4.2 Cyclododecatriene hydrogenation (Fig. 12.18)

The hydrogenation of CDT to cyclododecane is a highly exothermic reaction:



It takes place in the liquid phase, at 200°C, under 1.4 · 10⁶ Pa absolute, in the presence of a nickel catalyst and excess hydrogen. Conversion and selectivity are practically total.

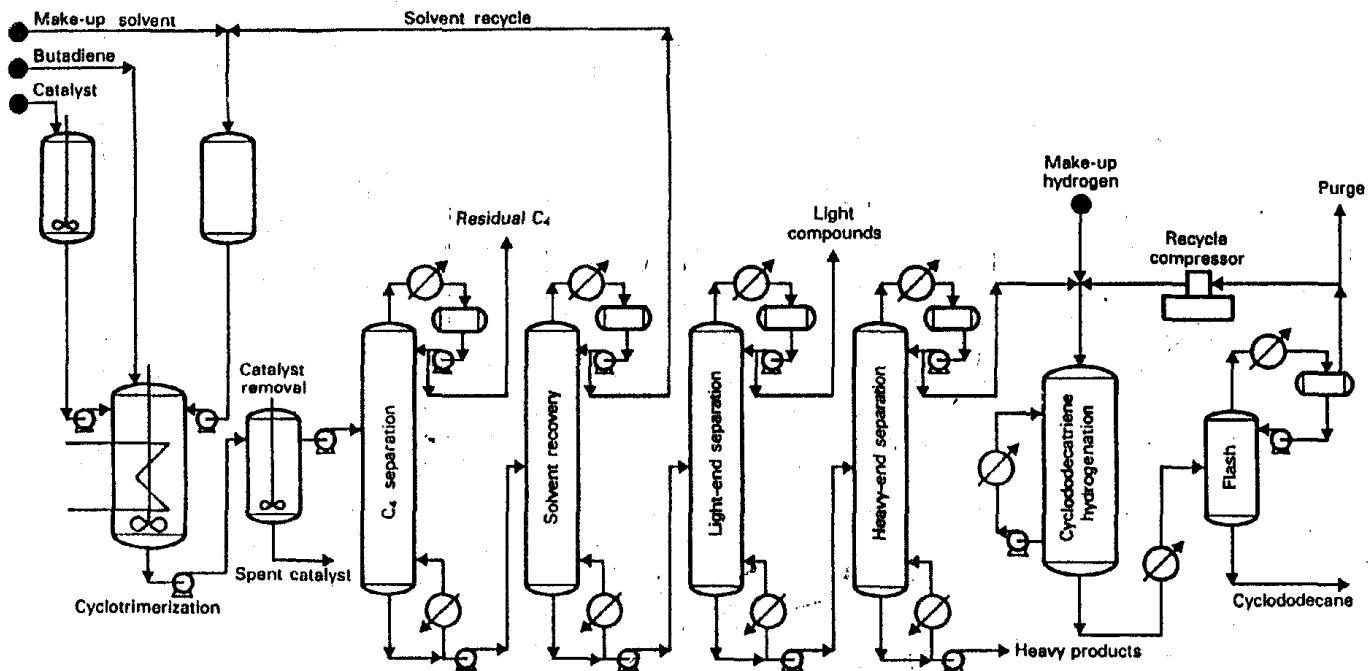


Fig. 12.18. Laurolactam manufacture. Cyclododecane synthesis by cyclotrimerization of butadiene and hydrogenation.

12.4.3 Synthesis of laurolactam

Two methods are currently industrialized, starting with cyclododecane, one by *Chemische Werke Hüls* in West Germany, and the second by *ATO Chem.* in France.

12.4.3.1 Hüls process (Fig. 12.19)

This process uses the same steps as the conventional process for manufacturing caprolactam from cyclohexane: oxidation, oximation of cyclododecanone, Beckmann rearrangement.

A. Cyclododecane oxidation

Cyclododecane is oxidized in the liquid phase, at 150°C, in a series of jacketed and agitated reactors. Air is introduced at the base and the temperature is controlled by circulating water in the outer shell. The operation takes place in the presence of boric acid. For a 7 per cent conversion, a molar yield of 92 per cent is obtained for cyclododecanol and cyclododecanone. The effluent from the final reactor is sent to a mixer, where the boric esters are hydrolysed, and then to a settler. Boric acid goes into solution in the aqueous phase, which is concentrated and subjected to crystallization. The acid recovered is centrifuged, dried, and then replaced in solution for recycling. The organic phase is washed with caustic soda and then with water. The first distillation column operating under vacuum (3 kPa, 60 trays) separates unconverted cyclododecane at the top, which is recycled. A second column (3 kPa, 10 to 15 trays) separates the heavy compounds and a residue at the bottom, with cyclododecanol recovered at the top, and sent to a dehydrogenation reactor.

B. Cyclododecanol dehydrogenation

Cyclododecanol is dehydrogenated to cyclododecanone around 200°C, in the liquid phase, in the presence of a catalyst consisting of copper on alumina. For a 75 per cent conversion, cyclododecanol selectivity is 98 molar per cent. The reactor effluent is first rid of the hydrogen formed by flash and fractionated in two successive light-ends and heavy-ends separation columns (7 kPa absolute, 25 to 30 trays each).

C. Cyclododecanone oximation

The oxime is obtained by the action of hydroxylamine hydrogen sulfate on cyclododecanone. This operation takes place in a solvent that is immiscible with water or with concentrated sulfuric acid, which are used in the next step. The most widely used solvent is isopropylcyclohexane (or hydrocumene) which dissolves the oxime at the reaction temperature of 100°C. Conversion is practically quantitative. It takes place in a series of reactors equipped with effective agitators, into which aqueous solutions of hydroxylamine sulfate are introduced, together with ammonia to keep the pH about 7. The effluent is cooled and settled. The aqueous layer containing ammonium sulfate is removed. The organic phase is washed with concentrated sulfuric acid. The oxime sulfate solution

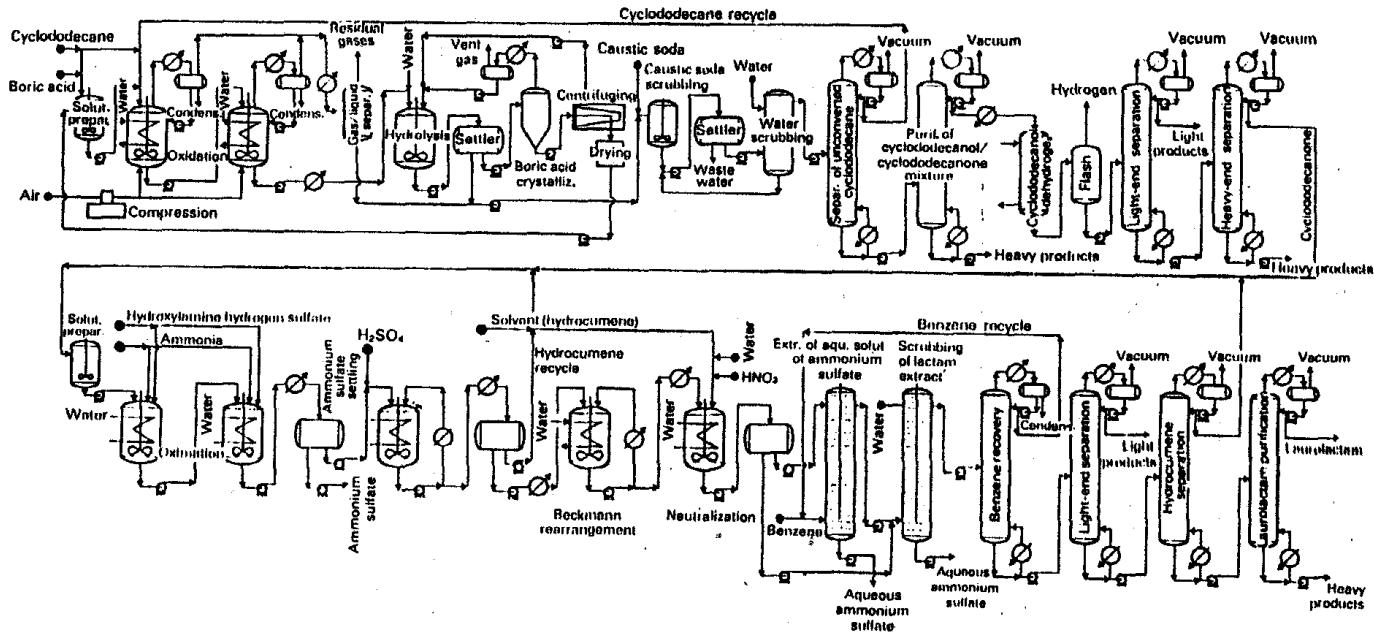


Fig. 12.19. Laurolactam production from cyclododecane. Hüls process.

obtained is then itself settled. The supernatant hydrocumene is collected and recycled, and the oxime sulfate solution is sent for the rearrangement reaction.

D. Beckmann rearrangement

This operation takes place in jacketed agitated reactors, operating at 110°C, in the presence of sulfuric acid. Conversion is practically quantitative with a molar yield of 92 per cent. The rearrangement product is then neutralized by ammonia in the presence of hydrocumene to favor the subsequent settling. The aqueous ammonium sulfate solution which appears is extracted with benzene to recover the lactam it contains. This lactam, which constitutes the bulk of the organic phase, is washed with water. The benzene is recovered (15 trays) and recycled. Final purification comprises a series of three distillation columns operating under high vacuum, and separating at the top, in succession, light compounds, hydrocumene and laurolactam to commercial specifications.

12.4.3.2 ATO Chem. process

In the ATO Chem. process, the cyclododecanone oxime is obtained directly from cyclododecane by photonitroization, in the same way as in the Toray PNC process for manufacturing caprolactam. The oxime hydrochloride is formed, and then undergoes the Beckmann rearrangement as in the Hüls process.

Nitrosyl chloride is formed *in situ* in the photonitroization reactor, by the reaction of hydrochloric acid with nitrosyl sulfuric acid. A 20 per cent weight solution of cyclododecane in carbon tetrachloride is introduced into the reaction system, with another solution containing 75 per cent weight of nitrosyl sulfuric acid in 85 per cent weight sulfuric acid, as well as hydrogen chloride gas. The mixture is irradiated at 15°C by mercury vapor lamps employing chromium, yttrium or holmium iodide to filter the low-wavelength radiation and to emit between 400 and 575 nm (nanometers). The elimination of 300 to 400 nm radiation has the effect of limiting tar deposits on the outer surface of the lamps. These detrimental by-products are also minimized by limiting the lamp temperature to a maximum of 70°C. A 10,000 t/year unit uses forty-six 60 kW lamps cooled by water circulation in a double wall.

The oxime, in the form of the hydrochloride, accumulates in the aqueous phase as it is formed. This product is continuously pumped to a separator, from where it is sent directly to the Beckman rearrangement reactor. Lamp consumption is 2.2 kWh/kg of laurolactam produced. For a once-through conversion of 68 per cent cyclododecane, molar selectivity of oxime is 88 per cent.

12.4.4 Other industrial methods for manufacturing laurolactam

12.4.4.1 SNIA Viscosa processes

The process originally proposed by *SNIA Viscosa* starts with cyclododecatriene converted selectively to mono-ozonide by the action of ozone at 20°C in a system of solvents which extracts the ozonide formed as soon as it appears in the medium, thus preventing the formation of polyozonides.

In a second step, the ozonide is decomposed at 30°C, in the presence of sodium or pyridinium acetate, under inert atmosphere, to unsaturated ω -aldehyde acid, with the following formula:



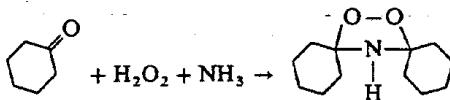
Ammonia is then caused to react with the aldehyde acid at between 15 and 20°C. The ammonium salt of the amino acid obtained is converted to the sodium salt and hydrogenated in an aqueous solution around 100°C, on a nickel/palladium catalyst which yields the saturated amino acid: aminododecanoic acid ($\text{NH}_2-(\text{CH}_2)_{11}-\text{COOH}$), a monomer of nylon-12, like laurolactam.

Another process also proposed by SNIA Viscosa is based on the technique employed by this company to manufacture caprolactam from toluene. It comprises the following steps:

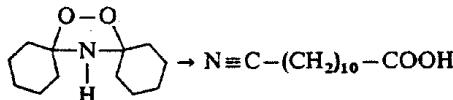
- Selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene.
- Hydroformylation of cyclododecene to the corresponding aldehyde,
- Air oxidation of this aldehyde to cyclododecane-carboxylic acid.
- Action of nitrosyl sulfuric acid on cyclododecane carboxylic acid in the presence of oleum, with the formation of the oxime, which is converted to laurolactam without being isolated.

12.4.4.2 Ube process

Ube proposes a totally different process from the above, starting with cyclohexanone. In the first step, cyclohexanone is converted to 1,1'-peroxydicyclohexylamine by the action of hydrogen peroxide and ammonia, in the presence of the ammonium salt of an organic acid and a peroxide stabilizer (zinc and nickel salt of ethylene diamine tetracetic acid):



In a second sequence, the peroxide obtained in the first step is pyrolysed at 500°C in the presence of steam:



11-cyanoundecanoic acid is formed with a molar selectivity of 60 per cent. The two main by-products of pyrolysis are cyclohexanone, which is recycled to the first step, and caprolactam. The 11-cyanoundecanoic acid is hydrogenated on a ruthenium-on-silica catalyst, at about 100°C and $4.5 \cdot 10^6$ Pa absolute. 12-aminododecanoic acid is obtained:



Laurolactam is manufactured by *Hüls* in West Germany (12,000 t/year), by *ATO Chem.* in France (8,000 t/year) and by *Daicel* in Japan (1,800 t/year).

12.4.5 Economic data

Table 12.15 lists some economic data concerning the processes for manufacturing laurolactam by the oximation of cyclododecanone and by the photonitroization of cyclo-dodecane.

TABLE 12.15
LAUROLACTAM PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 10,000 t/year

Process	Passage through cyclododecanone	Photonitroization
Typical technology	Hüls	ATO
Battery limits investments (10^6 US\$)	18	20
Consumption per ton of laurolactam		
Raw material		
Cyclododecane (t)	1.20	1.05
Chemicals		
Ammonia (t)	0.45	0.60
Caustic soda (50%) (t)	0.30	0.10
Sulfuric acid/oleum (t)	1.25	1.45
Hydrochloric acid (kg)	—	25
Boric acid (kg)	70	—
Hydroxylamine sulfate (t)	0.45	—
Emulsifier (kg)	50	—
Miscellaneous and catalysts (US\$)	30	20
By-product		
Ammonium sulfate (t)	1.65	1.90
Utilities		
Steam (t)	10	5
Electricity (kWh)	270	2,800
Fuel (10^6 kJ)	2.3	5.3
Cooling water (m^3)	40	210
Process water (m^3)	100	10
Labor (Operators per shift)	15	20

Chapter 13

MONOMERS FOR POLYESTER SYNTHESIS

Polyesters are polycondensation products of a diacid with a diol. A distinction is made between polyesters for fibers and polyester resins. Of the former, polyethylene terephthalate, the polycondensation product of terephthalic acid (or its methyl ester) and ethylene glycol, accounts for most of the fiber polyesters currently commercialized (Dacron, Tergal, Terlenka, Terylene, Trevira,...). As for the resins, a distinction is made between saturated polyesters employed in films (Mylar, Melinex,...) and injection molding and thermosetting unsaturated polyesters, whose essential markets are coatings and castings.

Apart from terephthalic acid already mentioned, the saturated diacids used include orthophthalic acid (in anhydride form) and adipic acid. The main unsaturated diacids are maleic acid (in anhydride form) and fumaric acid. As for diols, ethylene glycol is the most widely used, followed by 1,4-butanediol employed to manufacture a new polyester resin by injection molding, polybutylene terephthalate (PBT), which has been developed since 1970, and 1,4-dimethylolcyclohexane ($\text{HOCH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2\text{OH}$) which, with terephthalic acid, is used to manufacture the fibers Kodel and Vestan. Since ethylene glycol has been discussed in Section 7.3, only the latter two diols will be dealt with here.

13.1 DIMETHYL TEREPHTHALATE AND TEREPHTHALIC ACID

In most applications, and especially in the field of fibers, monomer purity is an essential factor in polymer quality. This is why dimethyl terephthalate is used in preference to the acid, which is more difficult to purify. Terephthalic acid ($d_{400}^{20} = 1.510$)⁽¹⁾ does not melt but sublimes at 300°C under 101.3 kPa absolute. It is also practically insoluble in water and in most organic solvents. However, dimethyl terephthalate ($d_{400}^{25} = 1.283$)⁽²⁾ melts at

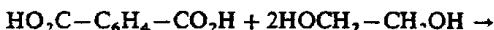
(1) Specific gravity, 68.0/39.2

(2) Specific gravity, 77.0/39.2

141°C and boils at 284°C, at atmospheric pressure. It is soluble in ether and hot methyl alcohol, and can be purified by crystallization or distillation.

However, the use of the methyl ester introduces additional constraints at the time of polycondensation (methanol recovery). This is why terephthalic acid purification processes have been developed in the past twenty years (*Amoco, Mobil, Mitsubishi, etc.*) to enable the direct use of the free acid.

One expedient designed to obtain a "fiber-grade" product consists in preparing the prepolymer, bis hydroxyethyl terephthalate, also called *Bishet*, and purifying it. The prepolymer is obtained by the reaction of two moles of glycol with one mole of acid:



Purification is relatively easy, because *Bishet* is soluble in water at 80 to 90°C and in various organic solvents. It melts at 110°C. However, if the terephthalic acid is very impure, supplementary purification treatment becomes necessary. This process, proposed by *Nippon Soda*, has not yet seen commercial development.

The most widespread industrial method to manufacture terephthalic acid and dimethyl terephthalate is based on the oxidation of *p*-xylene. Many attempts have been made to diversify the feedstocks and to reduce the influence of material cost in the final product cost; particularly by converting *o*-xylene and toluene. However, these methods remain limited owing to their complexity and the lack of selectivity.

13.1.1 Production of dimethyl terephthalate and terephthalic acid from *p*-xylene

13.1.1.1 Nitric oxidation of *p*-xylene

This was the first industrial process to manufacture terephthalic acid. It employs the liquid phase oxidation of *p*-xylene by nitric acid at 165°C and $1 \cdot 10^6$ Pa absolute, by the following overall reaction:



$$\Delta H_{298}^{\circ} \cong 750 \text{ kJ/mol}$$

The terephthalic acid formed, which is insoluble, is separated from the reaction medium by precipitation and centrifuging. After drying, it is esterified by methanol at 150°C in the presence of sulfuric acid catalyst. The total yield is 90 molar per cent, but the presence of nitrogen compounds makes purification difficult, and the recovery of nitrogen oxides seriously encumbers the economics of the system. This process, industrialized by *Du Pont*, was abandoned in the early 1970s.

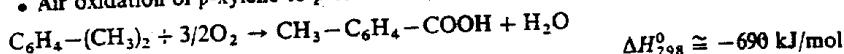
13.1.1.2 Witten process

A. Principle

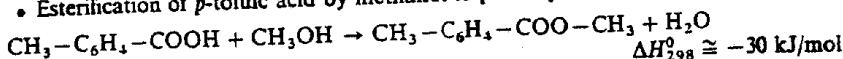
While the oxidation of a methyl group of *p*-xylene with the formation of *p*-toluic acid is easy, the oxidation of the remaining methyl group is more difficult. In the Witten

process, developed by *Dynamit Nobel* and *Hercules*, based on the synthesis conceived by *Katzschmann*, operations theoretically take place in four alternate oxidation and esterification phases:

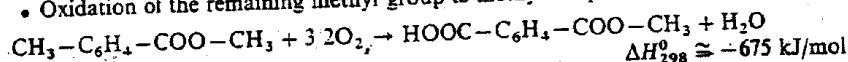
- Air oxidation of *p*-xylene to *p*-toluic acid:



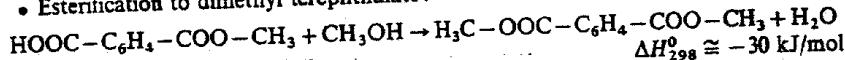
- Esterification of *p*-toluic acid by methanol to *p*-methyl toluate:



- Oxidation of the remaining methyl group to methyl terephthalate:



- Esterification to dimethyl terephthalate:



B. Industrial manufacture (Fig. 13.1)

Only three reaction sections are distinguished in practice, oxidation, esterification and purification:

- Oxidation. The reactors, placed in series, are fed with catalyst (cobalt naphthenate), fresh and recycled *p*-xylene, and methyl *p*-toluate. Air is introduced at the bottom. The operation takes place at a pressure between 0.4 and $0.7 \cdot 10^6 \text{ Pa}$ absolute and a temperature between 140 and 170°C, kept at this level by the vaporization of excess *p*-xylene to remove the heat generated.

- Esterification. The reactors, also placed in series, combine the transformations of toluic acid and methyl hydrogen terephthalate to the corresponding esters. The catalyst, diluted by methanol before its introduction into the reactor, is toluene sulfonic acid. Esterifications take place around 200 to 250°C.

- Purification. The effluent is sent to a series of distillations. The first (30 to 35 trays) separates a methanol/water mixture at the top, which is then sent to a dehydration tower (25 to 30 trays), while the bottom is sent to a column in which the ester is fractionated under partial vacuum (40 to 45 trays). Methyl toluate and excess *p*-xylene leave at the top and are recycled to the oxidation reactor. The withdrawal, consisting of crude terephthalate, is redistilled under vacuum to remove heavy compounds (20 trays), and then sent to a vacuum crystallizer (40 to 50 kPa absolute) using methanol as solvent. This may be followed by a second crystallization, or a countercurrent washing with methanol to complete the purification. The dimethyl terephthalate is finally centrifuged, melted to remove residual methanol, and vacuum distilled (30 trays). The molar yield of the operation in relation to *p*-xylene is about 87 per cent.

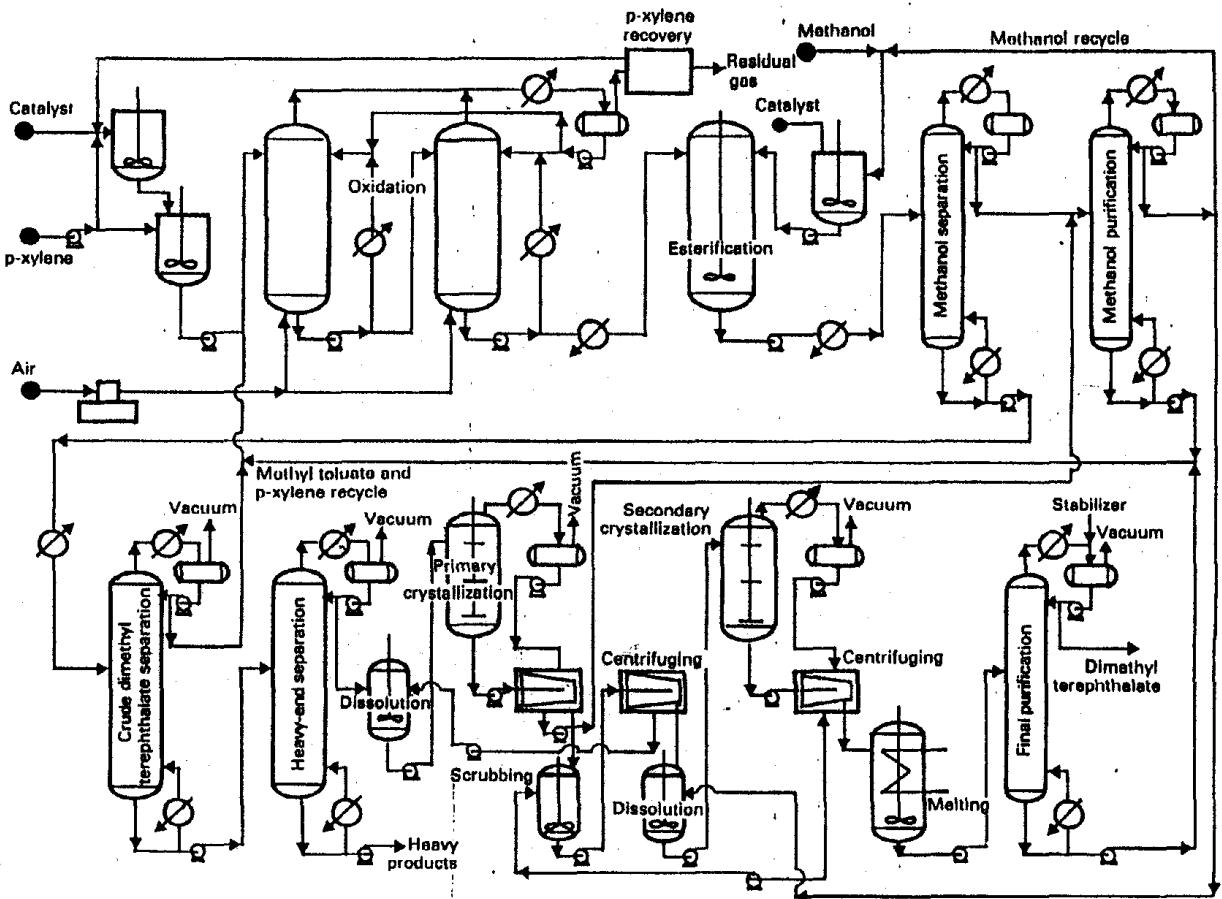


Fig. 13.1. Dimethyl terephthalate production from *p*-xylene by successive oxidations and esterifications. Witten process.

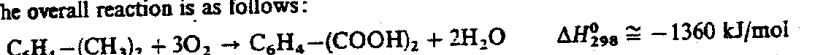
Other processes for manufacturing dimethyl terephthalate pass through the intermediate of free terephthalic acid (*Amoco, Du Pont, Eastman Kodak, ICI (Imperial Chemical Industries), Mitsubishi, Mitsui, Petrochemicals, Toray, etc.*) which is esterified around 250 to 300°C, in the presence of catalysts based on **antimony, tin, molybdenum, zinc, etc.**, with molar yields of 96 per cent and complete conversion, provided that water is removed as soon as it is formed.

13.1.1.3 Amoco process

This process produces fiber-grade terephthalic acid directly by the oxidation of *p*-xylene. It was developed originally by *Mid Century Corporation*, and the first plant went on stream in the United States in 1958. Since then, this technology has become the most widespread industrial process for the manufacture of terephthalic acid.

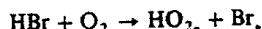
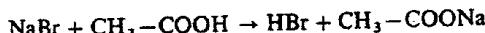
A. Principle

p-xylene is oxidized in solution in acetic acid, by air, at about 175 to 230°C (200°C), and between 1.5 and $3 \cdot 10^6$ Pa absolute. The catalyst system includes the catalyst itself (cobalt and manganese acetates) and an initiator containing bromine (sodium bromide). The overall reaction is as follows:

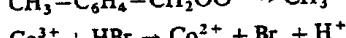
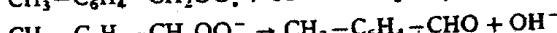
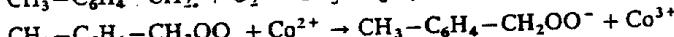
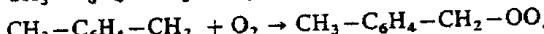
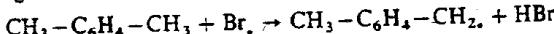


It is the result of a chain reaction mechanism culminating in the production of aldehyde, which can then be oxidized very rapidly to the acid, and which takes place as follows, according to a generally accepted but far from definitive interpretation:

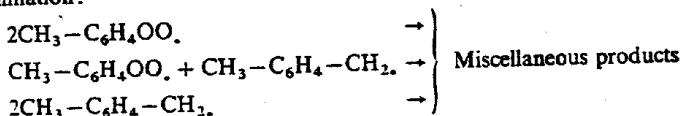
- Initiation:



- Propagation:



- Termination:



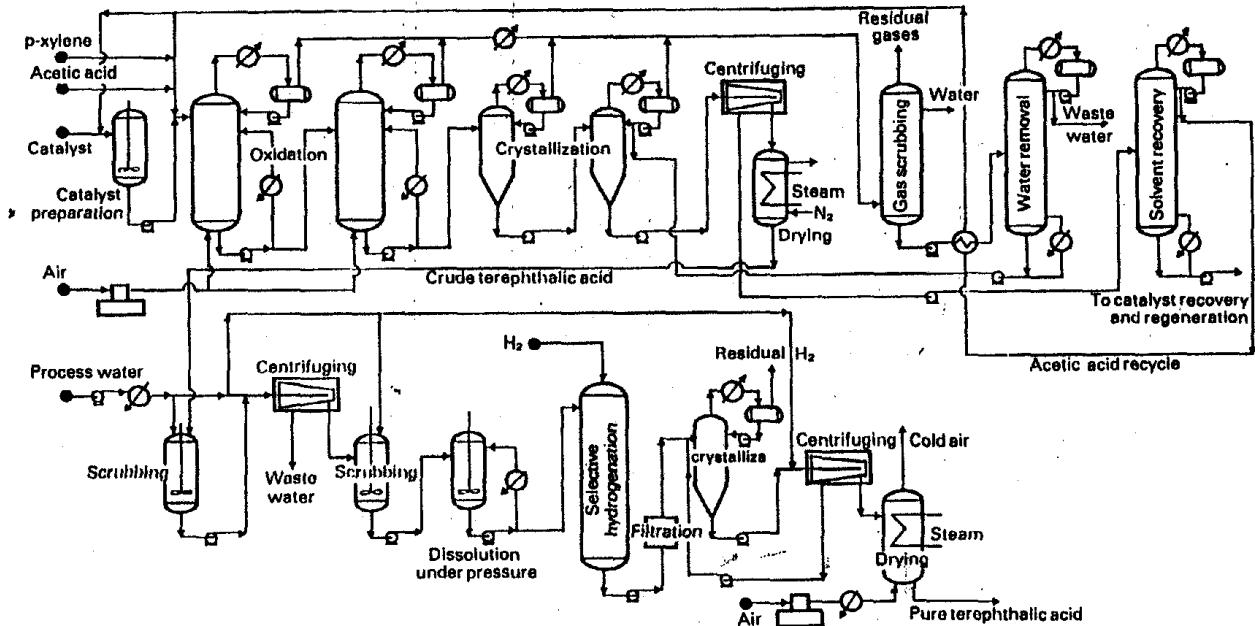


Fig. 13.2. Production of pure terephthalic acid by *p*-xylene oxidation. Amoco process.

B. Industrial manufacture (Fig. 13.2)

The installation includes the following sections:

- A reaction section, where operations are conducted in a reactor fed in descending stream with a mixture of *p*-xylene, acetic acid and catalyst solution prepared in a separate device. The reaction medium is agitated by the introduction of air at the bottom. The corrosive action of bromine and organic acids on carbon steels makes it necessary to use special stainless materials (Hastelloy C), both for the reactor and for certain parts of the equipment, particularly the heat recovery system. The temperature and oxygen content of the reaction medium must be carefully controlled to prevent the formation of undesirable side products. The heat of reaction is removed by vaporization of part of the reaction medium (acetic acid, *p*-xylene and water), and by condensation and reflux to the reactor. Residence time is about one hour, and the yield is up to 95 molar per cent.
- A crude terephthalic acid recovery and purification section. The reactor effluent is sent to a first crystallizer operating around 180°C, at between 0.5 and $0.7 \cdot 10^6$ Pa absolute, in which cooling is provided by the partial vaporization of acetic acid, unoxidized *p*-xylene and the water formed, a mixture which, after condensation, is fractionated by distillation (40 to 45 trays) to recycle the hydrocarbon and solvent to the reactor. It is cooled further in a second crystallizer operating at atmospheric pressure, around 110°C, also with partial vaporization of the medium. The suspension is then centrifuged and the crude terephthalic acid sent to the purification stage, while the acetic acid contained in the mother liquor is recovered by distillation (20 trays) and recycled. At this stage, the product purity is about 99.5 per cent weight.

The impurities it contains are aromatic acids resulting from the oxidation of *p*-xylene (*p*-toluic acid) and other aromatics in the feed (benzoic, isophthalic, *o*-toluic acids), aldehydes and ketones, but, above all, 4-carboxybenzaldehyde, which is responsible for the coloring of the polymers obtained from terephthalic acid by the chelation of metallic traces. The carboxybenzaldehyde content is higher with a lower oxidation temperature and with a lower oxygen content in the medium. This content, about 2000 ppm, is too high to allow direct polymerization, and it must not exceed 50 ppm. It can be reduced by catalytic hydrogenation. To achieve this, the crude acid is placed in suspension in water at 95°C, centrifuged, replaced in suspension in hot water, and sent to a dissolution tank raised to 250°C, at $4 \cdot 10^6$ Pa absolute.

The aqueous solution is sent to the hydrogenation reactor, operating in the same conditions in the presence of a catalyst bed of palladium on activated charcoal, and fed with a slight stream of hydrogen. The hydrogenated product is centrifuged, washed with water, and dried with air.

Another important parameter affecting the final purity of the product, and the energy expenditures involved to meet specifications, is the particle diameter of the crude terephthalic acid, usually about 150 μ . The influence of impurities resulting from the wetting of the crystals by the mother liquor is greater with smaller particle diameter.

13.1.1.4 Other techniques for the direct oxidation of *p*-xylene

The Maruzen Oil process operates in similar conditions to those of the Amoco process, so far as the solvent and catalyst are concerned. The temperature and pressure are

slightly lower, but the essential difference is in the design of the oxidation reactor. The Maruzen process uses an agitated reactor in which the *p*-xylene is introduced at three different levels. Furthermore, the recovery section features two and even three crystallizers. The first, smaller than the others, operates in the presence of air, resulting in supplementary oxidation which reduces the carboxybenzaldehyde content to about 200 ppm. These modifications made to the Amoco process, together with strict control of the operating conditions, serve to produce a medium-grade terephthalic acid without the need for purification by hydrogenation. This grade of terephthalic acid is acceptable for fibers, but generally unacceptable for films.

The remaining techniques proposed include:

- (a) The IFP (*Institut Français du Pétrole*) process operating by a technique similar to the one developed by Amoco, but in more moderate conditions (180°C, $1 \cdot 10^6$ Pa absolute).
- (b) The Toray process in which *p*-xylene oxidation is induced by that of the para-dehyde, which is easily oxidizable and generates hydroperoxide.
- (c) The Eastman Kodak process based on the same principle, but employing acetaldehyde as the oxidation initiator.
- (d) The Mobil process which uses a ketone, methyl ethyl ketone; this process was industrialized but abandoned in 1975.
- (e) The Teijin process uses an Amoco-type technique, but employs a large quantity of catalyst (20 to 100 per cent of *p*-xylene weight): after recovery, catalyst consumption does not exceed 1 per thousand.

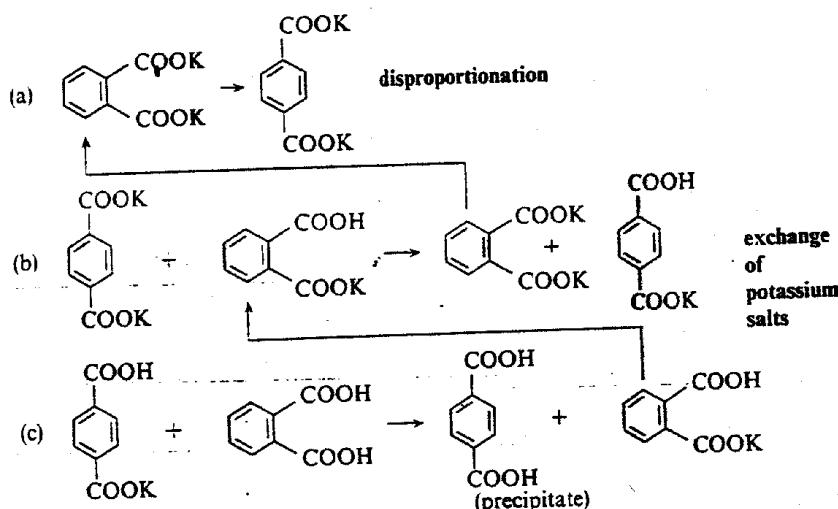
13.1.1.5 Other techniques for *p*-xylene conversion

The Lummus process converts *p*-xylene to terephthalic acid in a first step by ammonoxidation in the presence of a V_2O_5/Al_2O_3 -based catalyst. Terephthalic nitrile is converted to terephthalic acid in three steps. It is first hydrolysed by steam to form ammonium hydrogen terephthalate, and this salt is then pyrolysed to the diacid. The third step consists of a second hydrolysis to convert the amide which may have been formed in the trace state to the acid. This technique, which could be considered as a promising one, in so far as it allowed the production of fiber-grade terephthalic acid without special purification, has not yet enjoyed any industrial development.

13.1.2 Production of terephthalic acid from *o*-xylene, Henkel 1 process

This method is based on the potassium salts isomerization of phthalic acids. Developed to the industrial stage by Teijin and Kawasaki in Japan, it employs phthalic anhydride or its precursor, *o*-xylene, as the raw material. If the raw material is phthalic anhydride, the essential step is the potassium salts isomerization of phthalic acids. This reaction, conducted under carbon dioxide pressure at $2 \cdot 10^6$ Pa absolute and 400°C, in the presence of cadmium salts as catalyst, is followed by exchange reactions of the potassium salts.

During this operation, terephthalic acid can be isolated by crystallization, while the salts of the remaining isomeric acids are recycled to the isomerization step. The transformation scheme can be summarized as follows:



The operation is more complex in practice, and the balanced character of the isomerization and the presence of monopotassium salts of the different acids must be taken into account. The yield from phthalic anhydride is greater than 90 molar per cent. In principle, the same transformations can also be conducted from isophthalic acid.

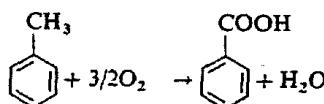
To obtain the total yield in relation to *o*-xylene, it is necessary to consider that of the phthalic anhydride production step, which barely exceeds 65 to 70 molar per cent in the gas phase oxidation (Von Heyden type reactor). At present, no industrial plant employs this process, which is uneconomical in comparison with other methods, given the lack of selectivity of the *o*-xylene conversion step.

13.1.3 Production of terephthalic acid from toluene

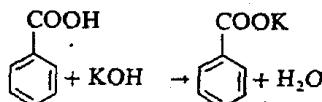
13.1.3.1 Henkel 2 process

Developed in Germany during the Second World War, this process was used in Japan by Mitsubishi in a 25,000 t/year plant, shut down in 1976. It is based on the disproportionation reaction of benzoic acid to terephthalic acid and benzene. Starting with toluene, it involves the following reactions:

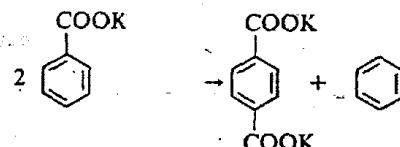
- Oxidation:



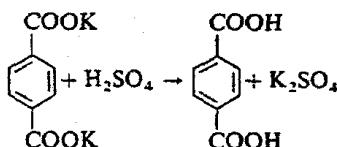
- Neutralization:



- Disproportionation:



- Acidification:



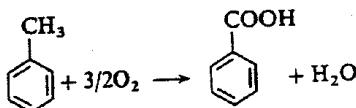
Toluene is oxidized in the liquid phase in the presence of a soluble cobalt-based catalyst. The neutralization of benzoic acid by potash yields insoluble potassium benzoate, which is separated by centrifuging. The disproportionation of potassium benzoate takes place between 400 and 430°C, under CO₂ pressure ranging from 1.5 to 3 · 10⁶ Pa absolute, in the presence of a catalyst consisting of cadmium or zinc oxides. The reaction takes place in the solid phase. Terephthalic acid is released from its salt by the action of sulfuric acid.

The industrial implementation of this process faces many difficulties, among which the most important appears to be the frequent clogging of the installation, due to the progress of the disproportionation reaction in a heterogeneous phase. This conversion is also unselective and does not allow high reaction rates. Another difficulty is the production of large amounts of potassium sulfate.

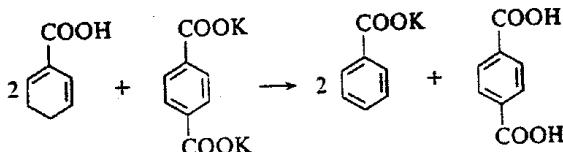
13.1.3.2 PRP process

Developed jointly by *Phillips Petroleum* and *Rhône-Poulenc* (PRP), this is a modification of the Henkel 2 process, using benzoic acid instead of sulfuric acid to liberate the potassium terephthalate from its salt. It conducts the disproportionation reaction of potassium benzoate in suspension in an organic dispersant, consisting of a mixture of terphenyls, in the presence of zinc oxide as catalyst. The three steps of the process are illustrated below:

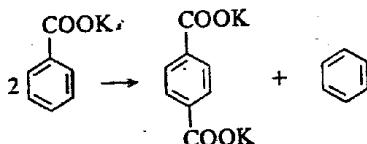
- Toluene oxidation (see Section 10.1.5.1):



- Metathesis:



- Disproportionation:



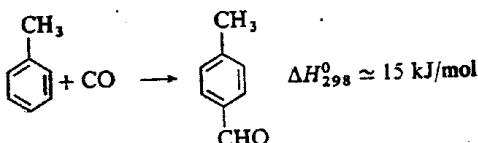
The metathesis and catalyst regeneration reaction (conversion of zinc benzoate to zinc oxide) takes place in the aqueous phase between 130 and 160°C. The disproportionation reaction takes place between 400 and 480°C, under CO_2 pressure of $5.5 \cdot 10^6 \text{ Pa absolute}$, in the presence of terphenyls.

The molar selectivity of terephthalic acid in the metathesis reaction is 97 per cent for a once-through conversion of potassium terephthalate of about 85 per cent. The potassium terephthalate molar selectivity of the disproportionation reaction is 85 per cent for a conversion of 90 per cent. This process, despite the improvements made to the Henkel 2 technology, and the value it offers by starting with toluene, which is cheaper than *p*-xylene, and co-production of easily marketable benzene, has nevertheless not yet been employed industrially.

13.1.3.3 Mitsubishi process

This is based on the Gatterman/Koch reaction, which consists in carbonylating toluene to *p*-toluic aldehyde, and then oxidizing the latter to terephthalic acid.

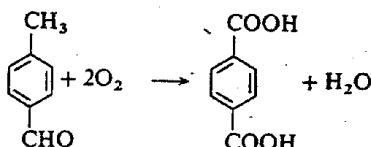
Toluene carbonylation corresponds to the following reaction:



It takes place at 0°C, under $1.5 \cdot 10^6 \text{ Pa absolute}$, in the presence of boron trifluoride BF_3 and hydrochloric acid HF , in the proportion of one mole of BF_3 and five moles

of HF per mole of toluene. The toluene/HBF₄ complex is first formed at low temperature (-25°C), using only half of the BF₃ required. It is heated to 0°C to form the *p*-toluic aldehyde/HBF₄ complex. The remainder of the BF₃ is added and the reaction completed. Some orthotoluic aldehyde is also formed. Molar selectivity for a once-through conversion of 90 per cent is 98 per cent for *p*-toluic aldehyde and 2 per cent for the ortho product. No meta isomer is formed.

The toluic aldehyde/HBF₄ complex is then decomposed by heating between 130 and 180°C in the presence of a solvent (benzene). The BF₃, HF and unconverted toluene are recovered and recycled. The *o*- and *p*-toluic aldehydes are separated by crystallization. Purified *p*-toluic aldehyde is air-oxidized (in solution in acetic acid) in the presence of manganese acetate, cobalt acetate and sodium bromide, by the technique employed for *p*-xylene. This takes place around 200°C , at $2 \cdot 10^6 \text{ Pa absolute}$:



This process is currently being developed in a 2000 t/year pilot plant at Mizushima in Japan.

13.1.4 Production of terephthalic acid from coal

The highly aromatic character of certain bituminous coals, with a C/H ratio of about 0.8, may offer an interesting source of benzene-carboxylic acids by oxidative cracking. In the presence of potassium salts, these aromatic acids are largely converted to diacids, essentially in the para position.

The process, recently proposed by *Occidental Research Corporation*, consists in oxidizing a bituminous coal in the presence of potassium acetate and water, in a weight ratio of 1/3.3/10, by oxygen at 260°C , at $10 \cdot 10^6 \text{ Pa absolute}$, with residence time of 30 min. The CO₂ formed is removed continuously and replaced by oxygen. The effluent collected after the reaction is rid of the free acetic acid it contains and the remaining product is mixed with cadmium iodide (6 per cent weight of coal employed). The mixture is heated to 400°C in the presence of CO₂, at $4 \cdot 10^6 \text{ Pa absolute}$, with a residence time of 2.5 hours. This operation has the effect of converting the ortho potassium salts to para potassium salts by isomerization, and potassium benzoate to potassium terephthalate by disproportionation.

After a number of separation operations, terephthalic acid is obtained with a weight yield of 34 per cent in relation to the coal feed. The acetic acid collected is neutralized by potassium carbonate and recycled. The process, which is unselective for terephthalic acid, is not economical today, but offers an interesting possibility for the use of coal in the future.

TABLE 13.1
PRODUCTION OF TEREPHTHALIC ACID AND DIMETHYL TEREPHTHALATE. ECONOMIC DATA.
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/year

Process	<i>p</i> -xylene oxidation			Toluene oxidation
	Terephthalic acid	Dimethyl terephthalate		
Typical technology	Amoco	Witten		Henkel 2
Battery limits investments (10 ⁶ US\$)	83	85		92
Consumption per ton of product				
Raw materials				
<i>p</i> -xylene (t)	0.68	0.63		—
Toluene (t)	—	—		1.35
Methanol (t)	—	0.38		—
By-products				
Benzene (t)	—	—		0.5
Chemical				
Acetic acid (kg)	60	—		—
Utilities				
Steam (t)	2	1.5		15
Electricity (kWh)	700	430		300
Fuel (10 ⁶ kJ)	9	6.5		11
Cooling water (m ³)	220	100		900
Process water (m ³)	0.2	0.1		20
Treated water (m ³)	10	—		—
Nitrogen (Nm ³)	15	—		—
Chemicals and catalysts (USS)	24	16		—
Labor (Operators per shift)	8	7		7

TABLE 13.2
AVERAGE COMMERCIAL SPECIFICATIONS OF TEREPHTHALIC ACID (TPA)
AND OF DIMETHYL TEREPHTHALATE (DMT)

Characteristics	TPA	DMT
Acid equivalent (mg KOH/g)	675±2	0.03 max.
As (ppm) max.	15	—
Metals (ppm) max.	10	—
4-formyl benzoic acid (ppm) max.	25	—
Moisture content (% Wt) max.	0.5	—
Color (Pt. Co) in 5% solution in DMF max.	10	—
Freezing point (°C)	—	140.6
Ester aldehyde (ppm) max.	—	30
Melted color (Pt Co) max.	—	25

TABLE 13.3
DIMETHYLTEREPHTHALATE AND TEREPHTHALIC ACID PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe		United States		Japan	
Product	DMT ⁽¹⁾	PTA ⁽¹⁾	DMT	PTA	DMT	PTA
Uses (% product)						
Polyethylene terephthalate (PET)						
Fibers	67	73	68	78	51	70
Films	10	9	14	5	21	11
Bottle resins			13	15	1	5
Polybutylene terephthalate (PBT)	23	18	3	2	5	14
Miscellaneous ⁽²⁾			2		22.	
Total	100	100	100	100	100	100
Production (10^3 t/year)	945	510	1,510	960	335	740
Capacity (10^3 t/year) ⁽³⁾	1,020	675	1,950	1,350	340	750
Consumption (10^3 t/year)	805	375	1,455	680	360	610

(1) DMT = dimethylterephthalate, PTA = purified terephthalic acid.

(2) Copolymers, specialty fibers and aramid fiber composite (tetraphthaloyl chloride), specialty polyesters....

(3) The worldwide production capacities of DMT and PTA were around 4.7 and $3.9 \cdot 10^6$ t/year in 1984 and approximately the same in 1986, with the following distribution (DMT/PTA):

United States	1.95/1.33	Western Europe	1.02/0.68	Middle East	0.06/-
Canada	~ / -	Eastern Europe	> 0.80 / > 0.10 ^(a)	Japan	0.39/0.75
Latin America	0.31/0.33	Africa	- / -	Asia and Far East ..	0.21/0.67

(a) A 115,000 t/year purified terephthalic acid plant will be built at Kursk in the USSR in the near future.

13.1.5 Economic data

Table 13.1 provides an order of magnitude of capital expenditures and various consumptions per ton of product for the main types of process to manufacture dimethyl terephthalate and fiber-grade terephthalic acid.

13.1.6 Uses and producers

Table 13.2 lists the average commercial specifications of terephthalic acid and dimethyl terephthalate used to manufacture fibers. Terephthalic acid and its methyl ester are utilized chiefly in the form of ethylene glycol polyester for fibers, films and resins. They are also used in the manufacture of polyesters of butylene glycol (PBT). Among the various applications is the manufacture of additives for lubricants, plasticizers and adhesives. Uses in Western Europe, the United States and Japan in 1984 are given in Table 13.3. This table also gives the production capacities of terephthalic acid and dimethyl terephthalate in Western Europe, the United States and Japan in 1984.

13.2 MALEIC ANHYDRIDE

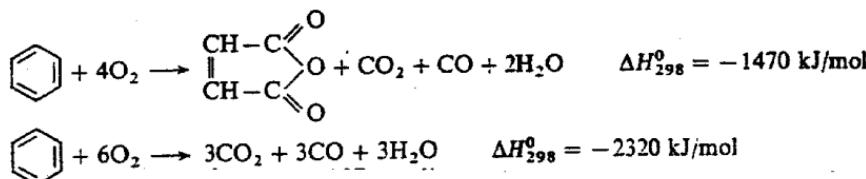
The vapor phase oxidation of benzene, *n*-butane or *n*-butenes offers the most important industrial method for producing maleic anhydride (d_{20}^{20})⁽³⁾ = 1.48, mp = 53°C, bp_{1.013} = 202°C). It is also obtained as a by-product of the manufacture of phthalic anhydride. Among these various raw materials, the oxidation of benzene has, for a long time, been the only commercial method yielding maleic anhydride. The increase in the price of benzene in comparison with that of butane and butenes has favored the latter two products, especially in Western Europe.

Whatever the feed employed, the oxidation processes are characterized by very high exothermicity, requiring costly heat transfer installations and accompanied by considerable production of energy in the form of steam. The lack of selectivity of this type of transformation also leads to the co-production of large amounts of carbon oxides, water and partly-oxidized by-products. Hence the maleic anhydride recovery and purification step is relatively complex.

(3) Specific gravity, 68.0/68.0.

13.2.1 Vapor phase oxidation of benzene

Benzene feedstock currently accounts for less than fifty per cent of world maleic anhydride production capacity. The basic reactions are as follows:



They are highly exothermic, so that once they have begun, the production unit is thermally self-contained and can even produce steam.

13.2.1.1 Halcon process (Scientific Design) (Fig. 13.3)

The benzene concentration in the feed mixture with air must be set outside the flammability limits, which are 1.4 and 7.1 per cent volume at 25°C. Operations are conducted below the lower limit at 1.2 to 1.3 per cent volume. The catalyst, placed in a fixed bed, consists of vanadium pentoxide and molybdenum oxide, deposited on a low surface area support (alumina). It also contains phosphorus pentoxide which stabilizes the catalyst. The reaction takes place between 350 and 400°C, at between 0.1 and $0.2 \cdot 10^6$ Pa absolute, in a multi-tube reactor, cooled by external circulation of a molten salt allowing the production of high-pressure steam. Residence time is about 0.1 s. Once-through conversion of benzene is up to 95 per cent, and the molar selectivity of maleic anhydride is 67 per cent, corresponding to a once-through yield of 64 per cent.

The gaseous effluent leaving the reactor, which contains about 1 per cent volume of maleic anhydride, is cooled by passage through a series of heat exchangers, which preheat the feed and produce low-pressure steam. Final cooling to around 60°C serves to recover nearly 50 per cent of the maleic anhydride directly in liquid form. The gas phase is sent to an absorption tower where the remainder of the anhydride is recovered in acid form by water scrubbing. The residual gases are incinerated to prevent the release of unconverted benzene into the atmosphere. The maleic acid solution is concentrated and dehydrated to the anhydride directly in thin layer evaporators operating under vacuum (60 to 30 kPa absolute), or by means of a water stripping agent (*o*- or *m*-xylene) by heteroazeotropic distillation (20 trays). The maleic anhydride initially condensed and that resulting from the dehydration are combined and distilled under vacuum in two columns, one for light-ends separation (20 kPa absolute) and the second for heavy-ends separation (10 kPa absolute), each with about 20 to 25 trays.

13.2.1.2 Other processes

The other benzene oxidation processes are usually distinguished from the Halcon process by the technique employed to recover and purify maleic anhydride. This applies

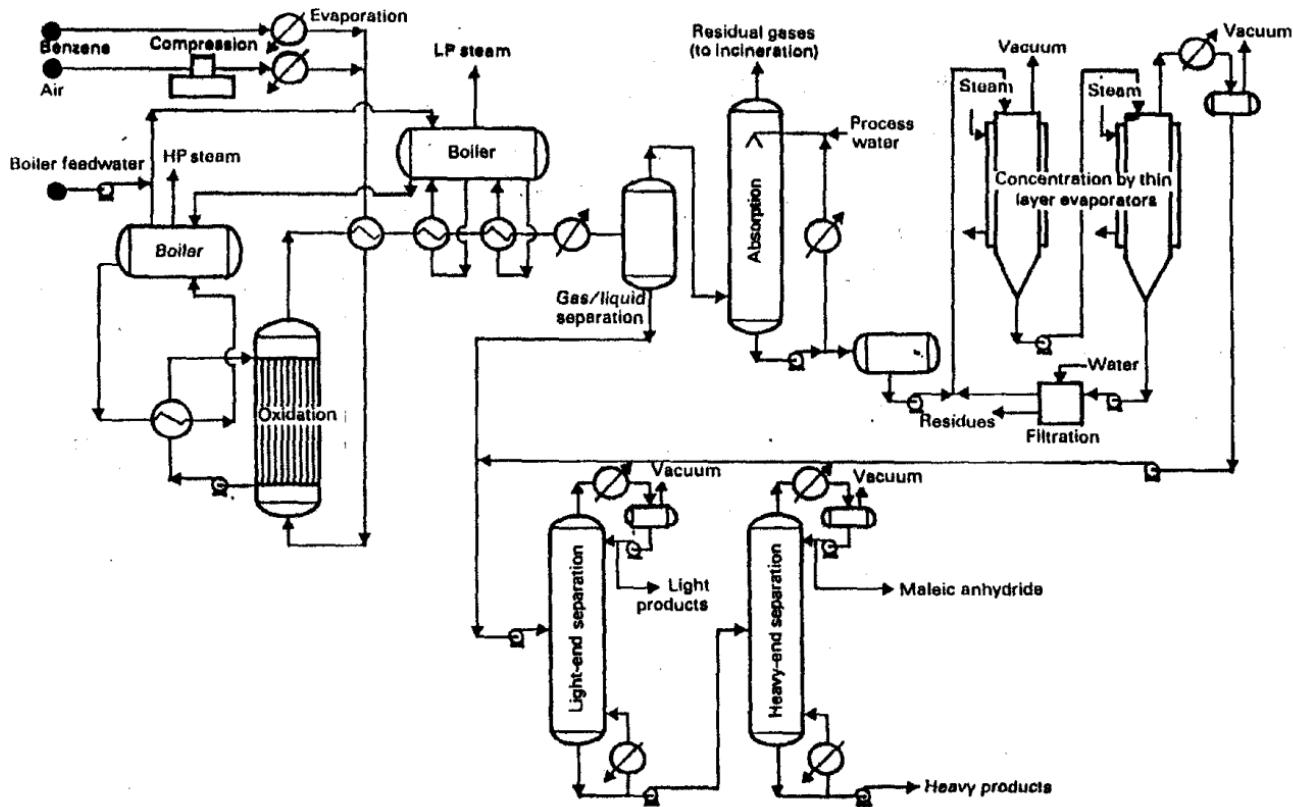


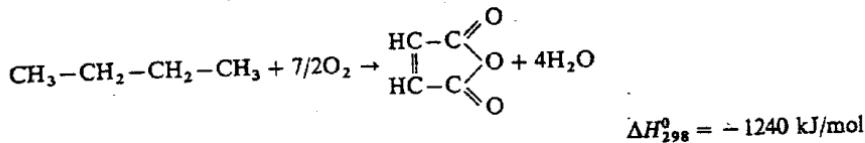
Fig. 13.3. Maleic anhydride production by benzene oxidation. Halcon/Scientific Design process.

to the Veba Chemie (ex-Bayer/RhuröI), Lonza and UCB (*Union Chimique Belge*) processes. In the Veba process, nearly 90 per cent of the maleic anhydride contained in the reactor effluent is condensed, by supplying it with dry air and by cooling the products below the anhydride melting point. The UCB process uses a catalyst, achieving at 375°C a molar selectivity of 95 per cent of maleic anhydride.

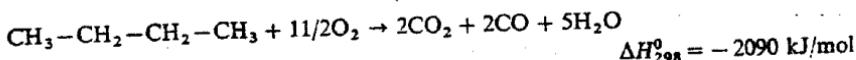
13.2.2 *n*-butane oxidation (Fig. 13.4)

The first industrial plant using *n*-butane to manufacture maleic anhydride was started up by *Monsanto* in 1984. At the time, 20 per cent of the maleic anhydride production capacity of this company switched from benzene to butane. Since then, three other manufacturers in the United States (*Amoco, Ashland* and *Denka Chemical*), and two in Western Europe (*Bayer* and *Hüls*) have followed a similar procedure, so that all maleic anhydride produced today in the United States is based on butane feedstock and nearly 50 per cent of worldwide installed capacity operates by this method. The *n*-butane is oxidized in the vapor phase, in a multi-tube reactor, on a fixed bed of catalyst based on phosphorus, vanadium and iron, deposited on a silica/alumina support.

The main reaction is as follows:



It is accompanied by the side reaction combustion of the feed:



One of the advantages offered by butane conversion is that all the carbon atoms it contains are theoretically found in the anhydride, whereas, in the case of benzene, two of them are lost in the form of CO₂. The operating conditions differ only slightly from those of the earlier processes starting with benzene, so that the plants could be revamped accordingly. The essential difference lies in the recovery of maleic anhydride by partial condensation of the transformation products. In the case of *n*-butane, the amount of water obtained per mole of anhydride formed is two times higher than in the case of benzene. This higher water content in the effluent limits the temperature to which it can be cooled, so that only about 30 to 35 per cent of the anhydride can be condensed before reaching the water dew-point.

The fraction contained in the gases is recovered by water scrubbing, or by absorption in an organic solvent (dibutyl hexahydrophthalate). In the case of scrubbing, the water is removed in thin layer evaporators operating under vacuum. In solvent absorption, the solvent is regenerated by stripping. Maleic anhydride is obtained to specifications by partial vacuum distillation in two light-ends and heavy-ends separation columns with 20 to 25 trays each.

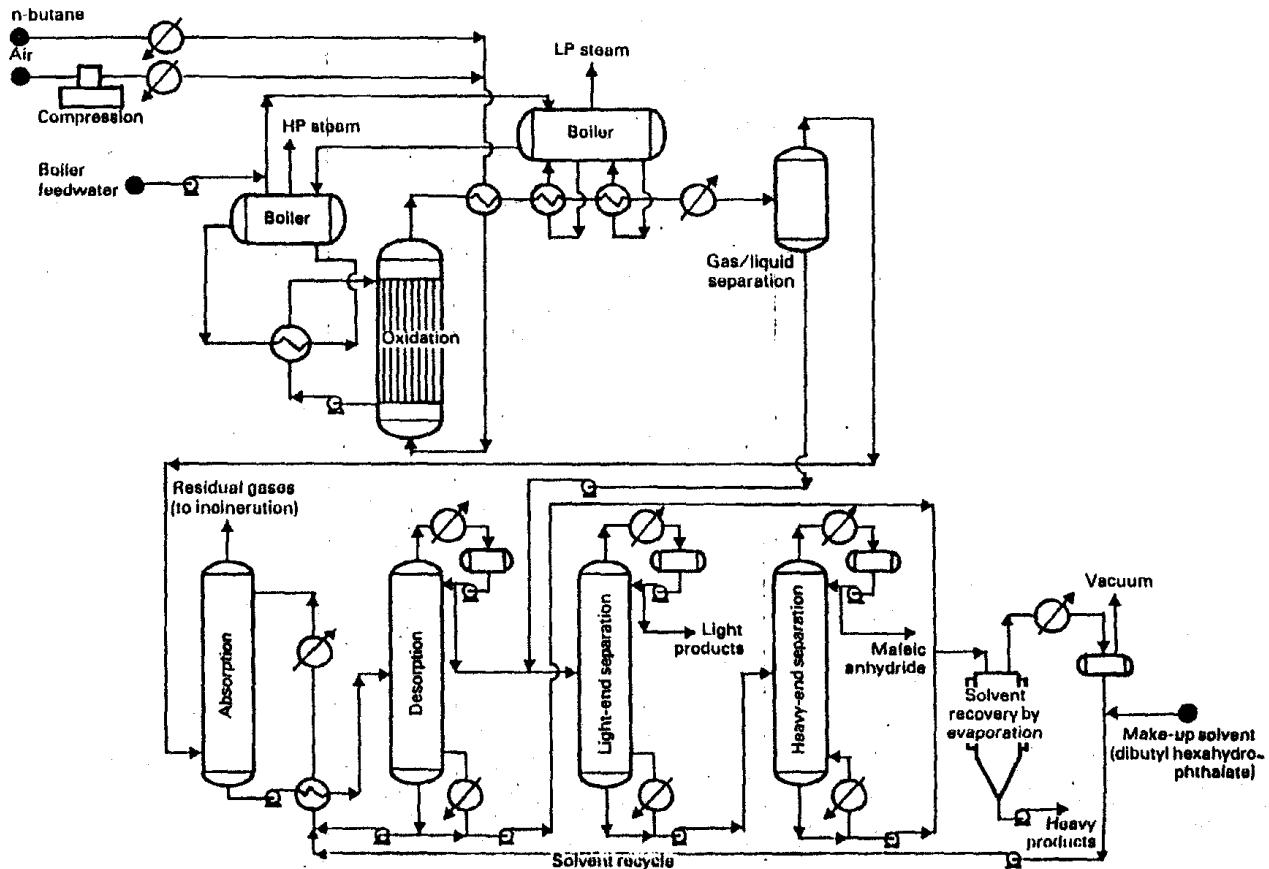


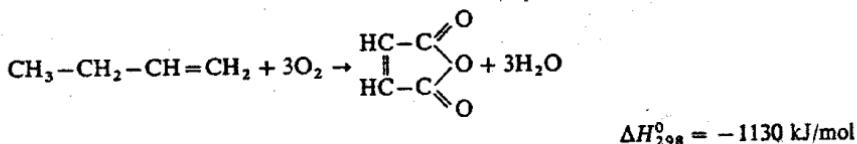
Fig. 13.4. Maleic anhydride production by *n*-butane oxidation

Among the companies which participated in developing a process starting with *n*-butane are *Amoco*, *Chevron*, *Mobil Oil*, *Petrotex* and *Standard Oil*. Moreover *Badger*, on the one hand, and *Lummus/Alusuisse Italia*, *Standard Oil* and *UCB* on the other, are currently developing fluidized bed *n*-butane oxidation processes.

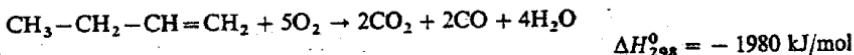
13.2.3 Oxidation of *n*-butenes

The first process which employed *n*-butenes to manufacture maleic anhydride was the Petrotex process in the United States in the early 1950s. At present, however, only Japan still uses this feed for about 35 per cent of its production, amounting to about 5 per cent of worldwide installed capacity. The process is carried out with the steam-cracked naphtha C₄ cut, rid of butadiene and isobutene, and containing approximately 90 per cent weight of 1-butene and cis and trans 2-butenes and 10 per cent butanes. The catalyst is a mixture of molybdenum, vanadium and phosphorus oxides.

The main reaction in the case of 1-butene is the following:



It is accompanied by the combustion reaction:



and a number of other side transformations, leading to the formation of various oxidized products (butyric and crotonic aldehydes, propionic, acetic, acrylic acids, etc.).

In normal operation, the butane feed is practically not oxidized, but is burned with the residual gases to produce steam. The operating conditions are closely similar to those used for the oxidation of benzene. *BASF* (*Badische Anilin und Soda Fabrik*) uses a fixed bed multi-tube reactor cooled by external molten salt circulation, operating between 360 and 440°C, also producing high-pressure steam. The maleic anhydride selectivity in relation to oxidizable butenes is about 50 molar per cent.

Bayer's 10,000 t/year plant in Uerdingen employs a similar technology. *Mitsubishi*, however, in an 18,000 t/year plant in Mizushima, uses a fluidized bed reactor with a catalyst similar to that of the fixed bed processes (Fig. 13.5). The fluidized bed technique offers many advantages. It facilitates the removal of the heat generated by the transformation, as well as temperature control. Operations can be conducted without any explosion hazard with *n*-butenes concentrations in air lying within the flammability range (between 1.4 and 9 per cent volume), allowing higher conversions per reactor volume. In this type of process, only part of the maleic anhydride is collected directly after cooling, by concentration. It is totally recovered by absorption in water. The dilute 40 per cent weight maleic acid solution is concentrated under vacuum. Maleic anhydride is then purified by distillation in two columns, which remove the light and heavy compounds in succession.

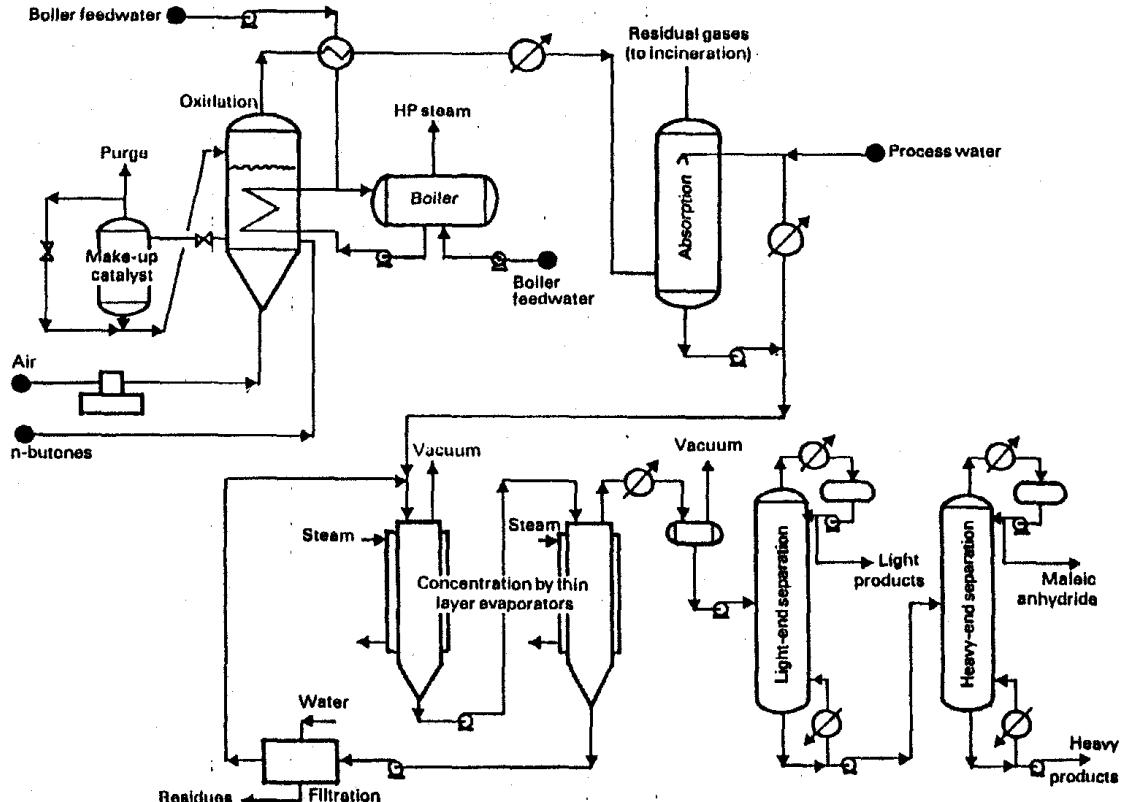


Fig. 13.5. Maleic anhydride production by fluidized bed oxidation of μ -butenes. Mitsubishi process.

13.2.4 Co-production of maleic anhydride in the manufacture of phthalic anhydride

This source of maleic anhydride accounts for less than 2 per cent of world production, but about 10 per cent of output in Western Europe. The manufacture of phthalic anhydride by the oxidation of naphthalene or *o*-xylene is accompanied by the production of 5 to 6 per cent maleic anhydride, which can be recovered in the plant wastes. These can be concentrated until they contain 15 to 20 per cent maleic anhydride and about 5 per cent of other acids (phthalic, benzoic, citraconic). UCB has developed a process it employs in its Ostend phthalic anhydride plant, from which 3000 t/year of maleic anhydride are extracted.

BASF has developed a similar technology, enabling it to co-produce 3000 and 2000 t/year of maleic anhydride in its phthalic anhydride plants in Ludwigshafen and Leverkusen.

TABLE 13.4
MALEIC ANHYDRIDE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 30,000 t/year

Process.....	Fixed bed benzene oxidation	Fixed bed <i>n</i> -butane oxidation	Fixed bed <i>n</i> -butenes oxidation
Typical technology.....	Scientific Design	Bayer	BASF
Battery limits investments (10 ⁶ US\$)	28	32	27
Consumption per ton of maleic anhydride			
Raw materials			
Benzene (t).....	1.18	—	—
<i>n</i> -butane (t).....	—	1.29	—
<i>n</i> -butenes (t).....	—	—	1.30
Utilities			
Steam (t)	(-)4.5	(-)8.0	(-)5.5
Electricity (kWh)	1,500	1,900	2,000
Cooling water (m ³)	280	350	360
Nitrogen (Nm ³)	10	10	10
Chemicals and catalysts (US\$) ...	16	18	7
Labor (Operators per shift).....	4	4	4

TABLE 13.5
AVERAGE COMMERCIAL SPECIFICATIONS OF MALEIC ANHYDRIDE

Characteristics	Values
Purity (% Wt) min.....	99.5
Melting point (°C) min.....	52.5
Color in melted state (Pt. Co) max.....	20
Ash (ppm) max.....	20
Solubility in water (4 g/10 ml H ₂ O).....	Total and clear solution

TABLE 13.6
MALEIC ANHYDRIDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acids (fumaric, maleic).....	3	15	28
Agricultural chemicals ⁽¹⁾	2	9	3
Unsaturated polyester resins.....	70	52	47
Lubricating oil additives.....	2	12	8
Copolymers.....	11 ⁽³⁾	5	{ 14
Miscellaneous ⁽²⁾	12	7	
Total	100	100	100
Sources (% product)			
Benzene	74	—	65
n-butane	20	100	14
n-butenes	—	—	21
Phthalic anhydride by-product	6	—	—
Total	100	100	100
Production (10 ³ t/year)	135	160	65
Capacity (10 ³ t/year) ⁽⁴⁾	175	180	85
Consumption (10 ³ t/year).....	130	160	60

(1) Alar, Captan, Disolatan, Endothall, Malathion, maleic hydrazide.

(2) Butyrolactone, chloroendic acid and anhydride, maleimides; pharmaceuticals, plasticizers, tetrahydrofuran, tetrahydrophthalic anhydride, surface active agents,...

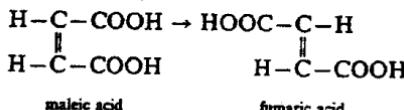
(3) Alkyd resins.

(4) The worldwide production capacity of maleic anhydride was around $0.57 \cdot 10^6$ t/year in 1984 and $0.60 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.18	Western Europe	0.17	Middle East	—
Canada	0.01	Eastern Europe	0.08	Japan	0.09
Latin America	0.05	Africa	—	Asia and Far East	0.02

13.2.5 Fumaric acid production

The different methods for producing maleic anhydride can also simultaneously produce fumaric acid, an isomer of maleic acid, by the treatment of a variable fraction of the absorber withdrawal stream:



Isomerization takes place in an aqueous solution at 100°C, in the presence of ammonium bromide and ammonium persulfate, or hydrochloric acid, or even thiourea. Pure fumaric acid is obtained by cooling the reaction medium, centrifugal drying, washing, and drying of the crystals obtained. Fumaric acid is used in the manufacture of polyester resins, adhesives and food additives (malic acid obtained by the hydration of fumaric acid).

13.2.6 Economic data

Economic data concerning the production of maleic anhydride from benzene, *n*-butane and olefinic C₄ cuts are given in Table 13.4.

13.2.7 Uses and producers

Table 13.5 gives the average commercial specifications of maleic anhydride.

The main uses of maleic anhydride in 1984 are expressed in per cent in Table 13.6. This table also gives the production capacities in Western Europe, the United States and Japan in 1984.

13.3 PHTHALIC ANHYDRIDE

Phthalic anhydride ($d_4^{20} = 1.527$ ⁽⁴⁾, mp = 131°C, sublimation at 284.5°C under 101.3 kPa absolute) is manufactured industrially from naphthalene or *o*-xylene by substantially similar oxidation techniques.

Naphthalene of carbochemical origin, the only material used until the end of the Second World War, was then gradually supplanted by *o*-xylene, available in large quantities in petroleum cuts. The advent of naphthalene of petroleum origin then revived interest in the initial raw material, so that in 1965 80 per cent of the feeds employed consisted of naphthalene, about half of petroleum origin. The situation has since been

(4) Specific gravity, 68.0/39.2.

reversed, so that today *o*-xylene accounts for more than 80 per cent of the synthesis of phthalic anhydride. Most processes using naphthalene or *o*-xylene operate in the vapor phase, but the liquid phase is also employed.

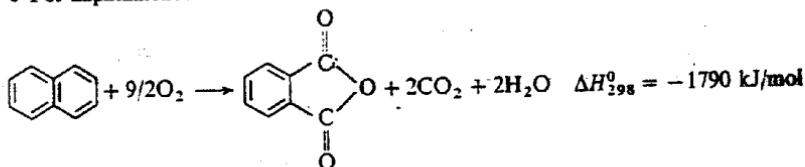
13.3.1 Vapor phase oxidation processes

13.3.1.1 Common features of the processes

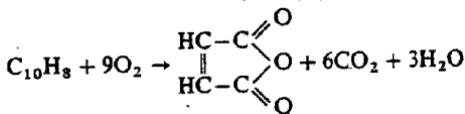
A. Synthesis

The reactions involved are as follows:

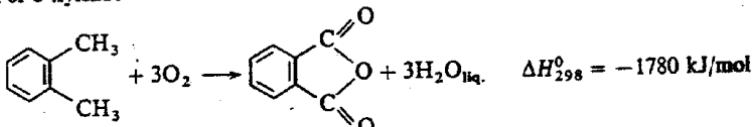
- For naphthalene:



with the main degradation reactions:



- For *o*-xylene:



Total combustion and the formation of maleic anhydride is also observed as a side transformation.

The above reactions, which are highly exothermic, take place in the presence of a catalyst. This catalyst may be in a fixed bed in multi-tube reactors with 5,000 to 20,000 tubes. Heat is removed by means of a coolant fluid consisting either of a bath of molten salts (nitrate/nitrite), or the sodium/potassium eutectic operating between 360 and 420°C. The catalyst may also be used in a fluidized bed traversed by cooling systems (coils, etc.). The heat generated is used to produce high-pressure steam.

Exothermicity is theoretically 10,500 kJ/kg of phthalic anhydride, but, in practice, it amounts to nearly 17,000 kJ/kg, in view of the total combustion. In the high-temperature process, it amounts to 7100 kJ/h . 1 of catalyst. The catalyst systems are based on supported vanadium pentoxide and titanium dioxide. Their life depends on the operating conditions and ranges between 2 and 3 years. Oxidation takes place in air. The air/hydrocarbon molar ratio is usually between 60 and 120, in order to operate beyond the low

limit of the flammability range (less than 1.7 molar per cent of *o*-xylene per mole of air) and to avoid degradation of the catalyst, which must always operate in the presence of a minimum amount of oxygen.

B. Product recovery and purification

The method most widely used today to recover phthalic anhydride from the reactor effluent consists in passing this stream through cyclic condensation systems. In some of them, operating as crystallizers, the anhydride solidifies by cooling in finned tubes, whereas in the others, hot oil is introduced to melt their content and to recover the previously-deposited product. In this way, up to 99 per cent of the phthalic anhydride in the effluent can be recovered.

The residual gases, which contain most of the maleic anhydride co-product, are scrubbed with water and then discharged into the atmosphere or burned. The scrubbing waters also contain small amounts of phthalic, benzoic and citraconic acids. Maleic acid is recovered in anhydride form (see Section 13.2.4). The crude phthalic anhydride, in a purity of 99 to 99.5 per cent weight, contains different acids (phthalic, maleic, benzoic). It is heated at atmospheric pressure to dehydrate the phthalic acid and to convert the colored impurities into high-boiling products that are easier to remove.

This is followed by vacuum distillation in two successive columns. In the first, maleic anhydride and benzoic and toluic acids are obtained in the distillate. In the second, phthalic anhydride is collected at the top. The high-boiling residues are removed at the bottom of the second column.

Throughout this distillation section, the lines must be steam traced and the pumps also heated. In the parts of the installation in contact with acids (phthalic, maleic, benzoic), it is necessary to use stainless steel.

13.3.1.2 Various types of process

Vapor phase processes include fixed bed and fluidized bed processes. Two types of fixed bed process formerly existed, characterized by the fact that some of them operated at low temperature (between 350 and 390°C) and low space velocity, and the others at high temperature (450 to 550°C) and high space velocity, with the latter offering a lower yield than the former. Progress achieved in catalysts now make it possible, by operating between 380 and 400°C, to reach high space velocities while preserving the high yields of the low-temperature processes. Among these technologies are those developed by *BASF*, *Flatital*, *Japan Catalytic Chemical*, *Lonza*, *Mitsui Toatsu*, *Mizushima Petrochemical*, *Rhône-Poulenc*, *Ruhröl*, *Scientific Design*, *Veba*, *Von Heyden*, etc.

Fluidized bed processes mainly use naphthalene, and their yield is lower than that of fixed bed processes, especially if they employ *o*-xylene. The main representative of these techniques is *Sherwin-Williams/Badger*.

A. *BASF* fixed bed process (Fig. 13.6)

The *o*-xylene, preheated to 140 to 150°C, and air, filtered, compressed and preheated to 160°C, are introduced into the multi-tube reactor consisting of 15,000 tubes 2.5 cm in diameter and 3.2 m high. The temperature is kept at 380°C by molten salt circulation.

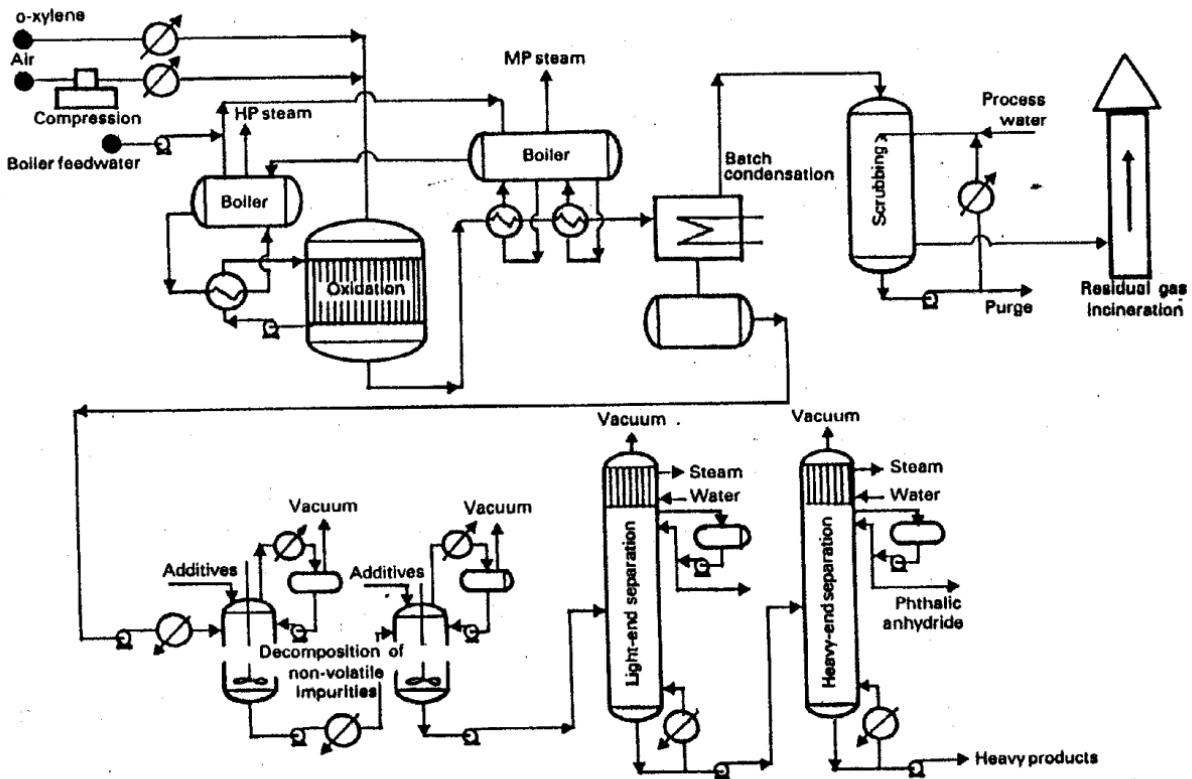


Fig. 13.6. Phthalic anhydride production by fixed bed air oxidation of *o*-xylene. BASF⁷ process.

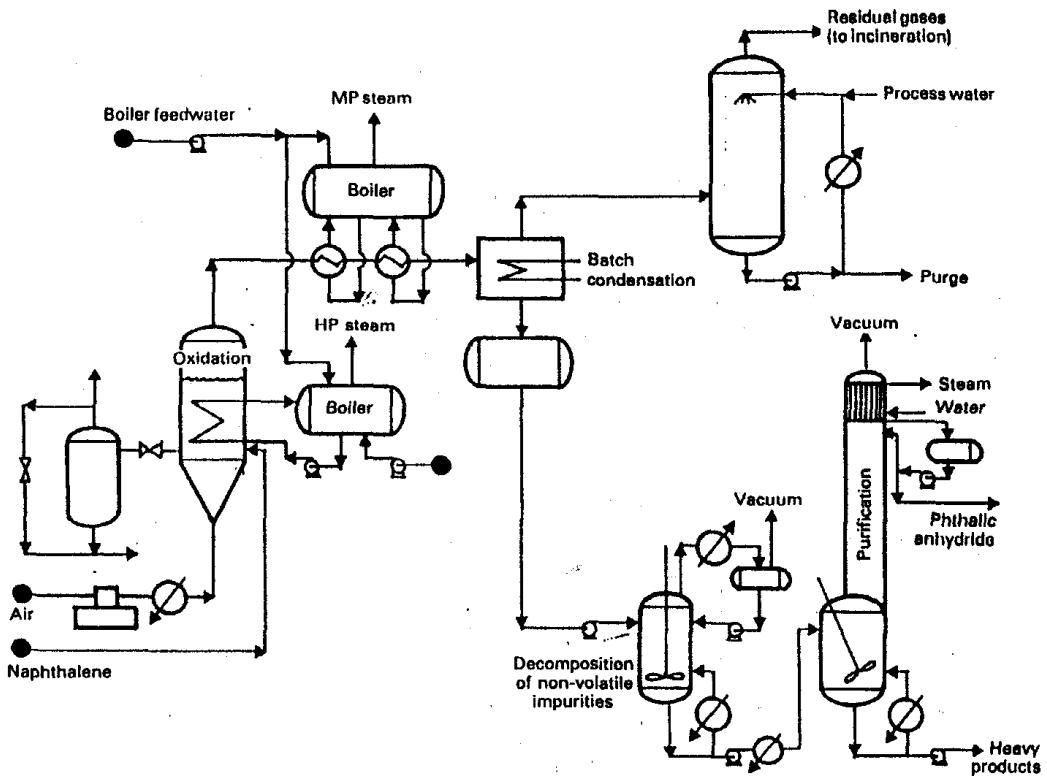


Fig. 13.7. Phthalic anhydride production by fluidized bed air oxidation of naphthalene.
Sherwin-Williams/Badger process.

A heat exchanger system installed on the coolant fluid circuit is used to produce high-pressure steam ($6 \cdot 10^6$ Pa absolute). The catalyst is a mixture of vanadium and titanium oxides deposited on an inert, non-porous support. The molar yield of phthalic anhydride is 74 per cent of stoichiometry, using 95 per cent *o*-xylene.

The gaseous reactor effluent is first cooled with the production of low-pressure steam ($1 \cdot 10^6$ Pa absolute), and the residual gases scrubbed with water and then discharged to the atmosphere. The condensed stream obtained is then sent to batch condensers, where it is melted at 130°C and sent to a storage tank. The crude product is vacuum preheated in the presence of additives to decompose the nonvolatile impurities (polymers and colored products). It then goes to a first vacuum distillation column (15 kPa absolute) which separates the maleic anhydride and benzoic and toluic acids at the top, and then to a second column where 99.5 per cent weight phthalic anhydride is recovered at the top.

B. Sherwin-Williams/Badger fluidized bed process (Fig. 13.7)

Pure naphthalene (mp > 80°C) is introduced in the liquid state at the base of a catalyst bed contained in the reactor. It is immediately vaporized and dispersed in the solid medium, where it enters into contact on the hot catalyst with air introduced below a grid placed at the base of the system. Naphthalene is vaporized and oxidized to phthalic anhydride at a uniform temperature, ranging between 340 and 385°C, due to the intense agitation of the reaction medium engendered by the fluidized bed. The catalyst consists of vanadium oxide on silica gel.

The heat of reaction is removed by water circulation in tubes placed in the catalytic bed, with the production of high-pressure steam. Solid particles entrained by the gas stream leaving the reactor are retained on a series of ceramic filters and returned to the reaction medium. The phthalic anhydride formed is condensed in the liquid and solid state. It is then sent to the purification section, where it is subjected to heat treatment intended to decompose the nonvolatile impurities liable to dye the final product, and then to vacuum distillation. The phthalic anhydride yields are not as high as those of fixed bed processes, especially those starting with *o*-xylene.

13.3.2 Liquid phase oxidation of *o*-xylene

A liquid phase process, similar to the Amoco *p*-xylene oxidation process, has been employed by Rhône-Poulenc since 1939 in its Chauny plant. This technique was subsequently replaced by a so-called low-energy consumption process operating in a fixed bed, in the vapor phase. The 19,000 t/year plant built in 1971 was supplemented by the 45,000 t/year unit installed in 1975.

13.3.3 Economic data

Various data of an economic type, concerning the production of phthalic anhydride from *o*-xylene and naphthalene, are given in Table 13.7.

TABLE 13.7
PHTHALIC ANHYDRIDE PRODUCTION, ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 50,000 t/year

Process	<i>o</i> -xylene oxidation		Naphthalene oxidation
	Conventional	Energy-optimized	
Typical technology	Von Heyden	BASF/RP	Badger
Battery limits investments (10^6 US\$)	25	22	27
Consumption per ton of phthalic anhydride			
Raw materials			
<i>o</i> -xylene (95%) (t)	0.95	0.97	—
Naphthalene (t)	—	—	1.03
Utilities			
Steam (t)	(-) 2.5	(-) 3.5	(-) 4.0
Electricity (kWh)	920	200	500
Cooling water (m^3)	250	—	40
Process water (m^3)	5	5	5
Nitrogen (Nm^3)	10	30	10
Chemicals and catalysts (US\$)	12	18	21
Labor (Operators per shift)	4	4	4

13.3.4 Uses and producers

Table 13.8 provides an indication of the average commercial specifications of phthalic anhydride. Its main uses in 1984 are expressed as per cent in Table 13.9. This table also

TABLE 13.8
AVERAGE COMMERCIAL SPECIFICATIONS OF PHTHALIC ANHYDRIDE

Characteristics	Values
Purity (% Wt) min.	99
Melting point (°C)	131
Color in the melted state	
Initial at 250°C (Pt/Co)	10
2 h stability at 250°C (Pt/Co)	30
Phthalic acid (ppm) max.	1,000
Maleic acid (ppm) max.	3,000
Benzoic acid (ppm) max.	1,000
Naphthoquinone (ppm) max. ⁽¹⁾	2
Solubility in benzene (1 g in 20 g at 25°C)	Completely soluble

(1) For phthalic anhydride obtained from naphthalene.

gives the production, capacities and consumption in Western Europe, the United States and Japan at the same time.

TABLE 13.9
PHthalic ANHYDRIDE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Alkyd resins	16	19	14
Phthalate plasticizers	63	51	63
Unsaturated polyester resins	19	25	15
Miscellaneous ⁽¹⁾	2	5	8
Total	100	100	100
Sources (% product)			
Naphthalene	8	15	29
<i>o</i> -xylene	92	85	71
Total	100	100	100
Production (10 ³ t/year)	635	395	260
Capacity (10 ³ t/year) ⁽²⁾	955	500	310
Consumption (10 ³ t/year)	625	395	235

(1) Cellulose acetate phthalate, diallyl phthalate, dyes and pigments, herbicides, isatoic anhydride, phenolphthalein, phthalimide, polyester-polymers, 4-sulfophthalic acid, tetrachloro and tetrabromophthalic anhydrides.

(2) The worldwide production capacity of phthalic anhydride was about $3.0 \cdot 10^6$ t/year in 1984 and $3.2 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.52	Western Europe	0.95	Middle East	0.08
Canada	0.04	Eastern Europe	≈ 0.75	Japan	0.31
Latin America	0.25	Africa	0.04	Asia and Far East	0.24

13.4 1,4-BUTANEDIOL

13.4.1 Synthesis processes

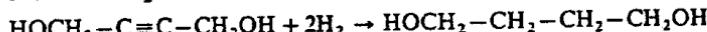
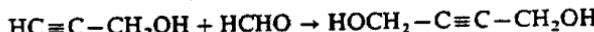
1,4-butanediol, $\text{HOCH}_2 - (\text{CH}_2)_2 - \text{CH}_2\text{OH}$ (mp = 20.2°C , bp_{1.013} = 228°C , $d_4^{20} = 1.017$)⁽⁵⁾ is manufactured industrially from acetylene, which accounts for over 90 per cent of its world output. The process employed was developed in Germany by Reppe during the Second World War in order to synthesize, by dehydration of the diol, the butadiene required for the manufacture of buna synthetic rubber.

(5) Specific gravity, 68.0/39.2.

13.4.1.1 Formaldehyde ethynylation

This consists in causing formaldehyde to react with acetylene in the presence of a copper-based catalyst. The ethynylation reaction yields 1,4-butyne diol and a few per cent of propargyl alcohol resulting from the condensation of a single molecule of formaldehyde. The 1,4-butyne diol is hydrogenated to 1,4-butanediol in a second step.

The conversions concerned are the following:

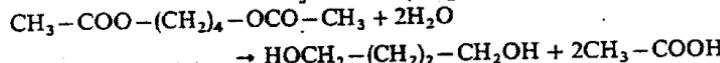
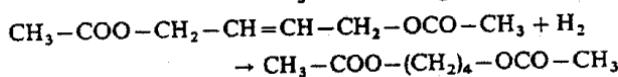
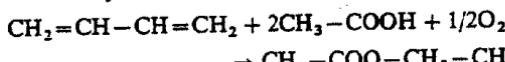


At present, three producers in the United States and two in West Germany employ this process, which has obviously been improved since its initial development in 1930.

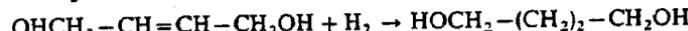
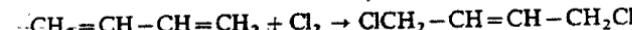
13.4.1.2 Processes starting with butadiene

In Japan, the techniques industrialized employ butadiene. *Mitsubishi* uses acetoxylation, and *Toyo Soda* employs the chlorination of butadiene by the following reactions:

- Acetoxylation:

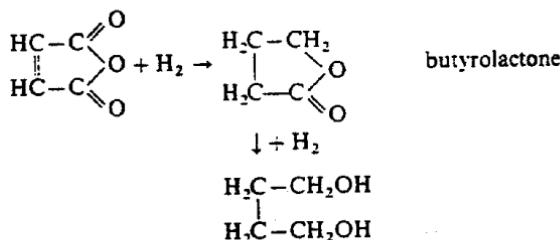


- Chlorination:



13.4.1.3 Maleic anhydride conversion processes

Maleic anhydride offers a third raw material for synthesizing 1,4-butanediol, and the process was industrialized by *Nippon Hydrofuran*, a Mitsubishi subsidiary, and by *ICI*, but these plants were subsequently shut down due to the excessively high price of maleic anhydride:

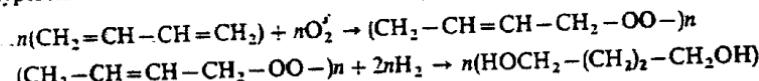


13.4.1.4 Other methods to manufacture 1,4-butanediol and suitable for industrialization

Many other processes have been proposed to synthesize butanediol starting from butadiene, and also using ethylene and propylene. None of them has yet been brought to the industrial stage.

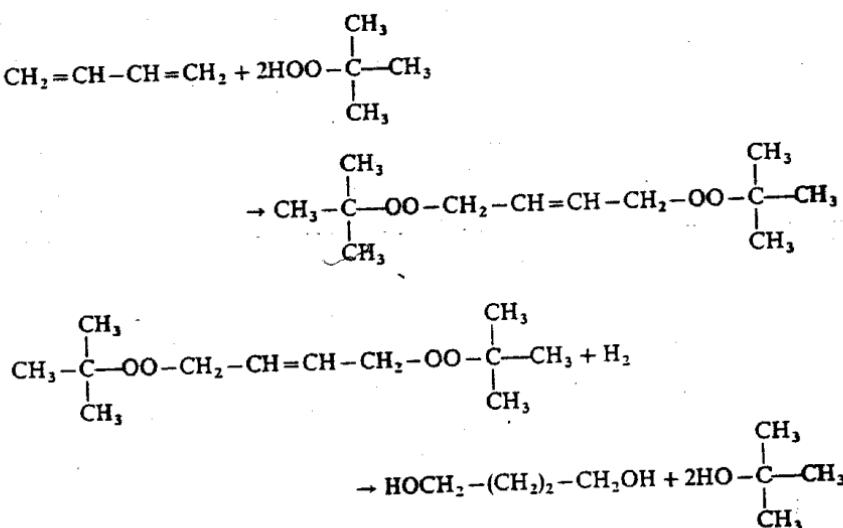
A. Butadiene conversion

- Starting with butadiene, *Phillips* and *Amoco* have proposed bromination which yields 1,4-dibromobutene, which is then hydrolysed to butanediol as in the chlorination process.
- Butadiene can also be polyperoxidized, a step followed by the hydrogenolysis of the polyperoxide:



However, apart from the fact that the polyaddition of oxygen takes place not only at 1,4- but also at 1,2-, causing the co-production of 1,2-butanediol, the hydrogenolysis step does not allow economically interesting diol yields.

- In a related area, Shell patents claim the catalytic addition of *t*-butylhydroperoxide to butadiene, followed by hydrogenolysis of the diperoxide obtained:

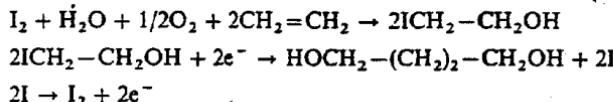


In this case also, a substantial share of the addition takes place at 1,2- and yields 1,2-butanediol that is difficult to utilize.

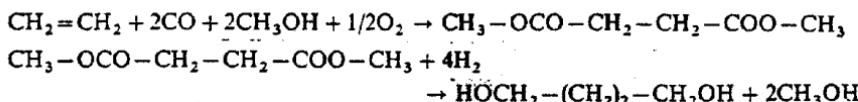
B. Ethylene conversion

The ethylene conversion process employs the following two main methods:

- Electrochemical coupling of two molecules of iodohydrin ethylene by the following reaction:



- Hydrogenation of methyl succinate obtained by the oxidative carboxyalkylation of ethylene by the following reactions:

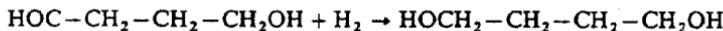
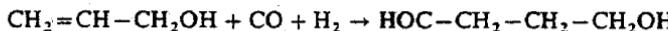


The first step is catalysed by palladium chloride and is similar to the Wacker process for manufacturing acetaldehyde from ethylene.

C. Propylene conversion

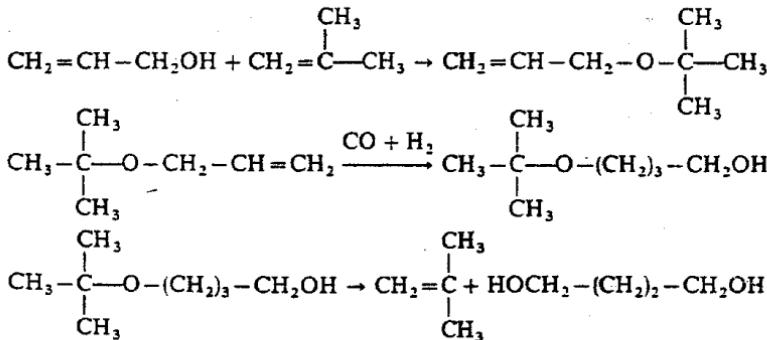
Synthesis methods starting with propylene are even more numerous. Most of them pass through allyl alcohol as an intermediate, which can be obtained by the hydrolysis of chlorine or of allyl acetate, by isomerization of propylene oxide, or by the hydrogenation of acrolein:

- Allyl alcohol is converted by hydroformylation to aldehyde/alcohol, which is then hydrogenated to 1,4-butanediol:



Allyl acetate can also be hydroformylated, yielding the monoacetate of 1,4-butanediol, which is then hydrolysed.

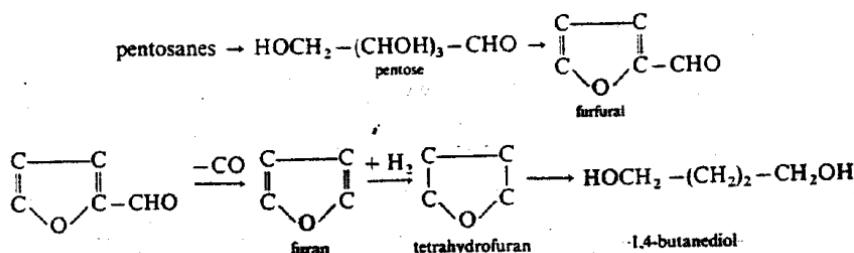
- It has also been proposed (*Davy/General Electric*) to cause isobutene to react with allyl alcohol. The allyl *t*-butyl ether obtained is hydroformylated, hydrogenated and decomposed to butanediol and recyclable isobutene:



• BASF, Celanese and Du Pont considered the hydroformylation of acrolein, after protecting the aldehyde function by acetalization by means of an alcohol. The acetal is then hydrolyzed and hydrogenated to the alcohol.

D. Upgrading of natural products

Biomass, through the intermediate of furfural, resulting from the hydrolysis of pentosanes of certain agricultural wastes, is another possible source, whose most important derivatives are butanediol and tetrahydrofuran. This method has been utilised by Quaker Oats in the United States:



This chapter is restricted to describing processes that have been industrialized.

13.4.2 Reppe process using acetylene

13.4.2.1 Synthesis of 1,4-diol 2-butyne (Fig. 13.8)

The condensation of formaldehyde on acetylene requires an extremely active and highly selective catalyst system to prevent explosions due to the use of excessively high acetylene partial pressures and the undesirable formation of cuprene, a polymer of acetylene. The catalyst used today is copper acetylidyde, deposited on a magnesium silicate support containing bismuth. Operations are conducted at low pressure ($0.1 \cdot 10^6$ Pa absolute) and at relatively moderate temperature (95°C) in a continuously fed system.

Make-up and recycle acetylene are introduced into the reactor in the gas phase, under pressure, at the same time as the dilution nitrogen. This feed passes through an aqueous solution containing 37 per cent weight of formaldehyde. Mechanical agitation ensures effective mixing of the reactants, and an external cooling circuit with water circulation removes the heat generated and helps to control the thermal level. A reflux condenser facilitates the return of vaporized liquefiable components to the reactor, while unconverted acetylene and nitrogen are removed in the gas phase continuously and recompressed before being recycled.

The conversion products are removed in the liquid state at the top of the reaction system. A fraction is recycled, and the remainder sent to a centrifuge to remove the catalyst content, which is returned to the reaction zone after the addition of unconverted recycled formaldehyde. The final traces of catalyst liable to remain after centrifuging are stopped by a filter. The aqueous solution of butynediol and propargyl alcohol obtained

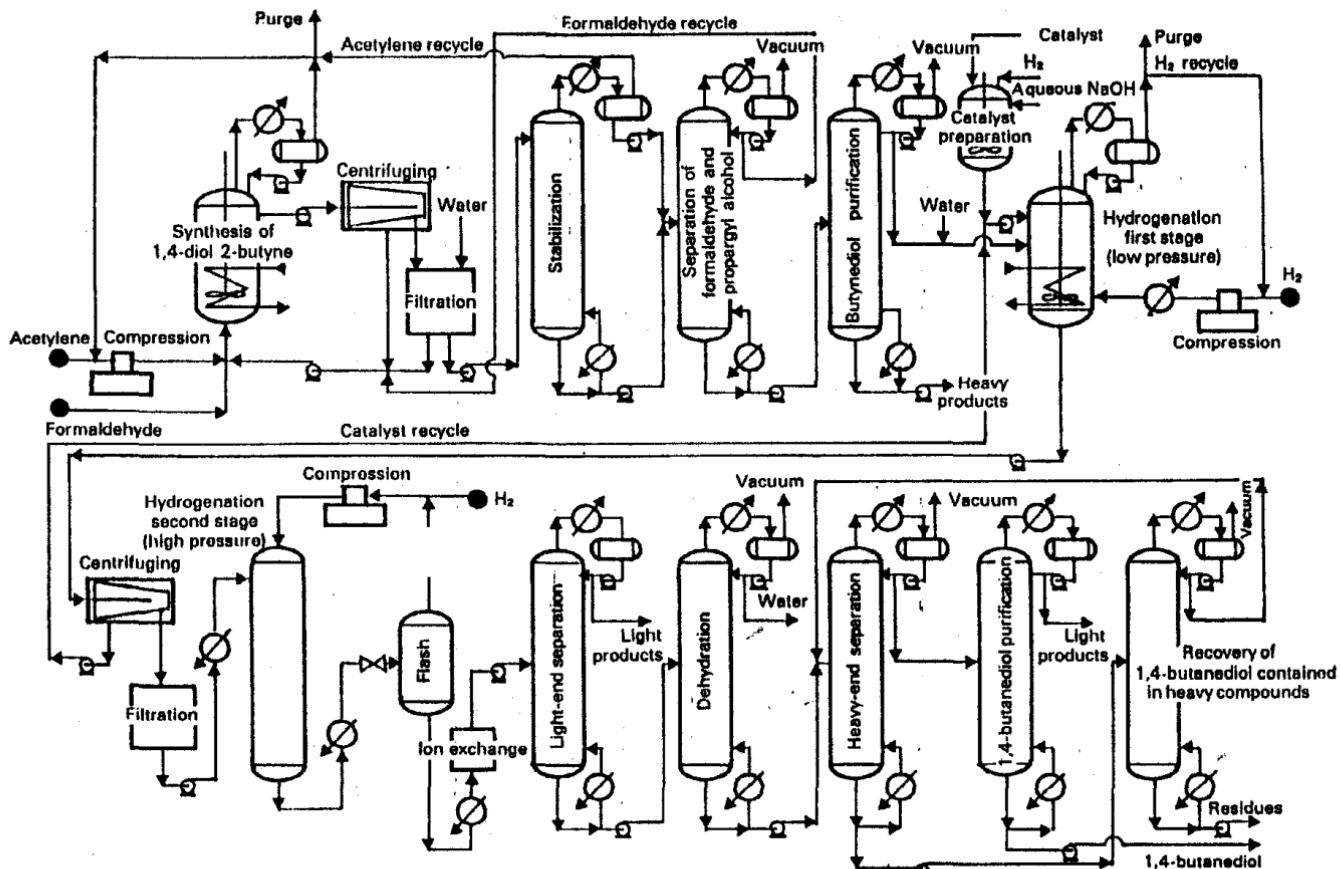
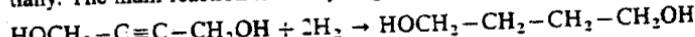


Fig. 13.8. 1,4-butanediol production by formaldehyde ethynylation. Reppe process.

is rid of dissolved acetylene in a stabilization column. The withdrawal and liquid distillate are vacuum distilled (20 trays) to separate formaldehyde and propargyl alcohol at the top, which are recycled to the reactor, and the heavy fractions at the bottom. These are sent to a third column also operating under vacuum (40 trays), where the heavy compounds are collected at the bottom and butynediol at the top, in the form of a 35 per cent weight aqueous solution.

13.4.2.2 Hydrogenation of 1,4-diol 2-butyne

The progress achieved by GAF (*General Anilin and Film Co.*) concerning the initial catalyst employed in the process has served to raise the 1,4-butanediol selectivity substantially. The main reaction is the hydrogenation of the triple bond:



$$\Delta H_{298}^0 = -250 \text{ kJ/mol}$$

Added to this are side reactions of hydrogenolysis and dehydration, yielding butanol and furan. Traces of acidity may also favor the production of butanediol and hydroxybutyraldehyde.

In the GAF process, hydrogenation takes place in two steps. The first is conducted in an agitated reactor around 50 to 60°C, at between 1.4 and $2 \cdot 10^6$ Pa absolute, in the presence of Raney nickel and copper acetate. The butanediol obtained contains hydroxybutyraldehyde and unsaturated compounds. It is sent to a second reactor, operating with a fixed bed, around 120 to 140°C, at between 14 and $20 \cdot 10^6$ absolute. The catalyst consists of nickel, copper and manganese deposited on alumina, in a weight ratio of 15/78/0.5.

After the hydrogen is removed by flash, the separation treatment comprises a series of five distillation columns which separate in succession the light compounds (15 trays), water (45 trays), heavy compounds (20 trays), butanediol (40 trays), and recover the product carried off in the heavy fractions (25 trays). The total hydrogenation yield is 95 molar per cent for butanediol, for virtually total butynediol conversion.

13.4.3 Butadiene acetoxylation

The butanediol synthesis process developed by Mitsubishi in Japan comprises three steps: acetoxylation of butadiene to 1,4-diaceoxy 2-butene, the hydrogenation of this compound to 1,4 diaceoxybutane, and, finally, hydrolysis to 1,4-butanediol.

13.4.3.1 Acetoxylation (Fig. 13.9)

This takes place in the liquid phase, at 80°C, under $3 \cdot 10^6$ Pa absolute, in the presence of a palladium- and tellurium-based catalyst deposited on activated charcoal and activated by nitric acid. Butadiene and make-up and recycle acetic acid are introduced at the same time as compressed air, at the base of the reaction system. The freshly prepared catalyst is kept in suspension in recycle acetic acid in a separate agitated vessel. It is continuously added near the top of the reactor. Residence time is about 2 h.

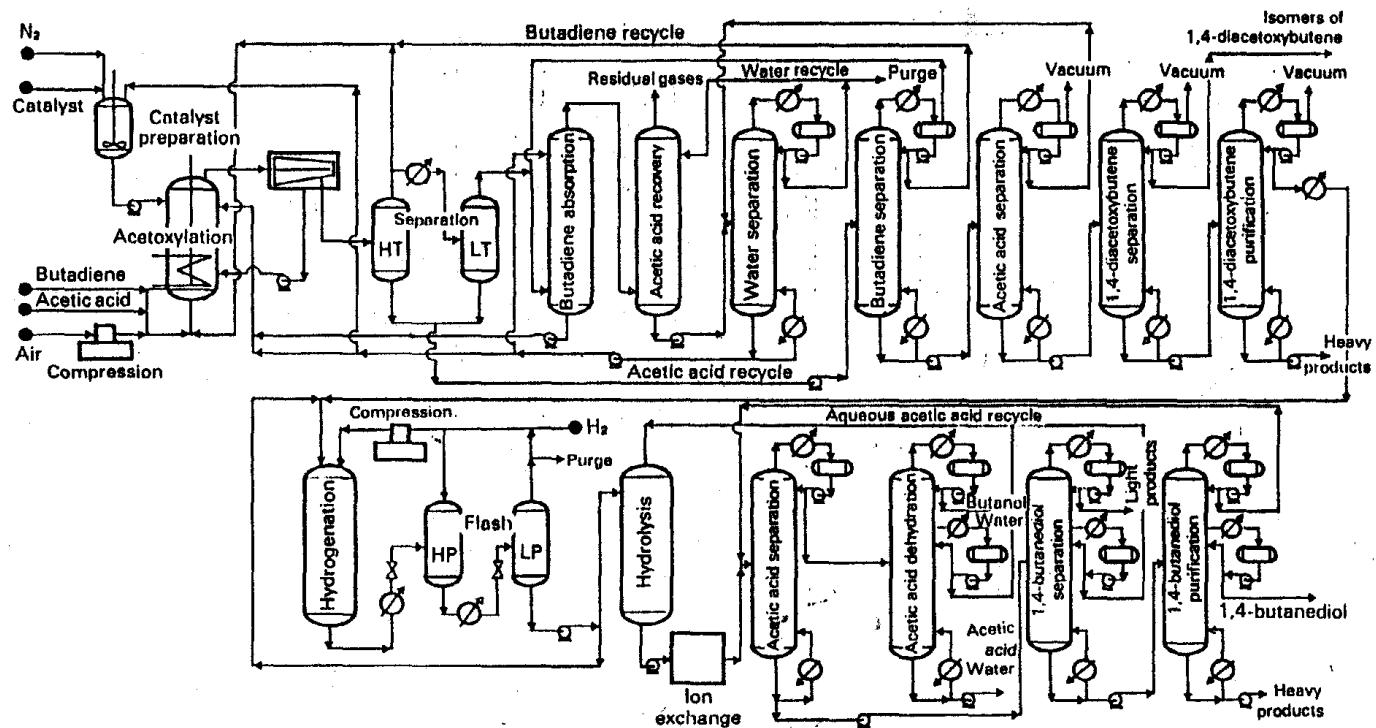


Fig. 13.9. 1,4-butanediol production by butadiene acetoxylation. Mitsubishi process.

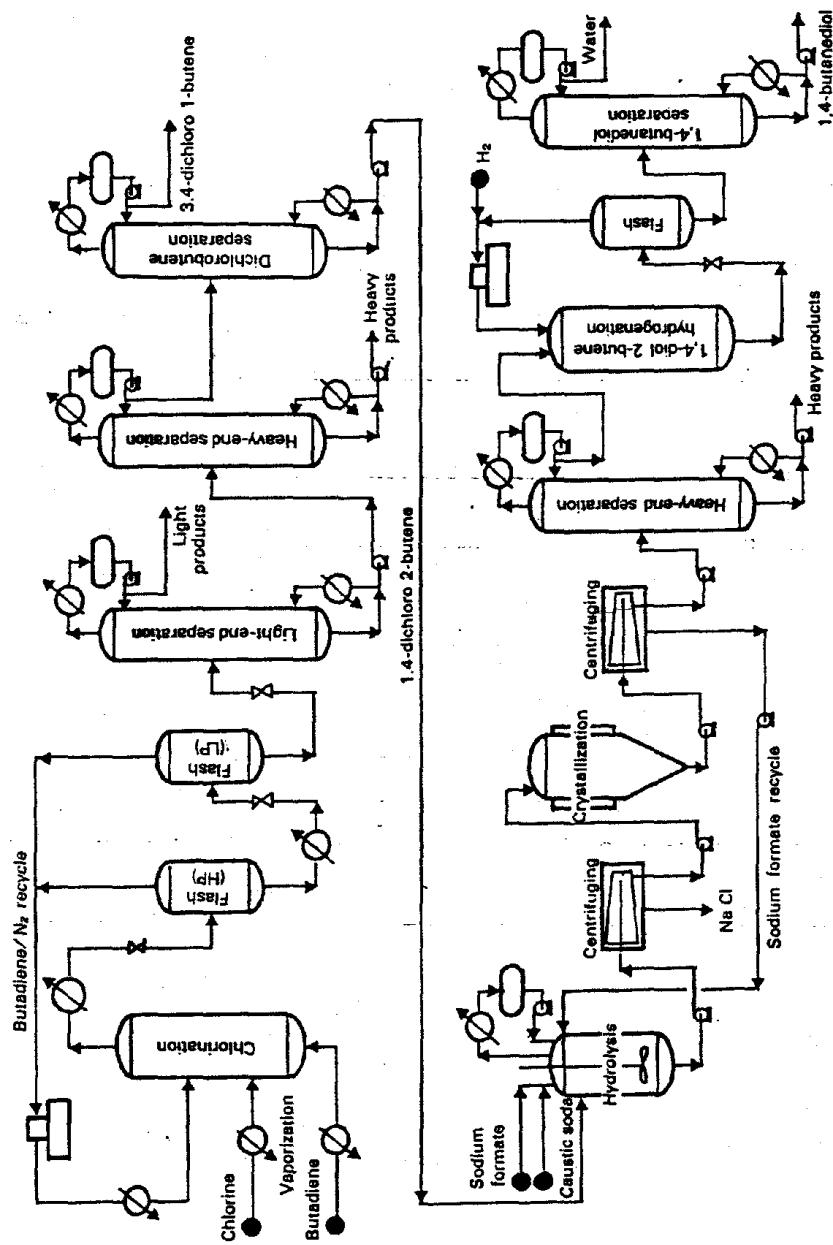


Fig. 13.10. 1,4-butanediol production by butadiene chlorination, Toyo Soda process.

The reaction products are withdrawn at the top by overflow and sent to a centrifuge to remove the catalyst system and recycle it directly. They are then sent to gas/liquid separators. The fraction in-vapor form is first rid of the butadiene it contains by absorption in acetic acid. This is then recovered by water scrubbing, while, in a final separation, by fractionation, the extract from the previous column and the light-ends from the subsequent separation of acetic acid by distillation are rid of the water they contain. This water, recovered in the distillate, is sent to acetic acid absorption, while the acid withdrawn is recycled.

The liquid fraction produced by the separators is treated in a series of four distillation columns. The first isolates the dissolved butadiene at the top, which is then recycled. The second (20 trays), operating under vacuum (10 kPa absolute), separates acetic acid which is also returned to the reactor. The third (9 kPa absolute, 35 trays) yields isomers of diacetoxybutene as the distillate. The fourth column (9 kPa absolute, 60 trays) is used to recover 1,4-diacetoxybutenes at the top, and the heavy compounds are removed at the bottom of the column.

13.4.3.2 Hydrogenation

This takes place in a fixed bed reactor, used in two stages at different temperatures (60°C for the first, 110°C for the second), in the presence of 1 per cent weight of palladium catalyst on charcoal. The cooling of a fraction of the hydrogenated product, which takes place outside the reactor, removes the heat generated by the reaction and maintains the temperature at the requisite level. Diacetoxybutane is obtained with a molar yield of 94 per cent, for virtually total conversion of diacetoxybutene.

13.4.3.3 Hydrolysis

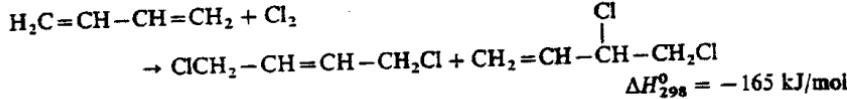
Butanediol diacetate is hydrolysed around 60°C. at atmospheric pressure, in the presence of an ion exchange resin. Effluent treatment includes the separation (20 trays) and concentration (75 trays) of acetic acid, and the recovery (70 trays) and purification (20 trays) of 1,4-butanediol in four successive distillation columns.

13.4.4 Butadiene chlorination

This process, employed by *Toyo Soda* in its Shin-Nanyo complex in Japan, carries out butadiene chlorination for the joint manufacture of chloroprene, 1,4-butanediol and tetrahydrofuran by dehydration of the diol.

13.4.4.1 Production of 1,4-dichlorobutenes (Fig. 13.10)

The addition of chlorine to butadiene takes place in the vapor phase, between 250 and 300°C. This is an exothermic reaction which produces two dichlorinated isomers, 1,4-dichloro 2-butene and 3,4-dichloro 1-butene:



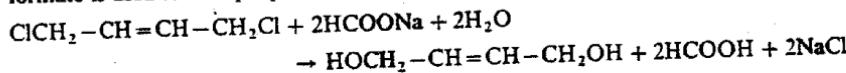
Tri and tetrachlorinated compounds may also be formed. To prevent the excessive production of these polychlorinated derivatives, a butadiene/chlorine molar ratio approaching 6/1 is maintained during the reaction, and the reaction mixture is diluted with nitrogen. Under these conditions, the selectivity of the dichlorinated components, for total conversion of chlorine, may be as high as 95 molar per cent. The 1,4-dichloro 2-butenes content in the mixture of the two dichlorinated compounds is about 60 per cent.

Chlorine and make-up butadiene, as well as recycled butadiene and nitrogen, are preheated around 120°C and then sent to the reactor, where the exothermicity of the reaction maintains the temperature at about 250°C. The reactor effluent is cooled, and the nitrogen and unconverted butadiene are separated from the liquid fraction and recycled to the reactor.

Three distillation columns successively separate the dichlorobutenes from the monochlorobutenes and tri- and tetrachlorinated compounds. The light compounds (1-chloro and 2-chlorobutadiene) are recovered at the top of the first (20 trays). The second (20 trays) leaves tetrachlorobutanes and trichlorobutanes at the bottom, and yields at the top the feed for the final column (30 to 35 trays), where 1,4-dichloro 2-butenes are separated in a withdrawal stream and 3,4-dichloro 1-butene is separated in the distillate, and then sent to the chloroprene manufacturing unit.

13.4.4.2 Hydrolysis of 1,4-dichloro 2-butenes

To prevent undesirable isomerizations and condensations, 1,4-dichloro 2-butenes are hydrolysed by the sodium salt of an organic acid and not by caustic soda. Sodium formate is used for the purpose:



The conversion takes place at the boiling point of the reaction medium (110°C) to remove the heat generated by vaporization.

Dichlorobutenes, sodium formate and caustic soda intended to neutralize the formic acid produced are introduced simultaneously into the reactor.

The effluent, which is first centrifuged to separate the sodium chloride formed, is then sent to a crystallizer operating under vacuum, and then into a second centrifuge, to separate the sodium salt from the organic acid initially introduced and to recycle it to the reactor in an aqueous solution. The mother liquor produced by the centrifuge is sent to a distillation column (25 to 30 trays) which separates the heavy compounds at the top, and from which the distillate is sent to the hydrogenation reactor.

13.4.4.3 Hydrogenation of 1,4-diol 2-butenes

This takes place at about 100°C, under $3 \cdot 10^6 \text{ Pa}$ absolute, in the presence of Raney nickel as catalyst. The hydrogenation reactor effluent is sent to a distillation column,

which separates the water formed at the top and 1,4-butanediol at the bottom to commercial specifications.

13.4.5 Economic data

Table 13.10 gives some economic data about the three main industrial methods for manufacturing 1,4-butanediol.

TABLE 13.10
1,4-BUTANEDIOL PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 20,000 t/year

Process.....	Formaldehyde ethynylation	Butadiene acetoxylation	Butadiene chlorination
Typical technology.....	Reppé	Mitsubishi	Toyo Soda
Battery limits investments (10^6 US\$)	37	38	23
Consumption per ton of 1,4-butanediol			
Raw materials			
Acetylene (t)	0.32	—	—
Butadiene (t)	—	0.72	1.25
37% Wt formaldehyde (t)	1.98	—	—
Acetic acid (t)	—	0.18	1.00
Chlorine (t)	—	—	270
95% vol. hydrogen (Nm^3)	600	300	—
By-products			
Butanol (kg)	(-)35	—	—
3,4-dichloro 1-butene (t)	—	—	(-)1.1
Utilities			
Steam (t)	9.0	12.0	20.0
Electricity (kWh)	180	660	1,000
Cooling water (m^3)	420	250	950
Process water (m^3)	4	1.5	—
Nitrogen (Nm^3)	25	240	—
Chemicals and catalysts (US\$)			
Caustic (kg)	3	4	—
Labor (Operators per shift).....	5	4	5

13.4.6 Uses and producers

Table 13.11 lists the average commercial specifications of 1,4-butanediol. Table 13.12 shows the main uses in 1984 expressed in per cent in Western Europe, the United States and Japan, as well as the production, capacities and consumption in these three geographic areas.

TABLE 13.11
AVERAGE COMMERCIAL SPECIFICATIONS OF 1,4-BUTANEDIOL

Characteristics	Values
Purity (%) min.	99
Melting point (°C) min.	19
Distillation range (°C)	221 to 231
Viscosity at 25°C (cP)	65 to 70
$d_4^{25(1)}$	1.012 to 1.016
Refractive index n_D	1.4435 to 1.4445
Appearance at 25°C	Colorless liquid
Color (Pt/Co) max.	20
Water (ppm) max.	4,000
Carbonyl index (mg KOH/g) max.	1.5

(1) Specific gravity, 77.0-39.2.

TABLE 13.12
1,4-BUTANEDIOL PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
γ-butyrolactone	9	23	—
Polybutylene terephthalate resins	8	13	47
Polyurethanes	29	9	39
Tetrahydrofuran	36	53	8
Miscellaneous ⁽²⁾	18	2	6
Total	100	100	100
Sources (% product)			
Acetylene	100	100	—
Butadiene acetoxylation	—	—	71
Butadiene chlorination	—	—	29
Total	100	100	100
Production (10 ³ t/year)	82	130	10
Capacity (10 ³ t/year) ⁽³⁾	120	173	21
Consumption (10 ³ t/year)	73	117	15

(1) Estimated values.

(2) Pharmaceuticals, plasticizers, polyesters, solvent uses.

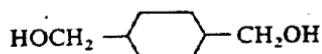
(3) The worldwide production capacity of 1,4-butanediol is that of Western Europe, the United States and Japan. In 1984 and 1986 the producers were the following:

United States: BASF Wyandotte (Geismar, La. = 30,000 t/year); Du Pont (La Porte, Tx. = 91,000 t/year); GAF (Calvert City, Ky. = 52,000 t/year). Western Europe: BASF (Ludwigshafen, West Germany = 90,000 t/year); GHC (GAF/Hüls) (Marl, West Germany = 30,000 t/year). Japan: Mitsubishi (Yokkaichi = 15,000 t/year); Toyo Soda (Shin Nanyo = 6,000 t/year).

In 1986 three companies raised their butanediol capacities. In the United States: GAF (Wyandotte to 70,000 t/year); in Western Europe: BASF (to 110,000 t/year) and GAF/Hüls (to 70,000 t/year). In Japan a new plant (18,000 t/year) was built by Du Pont/Idemitsu.

13.5 1,4-DIMETHYLOL CYCLOHEXANE

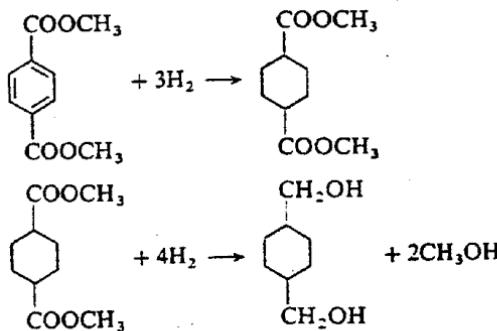
1,4-dimethylol cyclohexane or 1,4-dimethanol cyclohexane or 1,4 bis (hydroxymethyl) cyclohexane, with the following formula:



is a solid ($d_4^{25} = 1.038$ ⁽⁶⁾) (supercooled), mp = 41°C, bp_{1.013} = 280°C). It is used to manufacture the polyester fibers Kodel and Vestan, high-performance coatings and unsaturated polyesters, as well as a number of polyurethane foams. Since its industrial importance is very slight in comparison with ethylene glycol and butanediol, its manufacture will not be described in detail here.

It can be obtained by depolymerization and hydrogenation of polyethylene terephthalate in the presence of methanol, but it is produced industrially by *Tennessee Eastman* from dimethyl terephthalate.

The aromatic diester reduction takes place in two steps:



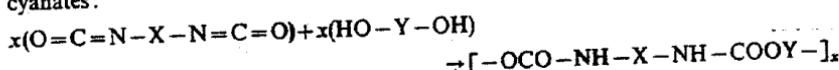
The first reaction takes place at between 160 and 180°C, under 30 to 40 . 10⁶ Pa absolute, in the presence of supported palladium. The operation is conducted in solution in the ester formed to prevent excessive temperature rise due to the exothermicity of the reaction. Molar selectivity of the saturated ester exceeds 95 per cent. The crude product obtained is sent to a hydrogenolysis reactor, where it is converted to dimethylol cyclohexane and methanol in the presence of copper chromite. The dimethylol cyclohexane obtained contains about 33 per cent of the cis isomer and 76 per cent of the trans isomer.

(6) Specific gravity, 77.0/39.2.

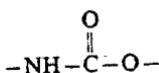
Chapter 14

MONOMERS FOR POLYURETHANE SYNTHESIS

Polyurethanes are macromolecules resulting from the polyaddition of diols and diisocyanates:



They are hence characterized by the repetition in their chain of the group:



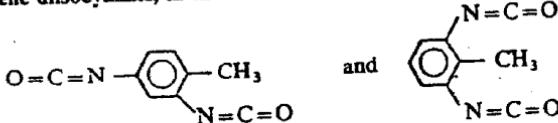
The variety of monomers helps to produce a very wide variety of products ranging from flexible foams to semi-rigid and rigid foams and elastomers, and including paints, surface coatings and adhesives.

14.1 MAIN MONOMERS USED INDUSTRIALLY TO SYNTHESIZE POLYURETHANES

The list of diisocyanates and polyols currently commercialized is relatively long. It mainly includes the following compounds, usually designated by an abbreviation.

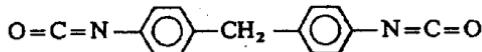
14.1.1 Diisocyanates

- TDI: tolylene diisocyanate, in the form of its 2,4- and 2,6-isomers:



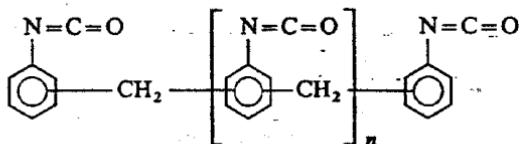
This is manufactured from toluene, by nitration to dinitrotoluene, which is then hydrogenated to tolylene diamine. This compound reacts with phosgene to yield TDI.

- MDI: diphenylmethane 4,4'-diisocyanate:

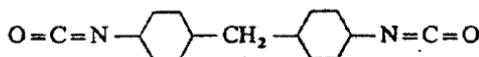


Its formation results from the condensation of formaldehyde and aniline, followed by the phosgenation of the resulting diamine.

- Polymeric MDI. The condensation of formaldehyde and aniline also causes the formation of the higher homologues, which are phosgenated to produce polyisocyanates:



- HMDI: hydrogenated diphenylmethane 4,4'-diisocyanate:



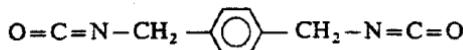
This is obtained by the phosgenation of the corresponding diamine, which is produced by the hydrogenation of the condensation product of aniline and formaldehyde.

- HDI: hexamethylene diisocyanate:



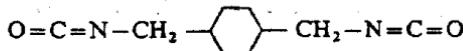
This is produced by the phosgenation of hexamethylenediamine.

- XDI: xylylene diisocyanate:



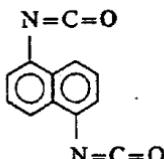
This is manufactured in three steps: ammonoxidation of *p*-xylene, hydrogenation of the resulting dinitrile to diamine, oxygenation of diamine.

- HXDI: hydrogenated xylylene diisocyanate:



The hydrogenation of the benzene ring is carried out on the diamine before phosgenation. Hydrogenated diamine can be obtained directly from the dinitrile.

- NDI: naphthalene diisocyanate:



This is produced by the phosgenation of the corresponding diamine.

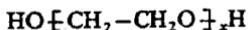
14.1.2 Polyols

The polyols employed in the manufacture of polyurethanes are divided into two main classes, polyether-polyols and polyester-polyols, the former being the most important commercially.

14.1.2.1 Polyether-polyols

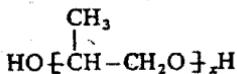
These are obtained by the reaction of a diol or triol with an epoxide. The most important are the following:

- PEG: polyethylene glycol:



This is obtained by the action of water or glycol on ethylene oxide.

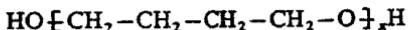
- PPG: polypropylene glycol:



This results from the action of water or propylene glycol on propylene oxide.

• PPG/PEG. This is a statistical or sequenced copolymer, and is manufactured by the addition of water or propylene glycol to a mixture of ethylene and propylene oxides.

- PTMG: polytetramethylene glycol:



This is produced by the action of water on tetrahydrofuran.

Other polyether-polyols, of lesser commercial importance, are obtained by the fixation on propylene oxide of polyols such as glycerin, trimethylolpropane, pentaerythritol, sorbitol, etc.

14.1.2.2 Polyester-polyols

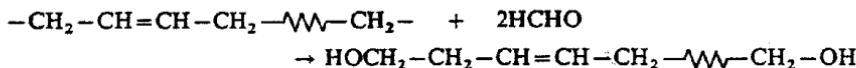
These compounds, widely employed at the outset of the development of polyurethanes, have been displaced from their market by polyether-polyols. For the production of rigid foams, however, use is still made of aromatic polyols produced by the transesterification of dimethyl terephthalate by glycol.

The esters of adipic acid are also used in the synthesis of thermoplastic elastomers and of certain flexible foams. The most widely used glycols for the esterification of adipic acid are ethylene glycol and 1,4-butanediol.

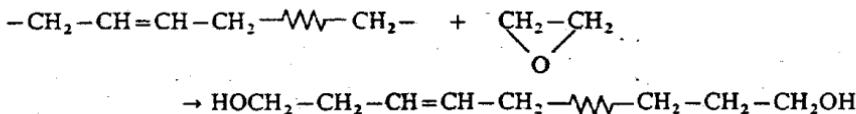
14.1.2.3 Other polyols

A third class of polyols, **polybutadiene-polyols**, is now emerging at the level of industrial development. They are obtained:

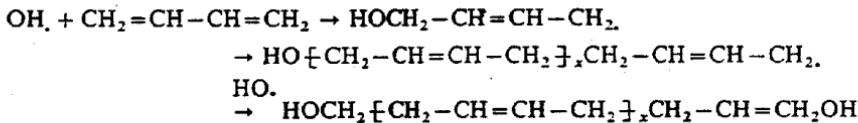
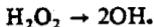
- By the anionic polymerization of butadiene and the functionalization of the active ends of the polymer by formaldehyde or ethylene oxide:



or:



- By free radical polymerization, in the presence of hydrogen peroxide, which acts as the reaction initiator and also as a reactant:



In both cases, butadiene is added at 1,4- and at 1,2-.

In this incomplete list of monomers for polyurethanes, the number of products that have witnessed significant industrial development is relatively small. With respect to diisocyanates, consumption in the United States in 1984 was about 490,000 t, essentially divided among TDI (50 per cent), MDI and polymeric MDI (47 per cent), with the remaining isocyanates accounting for about 3 per cent of the market.

For polyols, the demand distribution in the United States in 1984 was as follows: 94 per cent for polyether-polyols, less than 6 per cent for polyester-polyols, with polybutadiene-polyols accounting for less than 1 per cent of the market.

14.2 SYNTHESIS OF TOLYLENE DIISOCYANATE, TDI

Tolylene diisocyanate is a mixture of 2,4-tolylene diisocyanate (65 per cent) ($mp = 21.6^\circ\text{C}$) and 2,6-tolylene diisocyanate (35 per cent) ($mp = 8.3^\circ\text{C}$).

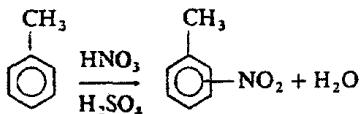
14.2.1 Conventional synthesis methods

Its manufacture, carried out on the industrial scale by *Allied*, *BASF* / *Badische Anilin und Soda Fabrik*, *Bayer*, *Dow*, *Du Pont*, *Mitsubishi*, *Mitsui*, *Mobay*, *Nippon Polyurethane*, *Nippon Soda*, *Olin*, *Progil*, *Sumitomo*, *Takeda*, *Union Carbide* etc., comprises three successive stages:

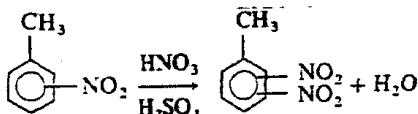
- Nitration of toluene to dinitrotoluene
- Reduction of dinitrotoluene to tolylene diamine.
- Phosgenation of diamine to tolylene diisocyanate.

14.2.1.1 Nitration of toluene to dinitrotoluenes (Fig. 14.1)

This conversion, initially developed by *Biazzini*, *Canadian Industries*, *Meissner*, etc., comprises two steps. In the first, a mixture of sulfuric and nitric acids is caused to react with toluene to form the three mononitrotoluenes (MNT) in the following proportions (per cent): ortho 59, meta 4, and para 37:



In the second step, using the same reagent, the mononitrotoluenes are converted to dinitrotoluenes (DNT), by controlling the acid concentration to prevent the formation of trinitrotoluenes:



A mixture of six isomers essentially containing 2,4-DNT (about 80 per cent) and 2,6-DNT (about 20 per cent) is obtained, hence the designation DNT 80/20. In fact, slightly less than 80 per cent of the 2,4-isomer is formed, and the total of the 2,3-, 2,5-, 3,4- and 3,5-isomers is up to 3 to 4 per cent. The first nitration stage is conducted in a series of agitated reactors equipped with internal or external cooling systems. The feed consists of toluene and a mixture of nitric and sulfuric acids, water, and traces of dinitrotoluenes resulting from the recycling of the aqueous phase collected at the end

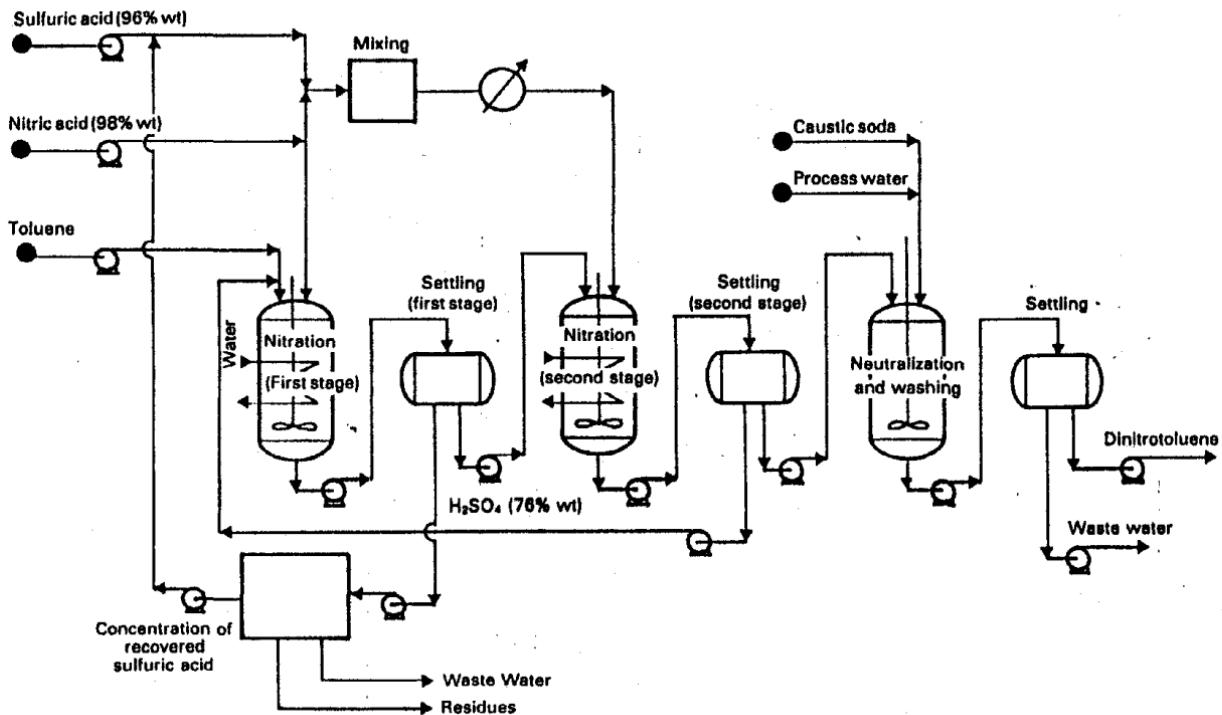


Fig. 14.1. Tolylene diisocyanate manufacture. Nitration of toluene to dinitrotoluenes.

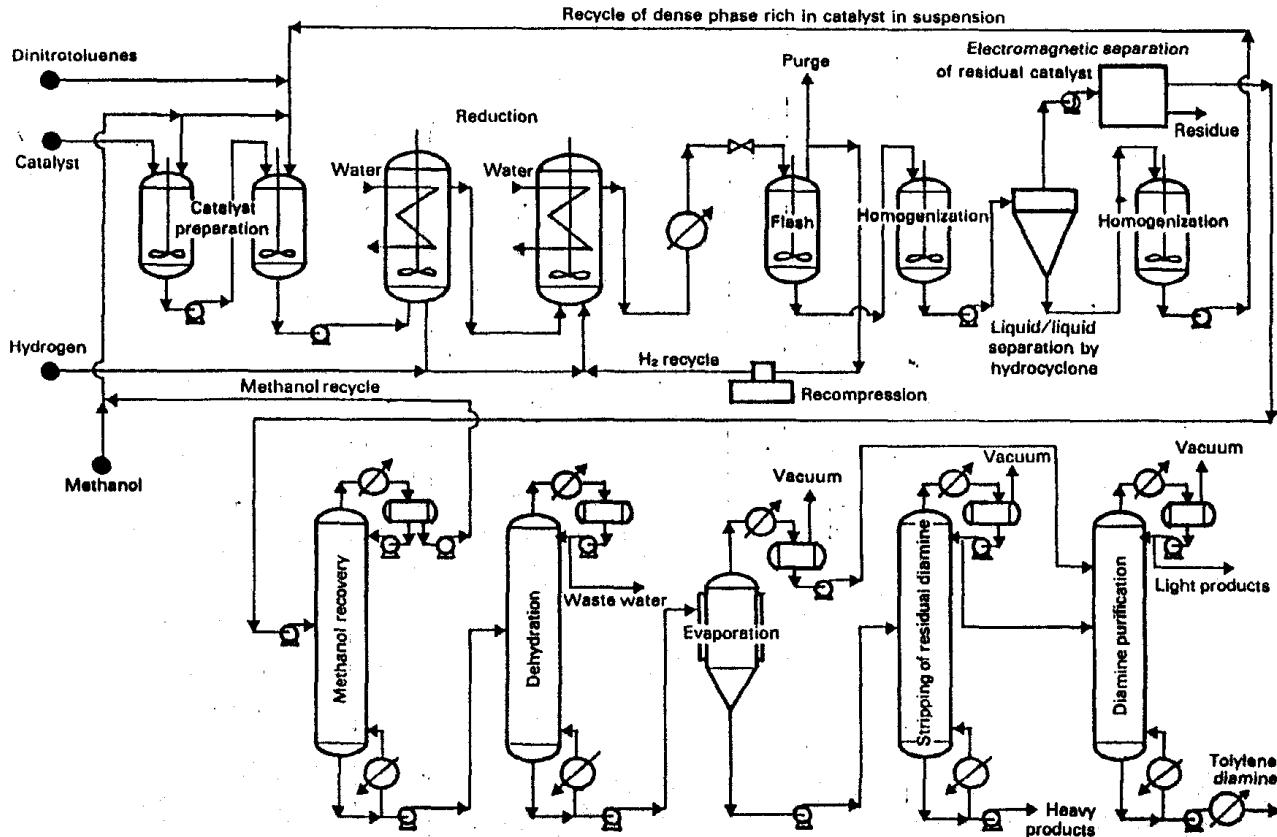


Fig. 14.2. Toluylene diisocyanate manufacture. Reduction of dinitrotoluenes to tolylene diamine.

of the second reaction step. The cooling system serves to maintain the temperature in the neighborhood of 50°C. The reactor effluent produces an aqueous phase by settling, containing sulfuric acid (74 per cent weight), nitric acid and mono- and dinitro-compounds. An organic phase containing the desired mononitro derivatives with some acids and water serves as a feed for the second series of nitration reactors, in which concentrated sulfuric and nitric acids are also introduced. This reactor operates at 65°C. The effluent obtained is sent to a second settler to separate the dilute acids, which are recycled to the first reaction step, and the nitrotoluenes which still contain water and traces of acid. These crude dinitrotoluenes are sent to a series of caustic soda neutralization and water scrubbing columns, operating in countercurrent contact. A final settler separates the water from the dinitrotoluenes, which may have to undergo final distillation.

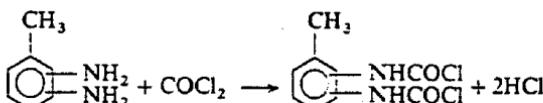
14.2.1.2 Reduction of dinitrotoluenes to tolylene diamine (Fig. 14.2)

The reduction of dinitrotoluenes to tolylene diamine occurs catalytically by hydrogen in the presence of Raney nickel, kept in suspension in the reaction medium by means of methanol used as a solvent. It is not accompanied by any isomerization. Diamine selectivity is up to 99 molar per cent.

The transformation takes place in agitated reactors in series, under a hydrogen partial pressure of $8.5 \cdot 10^6$ Pa absolute and at a temperature kept near 170°C by the circulation of water in coils placed in the upper and lower parts of the reactors. The effluent obtained is cooled to about 70°C and then flashed at about $0.8 \cdot 10^6$ Pa absolute. The hydrogen liberated is recompressed and recycled. The liquid withdrawal, after homogenization by agitation, is fractionated in a battery of hydrocyclones. The dense phase separated, containing about 9 per cent weight of catalyst, is recycled, while the lighter fraction, which still contains 0.05 per cent weight catalyst, is sent to an electromagnetic separator to reduce the catalyst content to about 0.02 per cent weight. The product is then purified by distillation. The first column separates methanol at the top ($\cong 20$ trays) which is recycled. The second ($\cong 15$ trays) removes the water in the distillate and leaves a product containing less than 0.4 per cent weight water at the bottom. By vacuum evaporation, this withdrawal produces vapors which are finally rectified (9 to 10 kPa absolute, $\cong 40$ trays) to produce the diamine in the required purity, while the residue is treated in a column (8 to 9 kPa absolute, 15 trays) to recover the diamine it contains at the top, which is then recycled to the previous distillation. The bottom effluent containing heavy compounds and tars is eliminated.

14.2.1.3 Phosgenation of tolylene diamine (Fig. 14.3)

Tolylene diamine reacts with phosgene in two steps. The first, which is very fast, takes place at low temperature (0 to 30°C) and leads to tolylene dicarbamyl dichloride:



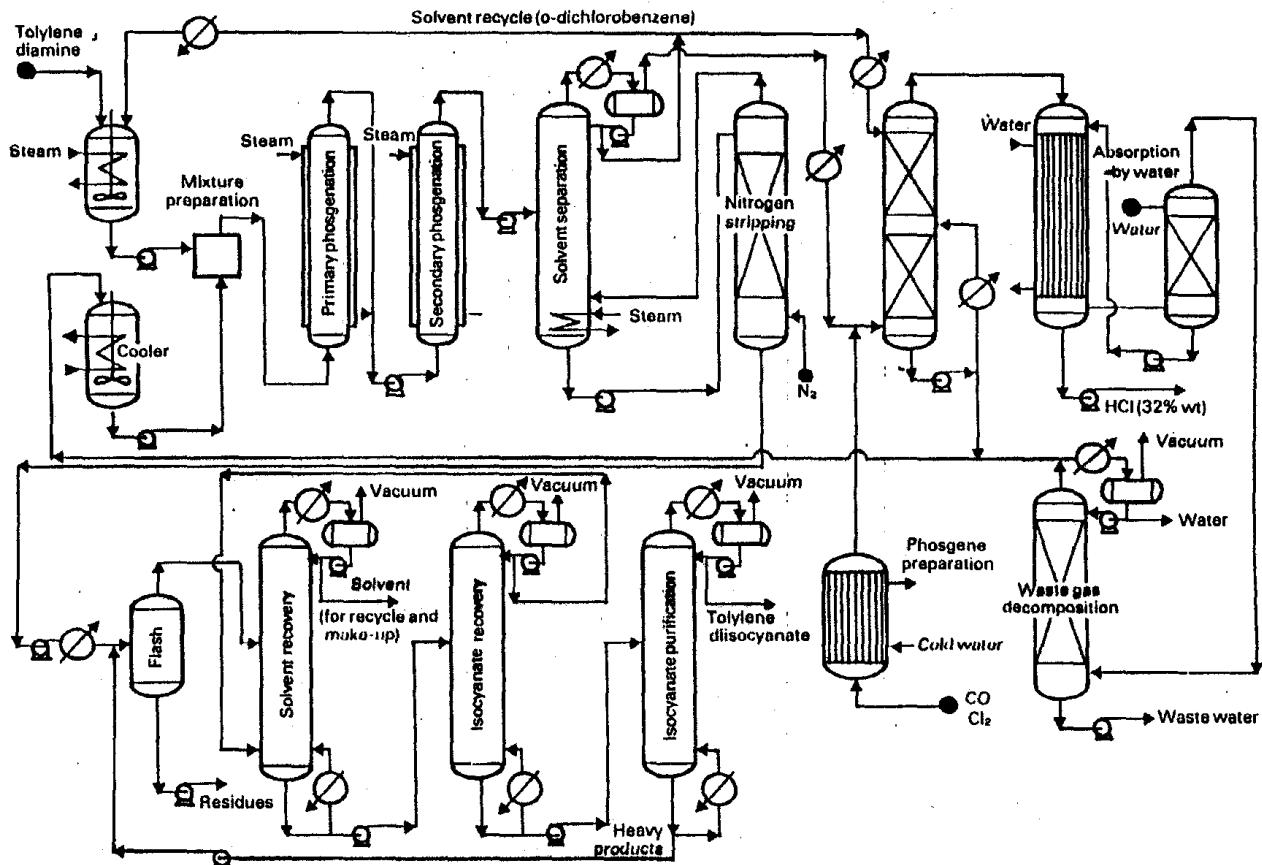
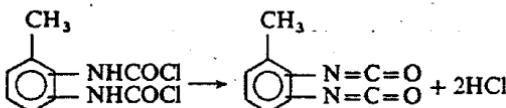


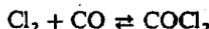
Fig. 14.3. Toluylene diisocyanate production by phosgenation of toluylene diamine.

The second, which is slower, is conducted around 170°C, with a residence time of 2 to 3 h:



Under these conditions, the conversion of tolylene diamine to tolylene diisocyanate may be up to 80 per cent. The remaining 20 per cent consists of a residue which, by alkaline hydrolysis, can reform the starting diamine, that can be recycled or commercialized as polymeric isocyanate.

Phosgene is manufactured by the reaction of excess chlorine with carbon monoxide in the presence of activated charcoal, at a temperature of about 50°C:



Thus the initial reactants consist of phosgene, in a 30 per cent weight solution in orthodichlorobenzene, and tolylene diamine, also in a 15 per cent weight mixture in the same solvent. These reactants are introduced into a series of so-called primary phosgenation reactors, after passage through a mixing valve to ensure a 50 per cent excess of phosgene over stoichiometry. The effluent obtained is then sent to finishing or so-called secondary reactors. Both of these reactors are vertical, jacketed vessels allowing for steam heating, and equipped with plates in a baffle arrangement to favor mixing of the reactants.

Separation treatment of the products formed comprises fractionation by absorption/desorption ($\cong 10$ trays) of the solvent, and of phosgene and hydrogen chloride in gaseous form, introduced at the base of an absorber operating in countercurrent contact with cold *o*-dichlorobenzene (15°C). The solution obtained at the bottom is recycled. The gaseous effluent recovered at the top, consisting of about 90 per cent hydrogen chloride, phosgene and inert gases, is sent to a new absorption step, with water in this case, producing a withdrawal containing 32 per cent weight of hydrochloric acid. The residual gases are decomposed by a countercurrent of water to CO_2 and HCl , on an activated charcoal bed, while the organic compounds they contain are absorbed. Crude tolylene diisocyanate is collected at the bottom of the initial absorption/desorption device and stabilized by nitrogen stripping to reduce its phosgene content to 0.04 per cent weight.

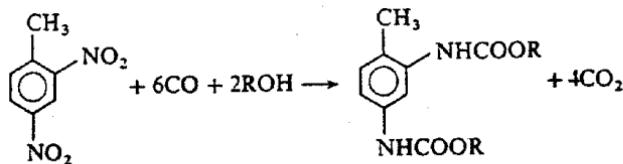
TDI purification involves the following steps in succession:

- Flash to remove the heavier components.
- Vacuum preconcentration (10 kPa absolute, $\cong 20$ trays) to complete the previous separation, of which the withdrawal is redistilled (10 kPa absolute, $\cong 30$ trays) to recover the TDI it contains.
- A finishing column (10 kPa absolute, packings).

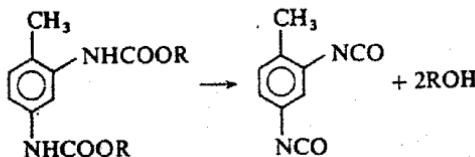
High-alloy steel is used as the material in the final column, and carbon steel in the others.

14.2.2 Other industrial methods: direct carbonylation of dinitrotoluenes to TDI

The problems raised by the handling of phosgene and the hazards this entails have led to the development of different methods to synthesize TDI. *Mitsui Toatsu Chemicals* in Japan has developed a process based on the carbonylation of dinitrotoluenes in the presence of an alcohol. The catalyst employed to do this is palladium-on-charcoal. It operates in the presence of ferric chloride and pyridine. The diurethane (or dicarbamate) of the alcohol used is obtained:



The diurethane is then thermally decomposed to diisocyanate and alcohol:



The carbonylation reaction takes place at 160°C , and $7 \cdot 10^6 \text{ Pa}$ absolute. Dinitrotoluene conversion is virtually complete, for a residence time of 2 1/2 hours. After cooling to 60°C , the effluent obtained is flashed. The CO_2 formed is extracted by diethanolamine, and excess CO is recycled. The liquid fraction is filtered to remove the catalyst. Distillation is then practised at atmospheric pressure to separate the alcohol (methanol), followed by the carbamate, which is decomposed under vacuum in a series of three reactors, around 250°C , in the presence of zinc naphthenate as catalyst.

The molten carbamate is first mixed with a paraffin fraction. A stream of nitrogen removes the methanol as it is formed, to prevent the recombination of isocyanate with alcohol. The effluent from the final reactor is purified in a series of three distillation columns. The first separates methanol at the top, the second the paraffin fraction, and the third, operating under vacuum, serves to collect the TDI at the bottom.

The economic advantages of this process over conventional phosgenation do not appear to be adequate for the promotion of its industrial development today.

14.2.3 Economic data

Table 14.1 provides some data of an economic nature concerning the production of tolylene diisocyanate.

TABLE 14.1
TOLYLENE DIISOCYANATE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Process	Nitration of toluene to dinitrotoluenes	Reduction of dinitrotoluenes to tolylene diamine	Phosgenation of tolylene diamine
Production capacity (t/year)	60.000	40.000	50.000
Battery limits investments (10^6 US\$)	18 ⁽¹⁾	17	26
Consumption per ton of product			
Raw materials			
Toluene (t)	0.52	—	—
Dinitrotoluenes (t)	—	1.56	—
Tolylene diamine (t)	—	—	0.82
By-products			
Hydrochloric acid (t)	—	—	(—)0.90
Heavy products (kg) ⁽²⁾	—	—	(—)80
Chemicals			
Hydrogen (kg)	—	140	—
Carbon monoxide (t)	—	—	0.43
Chlorine (t)	—	—	0.96
98% nitric acid (t)	0.74	—	—
96% sulfuric acid (t)	5	—	—
58% caustic soda (kg)	7	—	—
<i>o</i> -dichlorobenzene (kg)	—	—	15
Utilities			
Steam (t)	0.3	2.5	0.3
Electricity (kWh)	55	300	450
Fuel (10^6 kJ)	2.0	10.0	14.0
Cooling water (m ³)	80	400	250
Process water (m ³)	0.5	—	4
Nitrogen (Nm ³)	30	30	100
Catalysts and miscellaneous (US\$)	2	12	4
Labor (Operators per shift)	4	3	5

(1) Including sulfuric acid reconcentration.

(2) Impure tolylene diamine.

14.2.4 Uses and producers

Table 14.2 offers an indication of the average commercial specifications of tolylene diisocyanate. Table 14.3 lists the main uses in 1984, expressed in per cent, in Western Europe, the United States and Japan, as well as the production capacities and consumption at the same date for these three geographic areas.

TABLE 14.2
AVERAGE COMMERCIAL SPECIFICATIONS OF TOLYLENE DIISOCYANATE

Characteristics	Values
Purity (%) min.	99.5
Content of 2,4-isomer (%)	80 ± 2
Content of 2,6-isomer (%)	20 ± 2
Melting point (°C)	14
Total chlorides (ppm) max.	500
Hydrolysable chlorine (ppm) max.	70
Acidity (expressed as HCl) (ppm) max.	40
Color (Pt. Co) max.	50

TABLE 14.3
TOLYLENE DIISOCYANATE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Polyurethane foams	94	90	83
Flexible	92	90	75
Rigid	2	—	8
Non-foam uses	6	10	17
Elastomers	1	3	—
Coatings	—	5	12
Miscellaneous ⁽¹⁾	5	2	5
Total	100	100	100
Production (10^3 t/year)	285	305	75
Capacity (10^3 t/year) ⁽²⁾	375	315	80
Consumption (10^3 t/year)	180	245	65

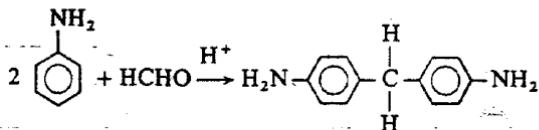
(1) Adhesives, sealants.

(2) The worldwide production capacity of tolylene diisocyanate was about $0.85 \cdot 10^6$ t/year in 1984 and $0.88 \cdot 10^6$ t/year in 1986 with the following distribution:

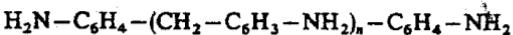
United States	0.28	Western Europe	0.38	Middle East	—
Canada	0.02	Eastern Europe	>0.05	Japan	0.08
Latin America	0.06	Africa	—	Asia and Far East	0.01

14.3 SYNTHESIS OF DIPHENYLMETHANE 4,4'-DIISOCYANATE MDI AND POLYMERIC MDI

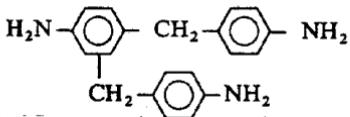
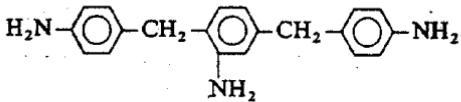
The industrial manufacture of MDI and polymeric MDI, particularly by *ARCO* (*Atlantic Richfield Co.*), *BASF*, *Bayer*, *ICI* (*Imperial Chemical Industries*), *Mitsui*, *Mobay*, *Montedison*, *Nippon Polyurethane*, *Olin*, *Takeda* and *Upjohn*, starts with the condensation of formaldehyde and aniline, with the formation of diaminodiphenylmethane or methylene diphenyldiamine:



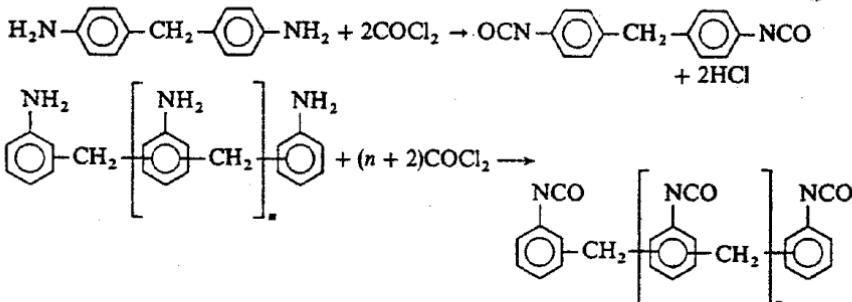
This condensation, catalyzed by acids, takes place chiefly at 4,4'- and, to a lesser extent, at 2,4'-, with the appearance of the 2,4'-isomer facilitated by raising the temperature or by excess aniline. However, an aniline deficiency favors the reaction of formaldehyde with the diamine produced, with the formation of polyamines with the general formula:



These triamines, tetramines, etc., are mixtures of 4,4'-, 2,4'-, 2,4'- and 2,2'-isomers:



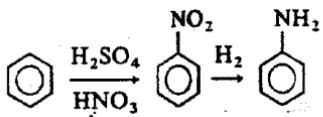
The phosgenation of methylene diphenyldiamine yields methylene diisocyanate, while that of the polyamines leads to polymeric MDI:



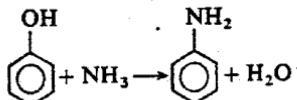
14.3.1 Aniline manufacture

60 to 70 per cent of the consumption of aniline ($d_4^{20} = 1.0217^{(1)}$, mp = -6.3°C , bp_{1.013} = 184.1°C) in the United States and in Western Europe is used to manufacture MDI and polymeric MDI. About 20 per cent is used in the rubber industry, while the remainder, less than 20 to 10 per cent, is consumed in the pharmaceutical industry, dyestuffs and different organic syntheses.

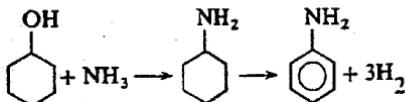
The most widely used process to synthesize aniline industrially consists in reducing nitrobenzene resulting from the nitration of benzene:



Another method, developed by *Mitsui* in Japan and currently being industrialized at *US Steel Chemicals* in the United States, carries out the vapor phase ammoniolysis of phenol on alumina:



Another process, developed by *Halcon*, but not yet at the industrial stage, consists in the ammoniolysis of cyclohexanol and the dehydrogenation of the cyclohexylamine obtained:



14.3.1.1 Nitrobenzene manufacture

A. Biazzì process (Fig. 14.4)

This represents the standard technology that is most widespread in the industry. Its specific aspect is the use of continuous liquid/liquid separators of the Biazzì type, with an inclined cylindrical shell, equipped with truncated cone top and bottom and allowing the introduction of the feed at the interface, thus accelerating the settling process.

In this process, the initial benzene is first introduced into an extractor where it is placed in contact with the acid residue resulting from the subsequent nitration, in order to absorb the residual nitrobenzene content. The mixture formed is settled in a Biazzì separator. The upper organic phase, representing the extract, is sent to the reaction

(1) Specific gravity, 68.0'39.2.

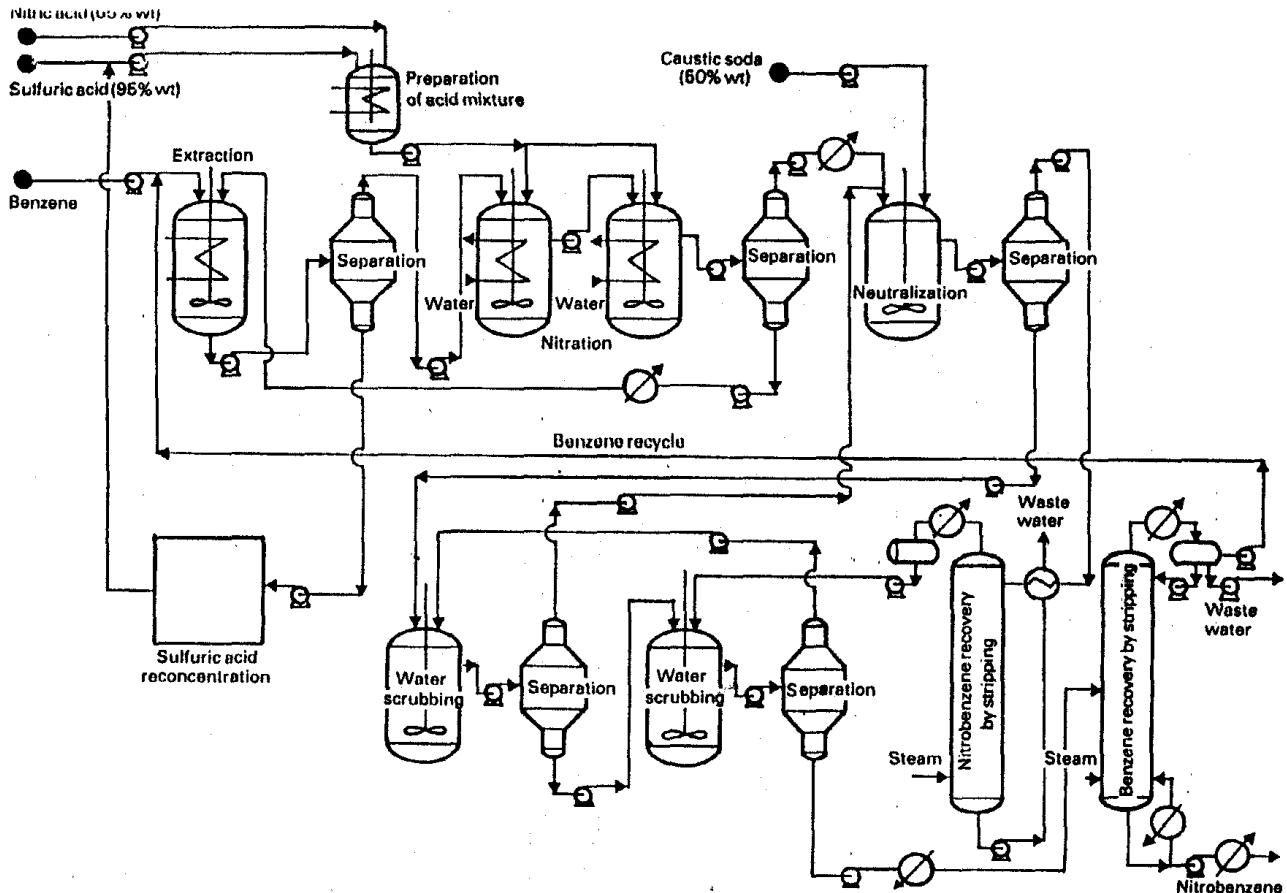


Fig. 14.4. Nitrobenzene manufacture. Biazzli process.

system, while the lower acid layer, consisting essentially of dilute sulfuric acid (68 per cent weight) is reconcentrated by evaporation (95 per cent weight) and then recycled.

Nitration is carried out in a series of agitated reactors, equipped with internal cooling coils, where the temperature is kept at about 60°C by means of cold water circulation. The feed consists of a mixture of sulfuric (95 per cent weight) and nitric (65 per cent weight) acids and the organic phase from the Biazz separator. A similar system is also employed to treat the reactor effluents and to settle a bottom acid phase, directly recycled to the initial extractor, and an upper organic phase rich in nitrobenzene.

The purification of this crude product comprises neutralization by 50 per cent weight caustic soda, followed by water washings conducted in a succession of mixers alternating with Biazz separators. Systematic recycling of the aqueous phases recovered to the previous stage ensures a pseudo-countercurrent which helps to remove the inorganic and organic acids (picric acid) nearly completely, together with the nitrophenols. The solution isolated at the end, in other words at the top of the neutralizer, is stripped by steam to recover its residual nitrobenzene content, and then eliminated. The organic layer from the final Biazz separator is rid of the benzene it contains, also by stripping.

B. Adiabatic nitration

To prevent the nitration reactors from cooling, the reaction should be carried out adiabatically. The process developed by *Du Pont* uses the heat of reaction for the azeotropic evaporation of benzene and water. Unfortunately, this variant is very costly in terms of investments.

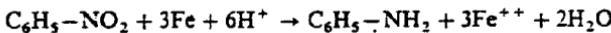
American Cyanamid has industrialized a process which limits the temperature rise. To do this, it uses a large excess of acid (14 times the weight of benzene to be nitrated, instead of 3 in the conventional method). Under these conditions, the acid absorbs the heat generated by the reaction, and the temperature does not exceed 145°C, thus preventing undesirable side conversions, but increasing the reaction rate in comparison with the conventional process. Before recycling, moreover, the acid is concentrated at this temperature, with a slight additional heat input.

14.3.1.2 Reduction of nitrobenzene to aniline

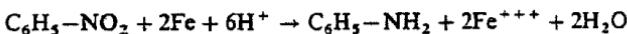
A. Béchamp process

This older technique, which uses a mixture of iron filings and hydrochloric acid to reduce nitrobenzene to aniline, is employed today only to produce iron oxide pigments, with aniline produced as a by-product.

The reactions in this type of process are as follows:



and



The ferrous and ferric ions appear in the form of the hydroxides Fe(OH)_2 and Fe(OH)_3 , which combine to form the magnetic oxide Fe_3O_4 . In the presence of other oxides and in accordance with the operating conditions, pigments are obtained ranging in color from yellow to brown or black.

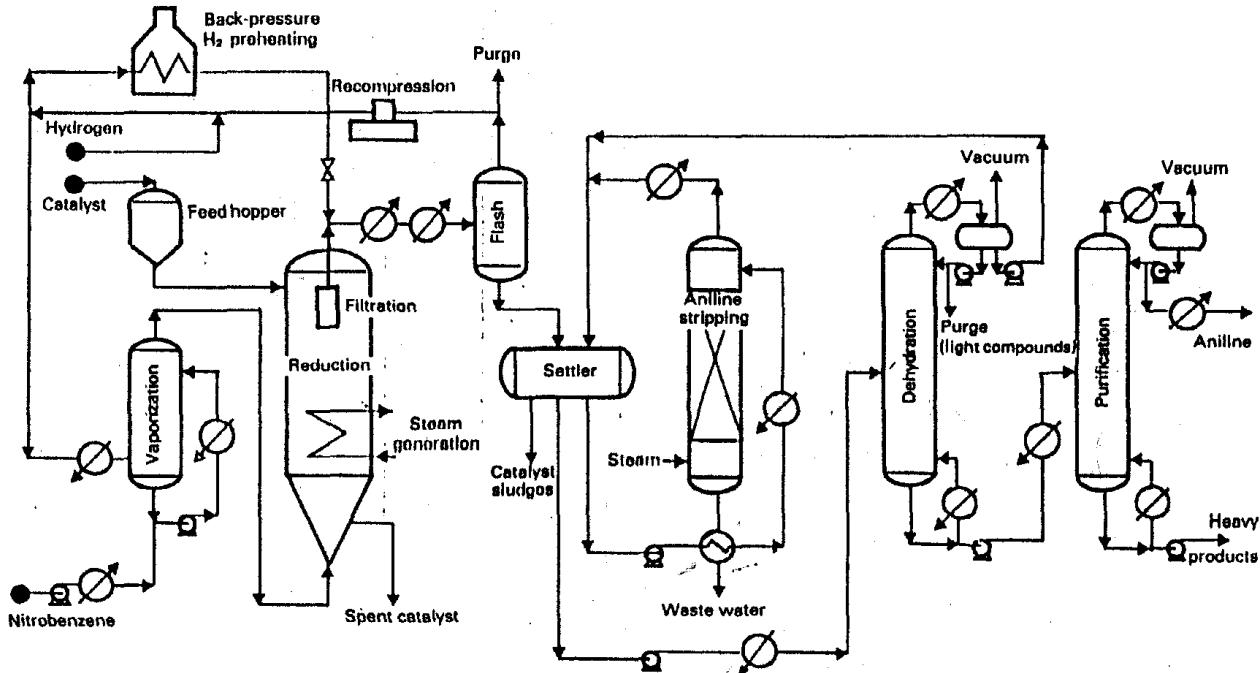


Fig. 14.5. Aniline production by vapor phase hydrogen reduction of nitrobenzene. Conventional process.

B. Conventional techniques (Fig. 14.5)

The method developed today are based on the catalytic reduction of nitrobenzene by hydrogen in the vapor phase. This can be carried out in liquid medium, but problems of recovery of the solvent employed to achieve this and of the catalyst entail substantially higher investments.

In the vapor phase techniques, nitrobenzene, first preheated to 180°C by heat exchange with the reactor effluent, is then partly vaporized, and the liquid fraction recirculated. Make-up and recycle hydrogen is then added to it, in a hydrogen/nitrobenzene molar ratio of about 9/1. The gaseous mixture obtained is introduced at the bottom of a hydrogenation reactor with a fluidized catalyst bed, consisting of copper-on-silica, in which water circulation in a tube bundle removes the heat generated by the transformation and produces medium-pressure steam ($1.7 \cdot 10^6$ Pa absolute). A disengagement zone, in the upper part of the reaction system, allows the direct recovery by gravity of most of the solid particles entrained in the gases produced. It is also equipped with metallic filters, periodically regenerated in halves by means of hot hydrogen back-pressure to remove catalyst deposits.

The reactor effluent, available at between 0.2 and $0.25 \cdot 10^6$ Pa absolute and at about 280°C, is cooled to 40°C, particularly by heat exchange with the hydrogen and nitrobenzene feeds. In this way it is partly condensed. The gaseous fraction, essentially containing hydrogen, is recycled after recompression. A previous purge prevents the buildup of impurities in this loop. The liquid part, mainly containing aniline and water, is settled. The lower aqueous phase is rid of the amine it contains by stripping. The water/aniline heteroazeotrope obtained at the top ($\text{bp}_{1.013} = 56.3^\circ\text{C}$, water content 84 per cent weight) is condensed and returned to settling. The upper organic phase is dehydrated by vacuum fractionation (30 to 40 kPa absolute, $\cong 30$ to 35 trays). The organic fraction resulting from the separation of the heteroazeotrope recovered at the top serves as reflux. The aqueous part is added to the previous aqueous phase. The crude aniline withdrawn is purified, also by vacuum distillation (30 to 40 kPa absolute, $\cong 50$ trays).

The catalyst system must be rid periodically of the deposits formed by controlled combustion with air, between 250 and 350°C. This operation, which lasts about 1 1/2 to 2 days, is preceded and followed by a nitrogen purge of the equipment. Before restartup, it also requires reduction by hydrogen, at about 250°C, of the copper oxide that may have been formed during the oxidizing treatment.

The molar selectivity for aniline is up to 99.6 per cent, for a nitrobenzene conversion of 99.7 per cent. The main impurities are nitrosobenzene, cyclohexylamine, diphenylamine, phenylcyclohexylamine and aminophenols.

14.3.1.3 Aniline synthesis by ammoniolysis of phenol (Fig. 14.6)

Two plants in the world use this process developed by *Halcon*. One belonging to *Mitsui Petrochemical* has been in operation in Ichihara in Japan since 1970 (30,000 t/year). The second is on stream in the *US Steel* complex in Haverhill in the United States (90,000 t/year).

Transformation takes place in the vapor phase, around 400 to 420°C, at about $1.6 \cdot 10^6$ Pa absolute (at the beginning of the cycle), with a large excess of ammonia in relation to phenol (molar ratio 20/1), and in the presence of a catalyst consisting of silica/alumina

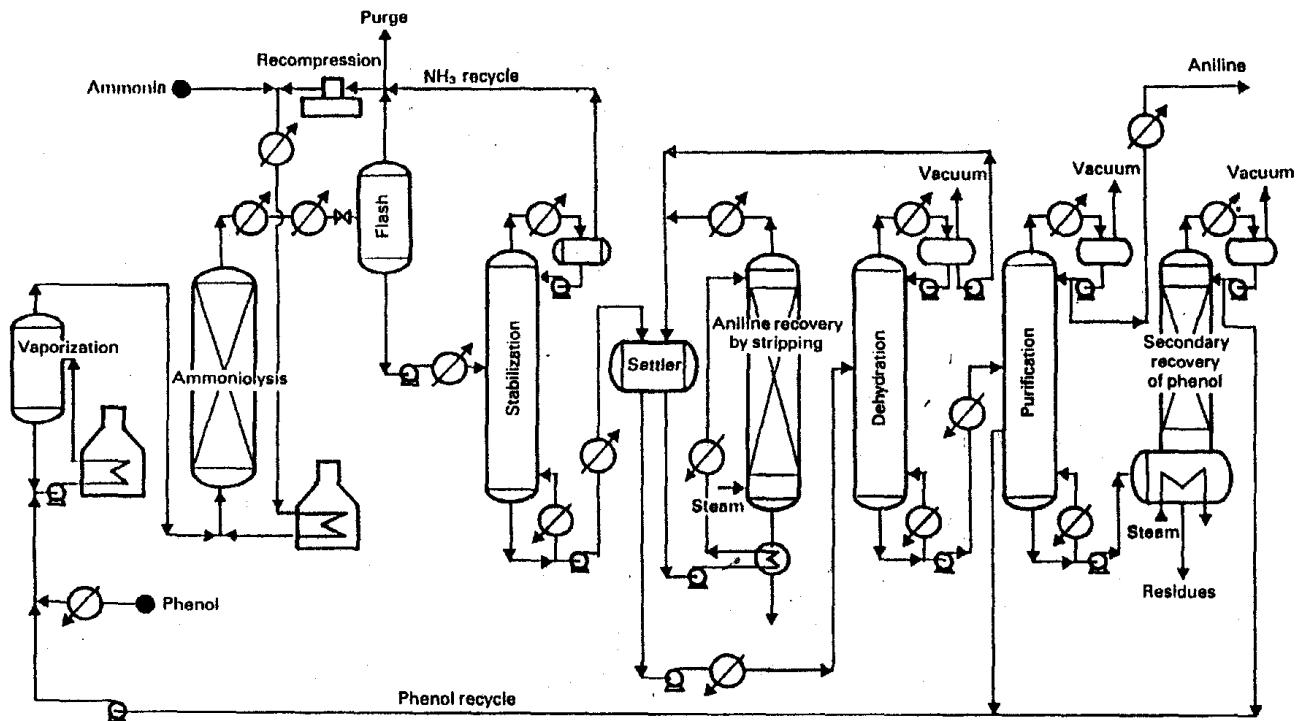


Fig. 14.6. Aniline production by phenol ammoniolysis. Halcon process.

placed in a fixed bed adiabatic reactor. The temperature must be raised progressively to offset the deactivation of the catalyst system. Once the temperature reaches 500°C, the catalyst is regenerated by controlled combustion with air, after the installation has been purged with nitrogen. Run length is about one to two months and reactivation lasts about 20 h. For a phenol conversion of 95 per cent, the molar selectivity of aniline is up to 98.3 per cent. 1.5 per cent of diphenylamine is formed with about 0.2 per cent of heavier impurities (triphenylamine, carbazole, etc.).

The reactor effluent is cooled to 60°C, particularly by heat exchange with the phenol and ammonia feeds, in order to condense the water and organic compounds. The gases are partly purged, but mostly recompressed and then recycled. The liquid fraction is first stabilized (15 to 20 trays), the ammonia recovered at the top is recirculated, and the liquid is then settled. The amine in the bottom aqueous fraction is recovered as above, by stripping, in the form of a heteroazeotrope with water. The upper organic phase, after vacuum dehydration (30 to 35 trays), is fractionated, also under vacuum (20 kPa absolute, ≥ 100 trays) to recover aniline to specifications at the top, and an aniline/phenol azeotrope at the bottom ($bp_{1.013} = 186^\circ\text{C}$, phenol content 42 per cent weight), which is returned to the reactor.

This process compares favorably with the conventional method, passing through nitrobenzene, in terms of investments, but its profitability is heavily influenced by the price of the phenol employed.

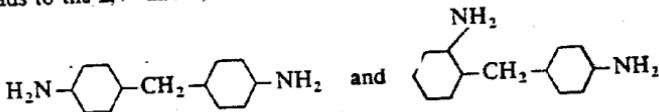
14.3.2 Synthesis of MDI and polymeric MDI

14.3.2.1 Conventional industrial methods

MDI and its polymers are synthesized in two steps. The first yields diphenylmethane diamine or polymethylene polyphenyl amines, and the second consists of the phosgenation of the amine obtained.

A. *Synthesis of polyamines* (Fig. 14.7)

The condensation of formaldehyde with excess aniline, in the presence of an acid (HCl), leads to the 2,4'- and 4,4'-diaminodiphenylmethanes:



Increasing the temperature or the aniline/formaldehyde ratio favors the formation of the 2,4'-isomer over that of the 4,4'-isomer. If the excess aniline is insufficient, a large proportion of the diaminodiphenylmethane continues its condensation with formaldehyde, forming a mixture of triamine, tetramine, etc., which constitutes the polymethylene polyphenylene amine (PMPPA), which is phosgenated to yield polymeric MDI.

Although the use of a suitable aniline/formaldehyde ratio makes it possible to produce the diamine only, MDI manufacturers integrate this production with that of the polyamines precursors of polymeric MDI. Hence only the manufacture of polyamines is

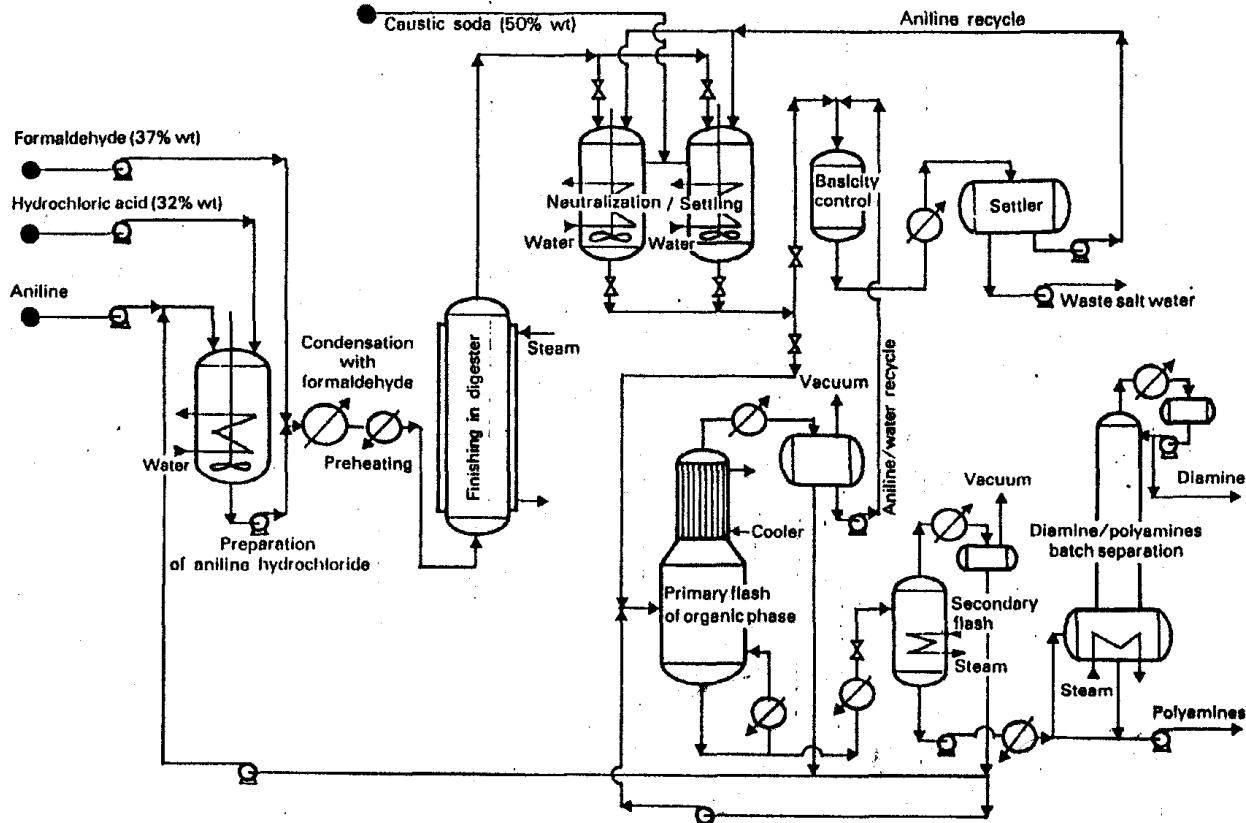


Fig. 14.7. Synthesis of MDI and polymeric MDI. Production of diaminodiphenylmethane and polymethylene polyphenylene amines. Conventional process.

described here, which consists in causing aniline hydrochloride to react with formaldehyde.

The hydrochloride is prepared semi-continuously in agitated reactors, in which a 33 per cent weight excess of aniline is caused to react with a 32 per cent weight hydrochloric acid solution. The heat generated by the reaction is removed by cooling water circulation in a double shell.

The aniline hydrochloride formed and a 37 per cent weight formaldehyde solution are then introduced into another so-called condensation reactor, in which the temperature is maintained between 50 and 70°C by cold water circulation. The reactor is a genuine double pipe heat exchanger in which the reaction is not pushed to its extreme. It is completed, after heating, in a "digester" operating between 100 and 105°C, at $0.35 \cdot 10^6$ Pa absolute, with a residence time of about 4 h. The product recovered at the top is neutralized with caustic soda (50 per cent weight), in sufficient quantities to reach a pH of between 10 and 12, while maintaining the temperature around 95°C. This is a batch operation in agitated and jacketed vessels placed in parallel. After settling, the bottom phase, consisting of salt water, whose basicity is ensured, is cooled, and then sent to a second settler in which the aniline, whose solubility is reduced, is separated and recycled to neutralization. The residual salt water is removed. The upper organic phase consists essentially of polyamines, and also contains aniline (10 per cent weight) and water (5 per cent weight).

Purification comprises a preliminary removal of excess aniline by vacuum flash distillation at about 170°C, under 8 to 9 kPa absolute. The water and amine recovered at the top are condensed and settled. The liquid fraction is again flashed at about 230°C, under high vacuum (<1 kPa absolute), allowing recovery of the remaining aniline at the top and its recycle. The polyamines obtained at the bottom are cooled and stored at 100°C for subsequent phosgenation.

If the desired product is the pure diamine, a fraction of the polyamines produced is subjected to batch distillation, providing diamine in the distillate. The withdrawal is sent to polyamine storage.

A variant of the process for manufacturing the mixture of polyamines consists in performing the condensation of formaldehyde and aniline in the presence of a sodium chloride solution (Mobay process). This alternative offers the advantage of avoiding the costly operation of the neutralization of the starting amine by hydrochloric acid.

B. Phosgenation of polyamines (Fig. 14.8)

Phosgene, produced by the reaction of chlorine with carbon monoxide, is absorbed in monochlorobenzene to a concentration of 20 per cent weight. The solution obtained is kept at a temperature below 10°C to prevent the phosgene from evaporating. Polyamines are also dissolved in monochlorobenzene to a content of about 18 per cent weight, and kept at 70°C to reduce the viscosity. The two solutions are mixed in proportions such that the excess phosgene is 200 molar per cent and the solvent/amine molar ratio is between 17/1 and 20/1. The mixture of the two reactants, which have already partly reacted by simple contact, is then sent to a series of three phosgenation reactors where the temperatures rise progressively from 50 to 120°C and then to 140°C at the outlet.

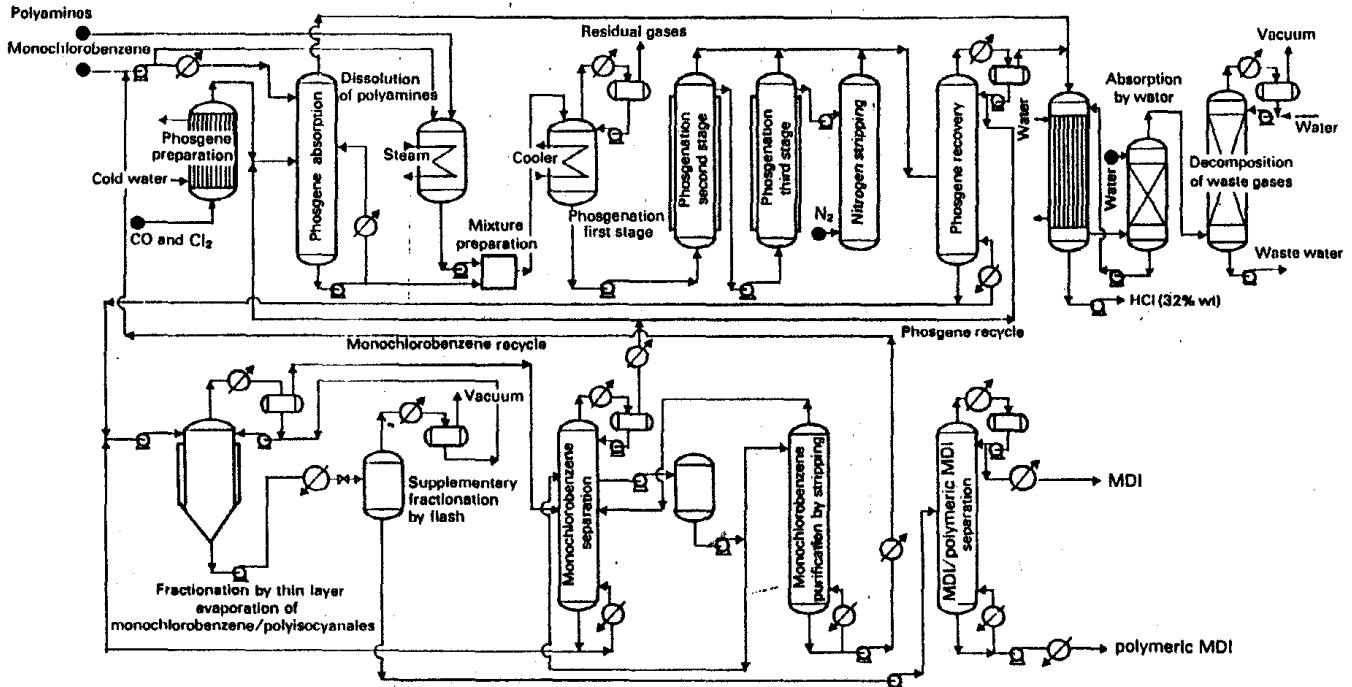


Fig. 14.8. Production of MDI and polymeric MDI by phosgenation of polymethylene polyphenylene amines. Conventional process.

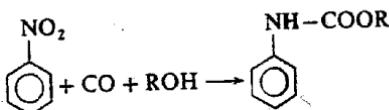
Most of the excess phosgene and hydrochloric acid formed, as well as about 80 per cent of the monochlorobenzene, are removed at the top of the phosgenation reactors and recycled. The liquid stream from the final reactor is sent to a purification train comprising the following main operations:

- (a) Stabilization during which phosgene and hydrochloric acid are removed by nitrogen stripping.
- (b) Phosgene recovery and separation of its two main impurities, monochlorobenzene and hydrochloric acid, by distillation (10 to 15 trays).
- (c) Passage in a thin layer evaporator, to remove the final remaining traces of phosgene and monochlorobenzene, without the risk of decomposition of the polyamines.
- (d) Purification of the polyamines by vacuum flash distillation (1.5 to 2 kPa absolute) at 180°C, the thermal level reached after preheating by HP steam in a double-pipe heat exchanger.

Furthermore, fractionation by distillation (20 to 25 trays), followed by stripping, is provided to recover the monochlorobenzene, together with an acid effluent treatment section to regenerate a 32 per cent weight hydrochloric acid after having removed the phosgene by absorption and decomposition by water to CO₂ and HCl.

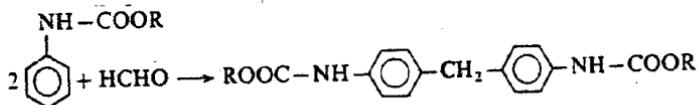
14.3.2.2 ARCO direct nitrobenzene carbonylation process

Atlantic Richfield Company (ARCO) has developed a method for synthesizing MDI and its polymers, which avoids the use of aniline and phosgene, and consequently the production of hydrochloric acid. In this process, carbon monoxide and an alcohol (methanol or ethanol) are first caused to react with nitrobenzene to form N-phenyl methylurethane:



where R = CH₃ or C₂H₅

In a second step, the condensation of urethane with formaldehyde yields methylene diphenylurethane and its oligomers:



The thermal decomposition of this product, between 250 and 280°C, leads to MDI and its polymers with the regeneration of the alcohol which can be recycled:

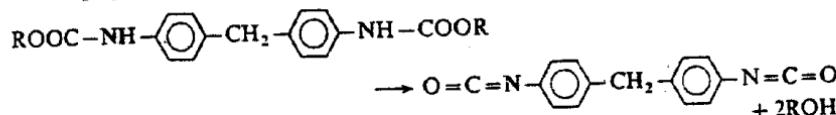


TABLE 14.4

MDI AND POLYMERIC MDI PRODUCTION, ECONOMIC DATA
(France conditions, mid-1986)

Product	Nitrobenzene		Aniline		MDI and polymeric MDI		
	Conventional benzene nitration	Adiabatic benzene nitration	Catalytic reduction of nitrobenzene	Phenol ammoniolyisis	Conventional aniline phosgenation	Aniline phosgenation in the presence of salt	Direct carbonylation of nitrobenzene
Process	Biazzi	Du Pont	Biazzi	Mitsui	Biazzi	Mobay	Arco
Typical technology							
Production capacity (t/year)	100,000	100,000	75,000	75,000	50,000	50,000	50,000
Battery limits investments (10^6 US\$)	17	11	13	18	25	27	39
Consumption per ton of product							
Raw materials							
Benzene (t)	0.65	0.63	—	—	—	—	—
Nitrobenzene (t)	—	—	1.35	—	—	—	1.08
Aniline (t)	—	—	—	—	0.79	0.79	—
Phenol (t)	—	—	—	1.05	—	—	—
By-products							
Hydrochloric acid (as 32% Wt) (t)	—	—	—	—	0.60	1.90	—
Diphenylamine (kg)	—	—	—	10	—	—	—
Chemicals							
Hydrogen (kg)	—	—	—	—	—	—	—
Formaldehyde (as 37% Wt) (t)	—	—	80	—	0.42	0.42	0.14
Methanol (kg)	—	—	—	—	—	—	80
Ammonia (t)	—	—	—	0.25	—	—	—
Chlorine (t)	—	—	—	—	0.67	0.67	—
Carbon monoxide (t)	—	—	—	—	0.28	0.28	0.90
Nitric acid (t)	0.53	0.52	—	—	—	—	—
Sulfuric acid (kg)	12	5	—	—	5	—	—
Caustic soda (kg)	9	7	—	—	160	—	—
Sodium chloride (kg)	—	—	—	—	50	—	—
Utilities							
Steam (t)	0.3	0.5	(—) 1.0	1.0	5.5	5.5	6.0
Electricity (kWh)	50	15	80	85	1,100	1,100	2,400
Fuel (10^6 kJ)	3	—	—	1.5	—	—	—
Cooling water (m ³)	120	150	100	100	900	900	1,000
Process water (m ³)	0.2	0.2	0.2	0.2	—	—	15
Nitrogen (Nm ³)	—	—	2	—	160	160	180
Catalysts and miscellaneous (US\$)	2	2	7	4	18	26	210
Labor (Operators per shift)	3	3	3	3	7	6	9

This process does not yet appear to have reached the industrial stage. The carbonylation step is catalyzed by selenium metal and lithium acetate. Nitrobenzene in 10 per cent weight solution in alcohol reacts with carbon monoxide in agitated and jacketed reactors placed in series, kept by cooling at 150°C and operating under a pressure of about $6 \cdot 10^6$ Pa absolute. With a residence time of about 1 1/2 h, conversion is virtually total and molar selectivity of urethane is 98 per cent. The two main by-products of the reaction, aniline and diphenylurea, are separated and recycled to the reactor. It is important to recover the maximum of selenium due to its high price and its toxicity.

The condensation step also takes place in a series of agitated reactors with excess formaldehyde (10 to 15 per cent in relation to stoichiometry). The operation is conducted at 100°C. in the presence of an acid catalyst (HCl or BF_3). The molar yield of diurethane is 97 per cent.

The final decomposition step consists in dissolving the diurethane in a high-boiling solvent (hexadecane or alkylbenzene) and in passing this solution through a series of reactors kept at 220°C, operating in a stream of nitrogen. The alcohol and solvent are recovered by distillations (10 to 15 trays each) to recycle them. Molar selectivity of polyisocyanates is nearly 90 per cent.

14.3.3 Economic data

Table 14.4 provides some economic data concerning the production of nitrobenzene, aniline, MDI and polymeric MDI.

14.3.4 Uses and producers

Table 14.5 offers an indication of the average commercial specifications of MDI and polymeric MDI. The main uses of aniline and MDI in 1984 in Western Europe, the United States and Japan are listed in Tables 14.6 and 14.7, which also give the production, capacities and consumption of these products at the same date in these three geographic areas.

TABLE 14.5
AVERAGE COMMERCIAL SPECIFICATIONS OF MDI AND POLYMERIC MDI

Isocyanate	MDI	Polymeric MDI
Purity (%) min.	99.5	132 to 135 ⁽¹⁾
<i>o</i> -, <i>p</i> -isomer content (%) max.	7	—
Melting point (°C) min.	35	—
Total chlorides (ppm) max.	1,000	—
Hydrolysable chlorides (ppm) max.	500	3,000
Acidity (expressed as HCl) (ppm) max.	500	3,000
Insolubles (ppm) max.	200	0
Heavy metals ⁽²⁾ (ppm) max.	—	200
d_{20}^{20} ⁽³⁾	1.19	1.2

(1) Isocyanate equivalent.

(2) Va. Cr. Mn. Zn. Ga. Fe. Co and Ni.

(3) Specific gravity, 68.0 68.0.

TABLE 14.6
ANILINE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Agricultural chemicals	1	7	2
Diphenylmethanediisocyanate	70	62	61
Dyes and pigments	8	3	7
Pharmaceuticals	2	2	4
Rubbers	19	19	23
Hydroquinone		2	
Miscellaneous ⁽¹⁾		5	3
Total	100	100	100
Sources (% product)			
Nitrobenzene ⁽²⁾	100	84	72
Phenol	—	16	28
Total	100	100	100
Production (10 ³ t/year)	365	300	95
Capacity (10 ³ t/year) ⁽³⁾	485	565	120
Consumption (10 ³ t/year)	380	295	80

(1) Analytical reagent, corrosion inhibitor, cyclohexylamine, photographic chemicals, specialty organic fibers (Kevlar), specialty resins...

(2) About 98% of the nitrobenzene is subject to captive use for the production of aniline.

(3) The worldwide production capacity of aniline was about $1.3 \cdot 10^6$ t/year in 1984 and $1.4 \cdot 10^6$ t/year in 1986, with the following distribution:

United States	0.57	Western Europe	0.49	Middle East	—
Canada	—	Eastern Europe	>0.15	Japan	0.12
Latin America	0.01	Africa	0.01	Asia and Far East	0.04

TABLE 14.7
DIPHENYLMETHANEDIISOCYANATE PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Polyurethane foams	81	84	76
Flexible	10	15	30
Rigid	71	69	46
Non-foam uses	19	16	24
Elastomers (RIM) ⁽²⁾	5	8	
Other microcellular	5	2	
Miscellaneous ⁽³⁾	6	6	24
Total	100	100	100
Production (10 ³ t/year)	340	275	75
Capacity (10 ³ t/year) ⁽⁴⁾	370	355	105
Consumption (10 ³ t/year)	330	230	70

(1) Estimated values.

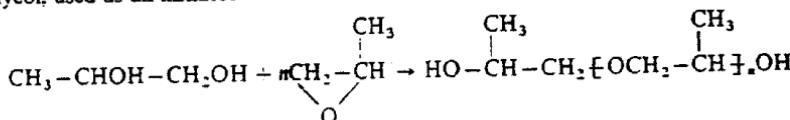
(2) RIM = Reaction Injection Molding.

(3) Adhesives and sealants, foundry core binders, Spandex fibers, thermoplastic polyurethanes.

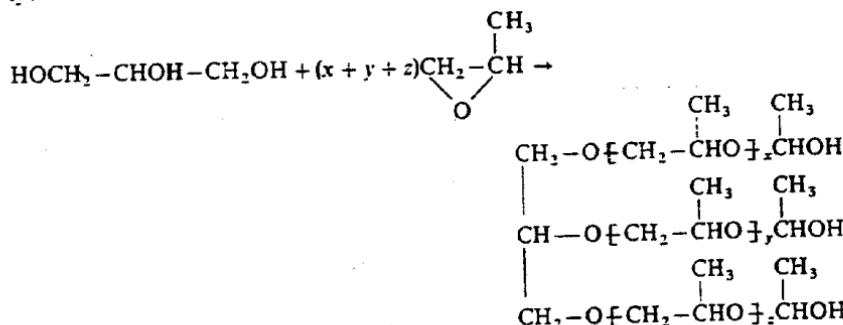
(4) The worldwide production capacity of diphenylmethanediisocyanate was about $0.9 \cdot 10^6$ t/year in 1984 and in 1986 (United States = 0.39, Western Europe = 0.37, Eastern Europe = >0.05, Japan = 0.11).

14.4 POLYETHER-POLYOOLS

Polyether-polyols are produced by the polyaddition of an epoxide (propylene or ethylene oxide) to an active hydrogen initiator (polyol, amine, acid, water, etc.). Polypropylene glycol (PPG) is obtained by the polyaddition of propylene oxide to propylene glycol, used as an initiator:



Among the polyether-triols, the adduct with glycerol is the most important industrially:



However, other polyols, with a larger number of terminal hydroxyl groups, are prepared by initiating the polyaddition by pentaerythritol or by sugars (glucose, raffinose, mannitol).

Propylene oxide can also react with the active hydrogen of hydroxyl groups, resulting from the opening of oxygenated rings, such as ethylene oxide and tetrahydrofuran.

14.4.1 Manufacturing technique

This operation can be described by a specific example, such as that of the production of an adduct with glycerin (Fig. 14.9). Although the manufacture of this polyether-polyol can be conducted continuously, most manufacturers operate with a batch process, in an inert atmosphere to prevent oxidation, which is responsible for staining the product, and in the absence of any trace of moisture that could lead to the formation of undesirable secondary derivatives.

Glycerin (usually the initiator) and caustic pellets, used as a catalyst, are introduced into a reactor equipped with an agitation system, whose power depends on the molecular weight of the desired product. The reaction system, kept under nitrogen atmosphere,

has a double shell conveying steam to preheat the glycerin and catalyst to 120 to 140°C. Propylene oxide is introduced at a rate controlled to maintain the pressure at about 350 kPa absolute, and adapted to the degree of advancement of the reaction. Since the reactivity of the growing polymer declines as its molecular weight increases, the rate of addition of propylene oxide must be decreased to maintain a constant pressure in the reactor.

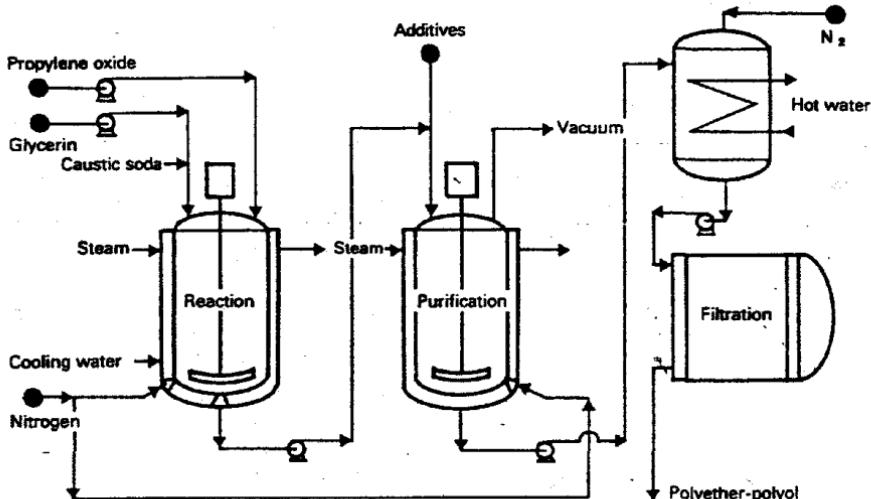


Fig. 14.9. Production of a polyether-polyol. Scheme for the formation of an adduct with glycerin.

The heat generated during the transformation is removed by the circulation of water in the double shell. At the end of the epoxide addition, which lasts about 12 h, the reaction is allowed to proceed to completion for about one more hour. Molar selectivity is 92 per cent in relation to glycerin and 94 per cent in relation to propylene oxide. The effluent obtained is purified in a second agitated and jacketed reactor, operating under nitrogen and kept under high vacuum (6 to 7 kPa absolute). A temperature of 100°C and a partial pressure lower than 1 kPa absolute favor the removal of the light compounds. A number of products intended to purify the polyol are also added. These include activated charcoal intended to bleach it, acid clays to neutralize the caustic soda, and additives to favor subsequent filtration. The product thus treated is stored in a tank where it is kept under nitrogen atmosphere at about 75°C. It is then sent to a filter press. All the equipment employed is of stainless steel.

14.4.2 Economic data

Table 14.8 offers an indication of the economics of polyether-polyol production, when the adduct used is glycerin.

TABLE 14.8

PRODUCTION OF POLYETHER-POLYOLS (USE OF GLYCERIN AS ADDUCT)
 ECONOMIC DATA (France conditions, mid-1986)
 PRODUCTION CAPACITY 20,000 t/year

Barely limits investments (10^6 US\$)	8
Consumption per ton of product	
Raw materials	
Glycerin (t)	0.025
Propylene oxide (t)	0.995
Utilities	
Steam (t)	0.5
Electricity (kWh)	35
Cooling water (m^3)	40
Chemicals and catalysts (US\$)	25
Labor (Operators per shift)	5

14.4.3 Uses and producers

The main outlets for polyether-polyols in 1984 in Western Europe, the United States and Japan are summarized in Table 14.9, which also gives the production, capacities and consumption for the same date in these three geographic areas.

TABLE 14.9
 PRODUCTION AND CONSUMPTION OF POLYETHER-POLYOLS FOR URETHANES IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Polyurethane foams	88	88	79
Flexible	63	76	62
Rigid	25	12	17
Non-foam uses ⁽¹⁾	12	12	21
Total	100	100	100
Production (10^3 t/year)	610	630	170
Capacity (10^3 t/year) ⁽²⁾	1,025	1,080	335
Consumption (10^3 t/year)	490	555	165

(1) Adhesives and sealants, cast elastomers, microcellular products, polyurethane stretch fibers (Spandex fibers), surface coatings, thermoplastic elastomers and malleable gums.

(2) The worldwide production capacity of polyether-polyols was about $2.9 \cdot 10^6$ t/year in 1984, with the following distribution:

United States	1.08	Western Europe	1.03	Middle East	—
Canada	0.01	Eastern Europe	>0.15	Japan	0.34
Latin America	0.16	Africa	0.02	Asia and Far East	>0.12

REFERENCES

(Volume 2)

Chapter 7 ETHYLENE AND PROPYLENE OXIDES

Ethylene oxide

- Van Oosten, R. P., "The manufacture of ethylene oxide"; *J. of the Inst. of Petroleum*, 46 (443) 347-352 (1960).
- Bata, G. L., Hazell, J. E., "Olefin oxides. How they are made and how they are used", *Oil and Gas J.*, 63 (40) 107-111 (1965).
- "Oxyde d'éthylène" (in French), *Inform. Chimie*, special issue (61) 27-50 (1968).
- Landau, R., Brown, D., Saffer, A., Porcelli, J. A., "The impact of new technologies", *Chemical Engineering Progress*, 64 (3) 27-34 (1969).
- Stobaugh, R. B., Ray, G. C., Spinek, R. A., "Ethylene oxide, how, where, who. Future", *Hydrocarbon Processing*, 49 (10) 105-115 (1970).
- Cranfield, J., "Oxygen route to ethylene oxide shows up to advantage in glycol production", *Petroleum and Petrochem. Internat.*, 13 (11) 28-30 (1973).
- Kiguchi, I., Kumazawa, T., Nakai, T., "For EO air and oxygen equal", *Hydrocarbon Processing*, 55 (3) 69-72 (1976).
- Gans, M., Ozeko, B. J., "For EO Air or Oxygen?", *Hydrocarbon Processing*, 55 (3) 73-77 (1976).
- De Maglie, B., "Oxygen best for EO", *Hydrocarbon Processing*, 55 (3) 78-80 (1976).
- Kuhn, W., "What's US PRO and EO outlook?", *Hydrocarbon Processing*, 58 (10) 123-128 (1979).
- Ozero, B. J., Procelli, J. V., "Can developments keep ethylene oxide viable?", *Hydrocarbon Processing*, 63 (3) 55-61 (1984).

Propylene oxide

- Fyvie, A. C., "Propylene and its derivatives", *Chem. Industry*, (10) 384-388 (1964).
- Landau, R., Brown, D., Russell, J. C., Kollar, J., "Epoxidation of olefins", 7th World Petroleum Congress, Mexico City (28 April 1967).
- "New catalyst aids oxidation of propylene" *Chem. and Engng News*, 22-23 (20 Nov. 1972).
- Yamagishi, K., Kageyama, O., Haruki, H., Numa, Y., "Make propylene oxide direct", *Hydrocarbon Processing*, 55 (11) 102-104 (1976).
- "Propylene oxide routes are ready to take off", *Chem. Engng*, 84 (23) 84-86 (1977).
- Simmrock, K. H., "Compare propylene oxide routes", *Hydrocarbon Processing*, 57 (11) 105-113 (1978).
- Landau, R., Sullivan, G. A., Brown, D., "Propylene oxide by the co-product processes", *CHEMTECH*, 602-607 (Oct. 1979).
- "Oxyde de propylène. un changement de dimension" (in French). *Inform. Chimie*, (213) 171-179 (1981).

Ethylene and propylene glycols

- "HALCON develops direct process for ethyleneglycol production", *European Chemical News*, 23 (9 August 1974).
- Brownstein, A. M., "Economics of ethyleneglycol processes", *Chem. Engng Progress*, 71 (9) 72-76 (1975).
- Weismantel, G. E., "New technology sparks ethyleneglycol debate", *Chem. Engng*, 86 (2) 67-70 (1979).
- Weiss, A. H., Trigerman, S., Dunnells, G., Likhobolov, V. A., Biron, E., "Ethyleneglycol from formaldehyde", *Industr. and Engng Chem. Process Design and Development*, 18 (3) 522-527 (1979).
- "Ethyleneglycol", *Chem. Week*, 134 (10) 32-35 (1984).
- Kollar, J., "Ethyleneglycol from syngas", *CHEMTECH*, 504-511 (August 1984).

Chapter 8 ACETIC DERIVATIVES

Acetaldehyde

- Jira, R., "Acetaldehyde via the direct oxidation of ethylene", *Europ. Chem. News*, Large Plant Suppl., 58-64, (20 Sept. 1965).
- "Acetaldehyde" (in French), *Inform. Chimie*, (58) 35-46 (1968).
- Smidt, J., "Production of acetaldehyde. Economics and technical processes", *Conference on Acetylene or Ethylene as Raw Materials for the Chemical Industry*, DecHEMA, Frankfurt-am-Main (27/28 March 1968).
- Jira, R., Blau, W., Grimm, D., "Acetaldehyde via air or oxygen", *Hydrocarbon Processing*, 55 (3) 97-100 (1976).

Acetic acid and anhydride

- Situg, M., *Acetic Acid and Anhydride*, Noyes Development Corporation, New York (1965).
- Kronig, W., "Production of acetic acid from n-butane", *7th World Petroleum Congress* Mexico City, (2/8 April 1967).
- Paris, A., "L'acide acétique et l'acétaldéhyde. Divers procédés de synthèse" (in French), *Industrie Chimique*, 55 (615) 421-431 (1968).
- "Acide acétique" (in French), *Inform. Chimie*, (65) 59-76 (1968).
- "Anhydride acétique" (in French), *Inform. Chimie*, (65) 79-80 (1968).
- Ellwood, P., "Acetic acid via methanol and synthesis gas", *Chem. Engng*, 76 (11) 148-150 (1969).
- Schwerdtel, W., "Make acetic acid from n-butenes", *Hydrocarbon Processing*, 49 (11) 117-120 (1970).
- Morrison, J., "Hüls develops acetic acid from butenes route", *Oil and Gas J. Internat.*, 11 (10) 26-29 (1971).
- "Rhône-Poulenc/Melle-Bezons improve acetic acid process", *Europ. Chem. News*, 27 (20 Oct. 1972).
- Grove, H. D., "Lowest cost acetic via methanol", *Hydrocarbon Processing*, 51 (11) 76-78 (1972).
- Lowry, R. P., Aguiló, A., "Acetic acid today", *Hydrocarbon Processing*, 53 (11) 103-113 (1974).
- Bergier, A., "Acide acétique à partir de CO + H₂" (in French), *Pétrole et Techniques* (257) 23-26 (1978).
- "Eastman's new gamble: chemicals from coal", *Chem. Week*, 134 (16) 34-36 (1984).

Chapter 9 ALCOHOLS

- Wickson, E. J., "Monohydric alcohols. Manufacture, applications and chemistry", ACS Symposium Series 159. Washington, DC (1981).

Ethanol

- Ball, I. M. D., "Ethanol", ECMRA 2nd International Conference, London (27/28 March 1969).

- Margiloff, I. B., Reid, A. J., O'Sullivan, T. J., "Ethanol: manufacture and applications", *ACS 179th National Meeting*, Houston, Texas (25/26 March 1980).
- Revuz, B., "L'éthanol produit de fermentation" (in French), *Journée d'Étude Assoc. Fr. Techniciens du Pétrole*, Paris, 67-74 (21 Janv. 1981).
- "Ethanol dehydration", *Gasohol U.S.A.* 13-14 (April 1981).
- Mednick, R. L., Weiss, L. H., Xippolitos, E. G., "Ethanol from cellulosics", *Chem. Engng Progress*, 78 (8) 68-73 (1982).
- "Ethanol by continuous fermentation", *Europ. Chem. News*, Biotechnology Suppl., 20-21, (May 1983).
- Nystrom, J. M., Greenwald, C. G., Harrison, F. G., Gibson, E. D., "Making ethanol from cellulosics", *Chem. Engng Progress*, 80 (5) 68-74 (1984).

Isopropanol

- "Isopropanol" (in French), *Inform. Chimie* (38) 36-44 (1966).
- Horie, T., Emaizumi, M., Fujiwara, Y., "New low cost isopropanol process", *Hydrocarbon Processing*, 49 (3) 119-120 (1970).
- "VEBA fights challenge of new IPA processes", *Europ. Chem. News*, 22 (10 March 1972).
- Neier, W., Woelner, J., "Use cation catalyst for IPA", *Hydrocarbon Processing*, 51 (11) 113-116 (1972).
- Neier, W., Woelner, J., "Isopropanol alcohol by direct hydration", *CHEMTECH*, 95-99 (Feb. 1973).
- Onoue, Y., Mizutani, Y., Akiyama, S., Izumi, Y., "Isopropanol par hydratation directe du propylène en présence d'un catalyseur soluble" (in French), *Inform. Chimie* (159) 199-204 (1976).
- Onoue, Y., Mizutani, Y., Akiyama, S., Izumi, Y., "Hydration with water", *CHEMTECH*, 432-435 (July 1978).

Butanols

- Hohenschutz, H., "Oxo synthesis in large plants", *Europ. Chem. News*, Large Plant Suppl., 7-11 (30 Sept. 1966).
- "Synthèse Oxo" (in French), *Inform. Chimie* (57) 91-105 (1968).
- "Alcools butyliques" (in French), *Inform. Chimie* (78) 63-73 (1969).
- "Butanol outlets dominate return on 2-ethylhexanol", *Europ. Chem. News*, 50-60 (18/25 Dec. 1970).
- O'Rourke, Kavasmanec, P. R., Uhl, R. E., "Manufacture of n-butanol and 2-ethylhexanol by the rhodium Oxo process and applications of the alcohols", *ACS 179th National Meeting*, Houston, Texas (25/26 March 1980).
- Roche, M., "Butanols, produits de la pétrochimie, l'alcool butylique tertiaire" (in French), *Journée d'Étude Assoc. Techniciens du Pétrole*, Paris, Special Brochure, 75-81 (21 Janv. 1981).
- Guetens, E. G., Dejovine, J. M., Yogis, G. J., "TBA aids methanol/fuel mix", *Hydrocarbon Processing*, 61 (5) 113-117 (1982).
- "Production of ter-butanol and isobutylene", *Chem. Engng.*, 90 (25) 60 (1983).

The higher alcohols

- Lobo, P. A., Coldiron, D. C., Vernon, L. N., Ashton, A. T., "The Alfol alcohol process", *Chem. Engng Progress*, 58 (5) 85-88 (1962).
- Guccione, E., "Oxo process initiates 2-ethylhexanol synthesis", *Chem. Engng*, 72 (11) 90-92 (1965).
- Sittig, M., *Oxo Process and Products*, Noyes Development Corporation, Park Ridge, New Jersey (1966).
- Lemke, H., "Select best Oxo catalyst cycle", *Hydrocarbon Processing*, 45 (2) 148-152 (1966).
- "Les alcools Oxo" (in French), *Inform. Chimie* (58) 71-78 (1968).
- Stevens, N. J., Livingston, Y., "A new route for alcohols", *Chem. Engng Progress*, 64 (7) 61-66 (1968).
- Miller, S. A., "Alfene and Alfol processes", *Chem. and Process Engng*, 50 (10) 103-106 (1969).
- Ishikawa, Y., "Improved Mitsubishi 2-ethylhexanol process", *Chem. Econ. and Engng Rev.*, 2 (1) 31-33 (1970).
- Weber, H., Falbe, J., "Oxo synthesis gains worldwide importance", *Oil and Gas J. Internat.*, 10 (5) 90-97 (1970).
- Weber, H., "Production of 2-ethylhexanol from ethylene and propylene", *Joint Conference of the Chemical Institute of Canada/American Chemical Society*, Toronto, Ontario (24-29 May 1970).

- Weber, H., "Choosing raw materials for 2-ethylhexanol", *Oil and Gas J.*, 69 (17) 82-83 (1971).
- Cornils, B., Payer, R., Traenckner, K. C., "Oxo with rhodium catalysts", *Hydrocarbon Processing*, 54 (6) 83-91 (1975).
- Weber, H., Dimmling, W., Desai, A. M., "Make plasticizer alcohols this way", *Hydrocarbon Processing*, 55 (4) 127-132 (1976).
- Fowler, R., Connor, H., Baehl, R. A., "A new low pressure process for the hydroformylation of propylene", *AICHE 80th National Meeting*, Kansas City, Missouri (11/14 April 1976).
- Fowler, R., Connor, H., Baehl, R. A., "Hydroformylation propylene at low pressure", *Hydrocarbon Processing*, 55 (9) 247 (1976).
- Brewester, E. A. V., "Low pressure Oxo process features rhodium catalyst", *Chem. Engng.*, 83 (24) 90-91 (1976).
- "Low pressure Oxo process yields a better product mix", *Chem. Engng.*, 84 (26) 110-115 (1977).
- Mercier, S., "Synthèse des fonctions aldéhyde, alcool et acide par synthèse Oxo" (in French), *Pétrole et Techniques* (257) 26-30 (1978).
- Vincent, R. E., "Higher linear Oxo alcohols manufacture", *ACS 179th National Meeting*, Houston, Texas (25/26 March 1980).
- Washecheck, P. H., "Manufacture of higher straight-chain alcohols by the ethylene chain growth process", *ACS 179th National Meeting*, Houston, Texas (25/26 March 1980).
- Cornils, B., Mullen, A., "2-EH, What you should know", *Hydrocarbon Processing*, 59 (11) 93-102 (1980).

Chapter 10

PHENOL, ACETONE AND METHYLACETONE

Phenol

- Agnello, C. L., "Synthetic phenol", *Industr. and Engng Chem. Product Research and Development*, 52 (11) 894-900 (1960).
- Keading, W. W., "How DOW makes phenol from toluene", *Hydrocarbon Processing*, 43 (11) 173-176 (1964).
- Pecka, K., Singer, P., "Cumene/phenol purification by fractional melting", *Europ. Chem. News*, Large Plant Suppl., 82-84, (27 Sept. 1968).
- Mita, Y., Maketaka, N., "Up cumene yield with transalkylation", *Hydrocarbon Processing*, 47 (10) 122-124 (1968).
- Cociancich, R., Maffioli, R., "SRI plans for phenol expansion", *Europ. Chem. News*, Large Plants Survey, 86-88, (26 Sept. 1969).
- Zabotto, G., "Make pure phenol by extraction", *Hydrocarbon Processing*, 49 (2) 135-136 (1970).
- Fleming, J. B., Lambrix, J. R., Nixon, J. R., "Safety in phenol from cumene process", *Hydrocarbon Processing*, 55 (1) 185-196 (1976).
- Pujado, P. R., Salazar, J. R., Berger, C. V., "Cheapest route to phenol", *Hydrocarbon Processing*, 55 (3) 91-96 (1976).
- Perk, A., "Phénol" (in French), *ECMRA 12th International Conference*, Venice (9/11 Oct. 1978).
- Gelbein, A. P., Nislick, A. S., "Make phenol from benzoic acid", *Hydrocarbon Processing*, 57 (11) 125-128 (1978).
- Bonacci, J. C., Heck, R. M., Mahendroo, R. K., Patel, G. R., Allan, E. D., "Hydrogenate AMS to cumene", *Hydrocarbon Processing*, 59 (11) 179-183 (1980).
- Canfield, R. C., Unruh, T. L., "Improving cumene yields via selective catalysis", *Chem. Engng.*, 90 (6) 32-33 (1983).

Acetone and methyl ethyl ketone

- Smith, J., Krekeler, H., "New process for acetone and MEK", *Hydrocarbon Processing*, 42 (7) 149-152 (1963).
- Kunugi, T., Matsuura, T., Oguni, S., "Isopropanol oxidizes this way", *Hydrocarbon Processing*, 44 (7) 116-122 (1965).
- "New technology seen trimming acetone market", *Oil and Gas J.*, 76 (37) 61 (1978).

Chapter 11

VINYL MONOMERS

Vinyl acetate

- "Make vinyl acetate from ethylene", *Hydrocarbon Processing*, 46 (4) 146-149 (1967).
- Krekeler, H., Schmitz, H., "Vinyl acetate on the basis of ethylene in the liquid phase with palladium salt catalysts", *Conference on Acetylene or Ethylene as Raw Materials for the Chemical Industry*, DecHEMA, Frankfurt-am-Main (27-29 March 1968).
- Schwerdtel, W., "Vinyl acetate based on ethylene in the gas phase", *Conference on Acetylene or Ethylene as Raw Materials for the Chemical Industry*, DecHEMA, Frankfurt-am-Main (27/29 March 1968).
- "Ethylene or acetylene route to vinyl acetate?", *Chem. Engng.*, 75 (17) 94-96 (1968).
- Morrison, J., "Acetylene still has benefits for making vinyl acetate", *Oil and Gas J. Internat.*, 65 (5) 104-116 (1969).
- "Vinyl acetate. Vapor phase process", *British Chem. Engng.*, Process SCAN (May 1970).
- Bedell, K. R., Rainbird, H. A., "Make VAM from ethylene", *Hydrocarbon Processing*, 51 (11) 141-143 (1972).
- Ohmae, T., "Development of ethylene process, vinyl acetate and process comparisons", *Chem. Econ. and Engng Rev.* 4 (11, 55) 46-57 (1972).
- "USI's vapor phase process for VAM proves out", *Oil and Gas*, 71 (4) 80-81 (1973).
- Carroll, J. E., Galloway, B. F., "Vinyl acetate from ethylene", *Chemical Engng.*, 80 (9) 92-93 (1973).
- Manning, P. C. E., "Vinyl acetate", *ECMRA 10th International Conference*, Madrid (13/15 Oct. 1976).
- Verde, L., Moreno, S., Riccardi, R., "Combine C_2H_2/C_2H_4 for lowest cost", *Hydrocarbon Processing*, 57 (1) 162-164 (1978).
- Brown, R. D., Bennett, B. A., "Commercial routes to vinyl acetate", *Chem. Engng Progress*, 74 (11) 11-13 (1978).
- Ehrler, J. L., Juran, B., "VAM and Ac_2O by carbonylation", *Hydrocarbon Processing*, 61 (2) 109-113 (1982).

Vinyl chloride

- Burke, D., Miller, R., "Oxychlorination", *Chemical Week*, 95 (8) 93-108 (1964).
- Gomi, S., "Japan's new vinylchloride process", *Hydrocarbon Processing*, 43 (11) 165-168 (1964).
- Edwards, E. F., Weaver, T., "New route to vinylchloride", *Chem. Engng Progress*, 61 (1) 21-26 (1965).
- Sittig, M., *Vinyl Monomers and Polymers*, Noyes Development Corporation, Park Ridge, New Jersey (1966).
- Buckley, J. A., "Vinylchloride via direct chlorination and oxychlorination", *Chemical Engng.*, 73 (29) 102-104 (1966).
- Albright, L. F., "Vinylchloride processes", *Chem. Engng.*, 74 (7) 123-130 (1967).
- Albright, L. F., "Manufacture of vinylchloride", *Chem. Engng.*, 74 (8) 219-226 (1967).
- Remirez, R., "Dilute ethylene opens door to vinyl chloride production in small plants", *Chem. Engng.*, 75 (9) 142-144 (1968).
- Caudle, P. G., "Acetylene or ethylene as raw materials for vinyl chloride. A review of economic factors", *Chemistry and Industry* (45) 1551-1558 (1968).
- "Vinylchloride. Balanced chlorination process", *British Chem. Engng.*, Process SCAN (May 1969).
- Onoue, Y., Sakurayama, K., "Recent trends in vinylchloride processes", *Chem. Econ. and Engng Rev.*, 4 (11, 19) 17-20 (1969).
- "Chlorure de vinyle" (in French), *Inform. Chimie*, special issue (95) 125-136 (1971).
- "Chlore-éthylène, CHLOE, un nouveau procédé Pechiney/Saint-Gobain de production simultanée de chlorure de vinyle et de solvants chlorés" (in French), *Inform. Chimie* (96) 131-142 (1971).
- Baba, H., "EDC cracking furnace", *Chem. Econ. and Engng Rev.*, 3 (5, 37) 23-28 (1971).
- Riegel, H., Schindler, H. D., Sze, M. C., "Chlorinated hydrocarbons produced via Transcat", *AICHE 74th National Meeting*, New Orleans, Louisiana (11/15 March 1973).
- "KUREHA offers integrated oil cracking VCM process", *Europ. Chem. News*, 30 (12 Oct. 1973).
- Wimer, W. E., Feathers, R. E., "Oxygen gives low cost VCM", *Hydrocarbon Processing*, 55 (3) 81-84 (1976).
- Reich, P., "Air or oxygen for VCM?", *Hydrocarbon Processing*, 55 (3) 85-89 (1976).

- Machida, M., Tanaka, S., "Vinylchloride monomer production without pollution", *Chem. Econ. and Engng Rev.*, 8 (11, 100) 31-36 (1976).
- Sittig, M., *Vinylchloride and PVC Manufacture, Process and Environmental Aspects*, Noyes Development Corporation, Park Ridge, New Jersey (1978).
- Guglielmi, G., "Future trend of chlorine technology", ECMRA 12th International Conference, Venice (9/11 Oct. 1978).
- McPherson, R. W., Starks, C. M., Fryar, G. I., "Vinylchloride monomer... What you should know", *Hydrocarbon Processing*, 58 (3) 75-88 (1979).
- Schillmoller, C. M., "Alloy selection for VCM plants", *Hydrocarbon Processing*, 58 (3) 89-93 (1979).
- Saito, R., Suzuki, S., "Toagosei new Vinylene process", *Chem. Econ. and Engng Rev.*, 11 (6, 128) 27-31 (1979).
- "VCM/PVC, La crise" (in French), *Inform. Chimie*, special issue (226) 203-205 (1982).
- McNaughton, K. J., "Ethylene dichloride process", *Chem. Engng*, 90 (25) 54-58 (1983).

Acrylates and methacrylates

- "Propylene route to acrylic acid due soon", *Chem. and Engng News*, 45 (7) 48-53 (1967).
- "Les monomères acryliques" (in French), *Industrie Chimique*, 15 (614) 455-466 (1968).
- Nakatani, H., "Toyo's new acrylate process", *Hydrocarbon Processing*, 48 (5) 152-154 (1969).
- Yoshimura, I., "Making acrylic acid via air oxidation of propylene", *Chem. Engng*, 76 (15) 78-80 (1969).
- Sittig, M., *Acrylic and Vinyl Fibers*, Noyes Development Corporation, Park Ridge, New Jersey (1972).
- Ohara, T., Hirai, M., Shimizu, N., "Oxidize propylene to acrylics", *Hydrocarbon Processing*, 51 (11) 85-88 (1972).
- Olivier, K. L., Fenton, D. M., Biale, J., "New route to acrylic acid", *Hydrocarbon Processing*, 51 (11) 95-96 (1972).
- Sakuyama, S., Ohara, T., Shimizu, N., Kubota, K., "A new oxidation process for acrylic acid from propylene", *CHEMTECH*, 350-355 (June 1973).
- Weigert, W. M., "Acrolein from propylene aided by new catalyst", *Chem. Engng*, 80 (15) 68-69 (1973).
- Schaal, G. E., "Make acrolein from propylene", *Hydrocarbon Processing*, 52 (9) 218-220 (1973).
- "BASF improves Oxo catalysts, has new acrylic acid route", *Europ. Chem. News*, 36 (9 May 1975).
- Oda, Y., Gotoh, I., Uchida, K., Morimoto, T., Endoh J., Ueno, T., "New route to methyl methacrylate", *Hydrocarbon Processing*, 54 (10) 115-117 (1975).
- Davis, J. C., "Big changes in store for methyl methacrylate", *Chem. Engng*, 85 (15) 25-27 (1978).
- Hasuike, T., Matsuzawa, H., "Make MMA from spent BB", *Hydrocarbon Processing*, 58 (2) 105-107 (1979).
- Itakura, J., "Present state and prospects for acrylic ester industry", *Chem. Econ. and Engineering Review*, 13 (7/8, 150) 19-24 (1981).
- Nakamura, T., Kita, T., "A new feedstock for the manufacture of methyl methacrylate emerges", *Chem. Econ. and Engng Rev.*, 15 (10, 172) 23-27 (1983).

Acrylonitrile

- Vearch, F., Callahan, J. L., Idoi, J. D., Milberger, E. C., "New data on Sohio's acrylo process", *Hydrocarbon Processing*, 41 (11) 187-190 (1962).
- Sittig, M., *Acrylonitrile*, Noyes Development Corporation, Park Ridge, New Jersey (1965).
- Guccione, E., "Acrylonitrile's latest synthesis from propylene", *Chem. Engng*, 72 (6) 150-152 (1965).
- Spillane L. J. and Koons, R. E., "Kinetics of acrylonitrile formation", *Chem. Engng Progress*, 62 (5) 92-98 (1966).
- Lichtenberger, M. R., "La fabrication de l'acrylonitrile à partir du propylène" (in French), *Rev. Assoc. Fr. Techniciens du Pétrole* (183) 29-35 (1967).
- Covidalli, G., Nenz, A., Caporali, G., "Aspetti e caratteristiche del processo 'Montecatini Edison' per acrilonitrile da propilene" (in Italian), *Chimica Industria*, 49 (8) 809-813 (1967).
- Schonbeck, R., "OSW: Newest acrylonitrile process", *Hydrocarbon Processing*, 46 (8) 124-126 (1967).
- Dalin, M. A., Kolchin, I. K., Serebryakov, B. R., *Acrylonitrile*, Technomic Publishing Company, Westport, (1970).

- Stobaugh, R. B., Clark, S. G. McH., Camirand, G. D., "Acrylonitrile: How, where, who. Future", *Hydrocarbon Processing*, 50 (1) 109-120 (1971).
- Caporali, G., "Montecatini Edison's acrylonitrile process", *AICHE 65th National Meeting*, Dallas, Texas, (20/23 Feb. 1972).
- Caporali, G., "How Montedison makes acrylo", *Hydrocarbon Processing*, 51 (11) 144-146 (1972).
- Jones, M., "Ammoxidation processes for acrylonitrile manufacture. Past, present and future?" Symposium on Synthetic Fibre Processes, Royal Aeronautical Society, London (6 Dec. 1972).
- Olson, D. A., "Acrylonitrile", *AICHE 83rd National Meeting*, Houston, Texas (20/24 March 1977).
- Pujado, P. R., Vora, B. V., Krueging, A. P., "Newest acrylonitrile process", *Hydrocarbon Processing*, 56 (5) 169-172 (1977).
- Haggan, J., "Soviet work could give C₁ route to acrylonitrile", *Chemical and Engineering News*, 29-31 (17 Oct. 1983).

Chlorine

- Vandijk, C. P., Schreiner, W. C., "Hydrogen chloride to chlorine via the Kel-Chlor process", *Chem. Engng Progress*, 69 (4) 57-63 (1973).
- "PPG, de Nora develop bipolar chlorine cell process", *Europ. Chem. News*, 30 (8 June 1973).
- Davis, J. C., "Chlor-Alkali producers shift to diaphragm cells", *Chem. Engng*, 81 (4) 84-87 (1974).
- Kienholz, P. J., "Outlook for chlorine/caustic production", *Chem. Engng Progress*, 70 (3) 59-63 (1974).
- Liederbach, T. A., "Reducing chlorine loss in an electrolysis plant", *Chem. Engng Progress*, 70 (3) 64-68 (1974).
- Perry, R. H., "Mercury recovery from process sludges", *Chem. Engng Progress*, 70 (3) 73-80 (1974).
- "De Nora improves mercury chlorine cell technology", *Europ. Chem. News*, 34 (12 April 1974).
- Payer, S., "Recover chlorine from HCl", *Hydrocarbon Processing*, 53 (11) 147-150 (1974).
- Schreiner, W. C., Cover, A. E., Hunter, W. D., Van Dijk, C. P., Jongen-Burger, H. S., "Oxidize HCl for chlorine", *Hydrocarbon Processing*, 53 (11) 151-156 (1974).
- Stinson, S. C., "Electrolytic cell membrane development surges", *Chem. Engng News*, 22-25 (15 March 1982).
- "De Nora develops Hg recovery in chlorine production", *Europ. Chem. News*, 32 (27 Oct. 1972).

Chapter 12

MONOMERS FOR THE SYNTHESIS OF POLYAMIDES

Cyclohexane and cyclohexanol/one

- Dufau, A. F., Eschard, F., Haddad, A. C., Thonon, C. H., "Un nouveau procédé pour l'obtention de cyclohexane haute pureté" (in French), *Rev. Inst. Fr. pétrole et Ann. Combustibles Liquides*, 19 (9) 970-981 (1964).
- "Cyclohex has its heyday", *Chemical Week*, 97 (21) 41-48 (1965).
- Peer, W. A., Winsor, J., "New BP route to cyclohexane features low operating cost", *Oil and Gas J.*, 65 (10) 107-109 (1967).
- Field, S., Daison, M. H., "Economics of making cyclohexane", *Hydrocarbon Processing*, 46 (3) 169-174 (1967).
- Reilly, J. W., Sze, M. C., "Hydrogenating benzene to cyclohexane", *Chemical Engineering Progress*, 63 (6) 73-75 (1967).
- "Nylon intermediates by cyclohexane oxidation", *British Chem. Engng. Process Suppl.* (Nov. 1967).
- Alagy, J., Asselineau, L., Busson, C., Cha, B., Sandler, H., "Selectively oxidize cyclohexane", *Hydrocarbon Processing*, 47 (12) 131-135 (1968).
- Otani, S., Sato, M., "New process for hydrogenation of benzene to cyclohexane", *Japan Chem. Quarterly*, 1 33-34 (1969).
- Miller, S. A., "Cyclohexane, cyclohexanol and cyclohexanone", *Chem. and Process Engng.*, 50 (6) 73-75 (1969).
- "Boron has new oxidation applications", *Oil and Gas J.*, 67 (50) 74-75 (1969).
- Craig, R. G., "Route gives volume output of high purity cyclohexane", *Chem. Engng.*, 77 (12) 108-110 (1970).

- Nettesheim, G., "Extract cyclohexane with PA", *Hydrocarbon Processing*, 49 (8) 115-116 (1970).
- Haberle, M., "Hazards and loss prevention in cyclohexane air oxidation process", *European Federation of Chemical Engineers Meeting*, Newcastle on Tyne (1971).
- "Poland details new cyclohexanone from benzene process", *Europ. Chem. News*, 28 (4 May 1973).
- Cosyns, J., Derrien, M., Forge, A., Cha, B., "Cyclohexane route uses improved catalyst", *Petroleum Internat.*, 14 (10) 14-16 (1974).
- McCabe, J., "Reformer revamped for cyclohexane", *Oil and Gas J.*, 74 (11) 115-116 (1976).

Adipic acid

- Tanako, K., "Adipic acid by single stage", *Hydrocarbon Processing*, 53 (11) 114-120 (1974).
- "New catalytic route leads to adipic acid", *Chem. Engng*, 91 (10) 34 (1984).

Adiponitrile

- Hurd, R. M., "Adiponitrile made electrochemically", *Hydrocarbon Processing*, 43 (11) 154-156 (1964).
- "Japanese plan new adiponitrile route", *Chem. Engineering News*, 45 (2) 58-59 (1967).
- "Europeans focus on new route to adiponitrile", *Chem. Engng*, 77 (8) 56 b-d (1970).
- Van Eygen, C., Hendrickx, A., Ramiouille, J., Walravens, J., Verheyden, A., "Nouveaux procédés d'hydrodimérisation de l'acrylonitrile en adiponitrile développés par UCB" (in French), *Chimie et Industrie, Génie Chimique*, 104 (1) 71-82 (1971).
- Seko, M., "Development of electrolytic hydrodimerization of acrylonitrile", *Chem. Econ. and Engng Rev.*, 7 (10, 89) 20-24 (1975).
- Childs, W. V., Walters, H. C., "Adiponitrile via EHD", *Hydrocarbon Processing*, 57 (11) 139-144 (1978).
- Baizer, M. M., "The electrochemical route to adiponitrile, I", *CHEMTECH*, 161-164 (March 1980).
- Danly, D. E., "The electrochemical route to adiponitrile, II", *CHEMTECH*, 302-311 (May 1980).
- Danly, D. E., "Adiponitrile via improved EHD", *Hydrocarbon Processing*, 60 (4) 161-164 (1981).

Caprolactam and other lactams

- Sittig, M., *Caprolactam and Higher Lactams*, Noyes Development Corporation, Park Ridge, New Jersey (1966).
- Sherwood, P. W., "Les débouchés des produits pétrochimiques dans la fabrication des nouveaux types de nylon" (in French), *Chimie et Industrie*, 95 (3) 253-263 (1966).
- Hulme, P., Turner, P. E., "Photochemical route to caprolactam", *Chem. and Process Engng*, 63 (11) 96-100 (1967).
- Hulme, P., Turner, P. E., "Light paves the way to higher yields of caprolactam at lower costs", *Chem. Engng*, 75 (7) 80-82 (1968).
- "Caprolactam", *Europ. Chem. News, Process Survey* (2 May 1969).
- Morrison, J., "New caprolactam route cuts by-product output by half", *Oil and Gas J.*, 68 (34) 56-58 (1970).
- Taverna, M., Chiti, M., "Compare routes to caprolactam", *Hydrocarbon Processing*, 49 (11) 137-145 (1970).
- Tsuda, S., "New process for caprolactam", *Chem. Econ. and Engng Rev.*, 39-41 (Dec. 1970).
- Achilladelis, B., "A study in technological history, Part II: The development of the BASF caprolactam process", *Chemistry and Industry* (50) 1584-1588 (1970).
- Achilladelis, B., "A study in technological history, Part III: The development of the SNIA Viscosa caprolactam process", *Chemistry and Industry* (52) 1608-1611 (1970).
- Lucas, G., "Nouvelle conception de la réaction d'oximation par le chlorure de nitrosoyle" (in French), *Inform. Chimie* (99) 73-80 (1971).
- Damme, J., Van Gooren, J. T., De Rooij, A. H., "Cyclohexanone oxime made without by-product $(\text{NH}_4)_2\text{SO}_4$ ", *Chem. Engng*, 79 (15) 54-55 (1972).
- "Caprolactam, INVENTA processes", *Europ. Chem. News, Suppl. 3-4*, (29 Sept. 1972).
- Loysen, S. J., Nunnink, G. H. J., "Caprolactam via HPO process", *Hydrocarbon Processing*, 51 (11) 92-94 (1972).

- "Caprolactam route avoids by-products", *Chem. and Engng News*, 14-15 (9 April 1973).
- "KANEBO develops new caprolactam process", *Europ. Chem. News*, 35 (11 May 1973).
- Giuffre, L., Tempesti, E., Fornaroli, M., Sili, G., Mattone, R., Airolidi, G., "New caprolactam process", *Hydrocarbon Processing*, 52 (9) 199-204 (1973).
- "NYPRO trebles its caprolactam capacity", *Sulphur* (108) 24-27 (1973).
- De Rooij, A. H., De Vries, H. A. W., Heunks A.M.A., "Caprolactam without any ammonium sulfate by-product", *Chem. Engng*, 81 (6) 54-55 (1974).
- Sili, G., Giuffre, L., "Make caprolactam via PMK", *Hydrocarbon Processing*, 53 (7) 124-126 (1974).
- Heath, A., "Caprolactam from toluene without ammonium sulfate", *Chem. Engng*, 81 (15) 70-71 (1974).
- "NYPRO, a lesson not to be forgotten", *Chemical Age*, 14-15 (23 May 1975).
- "Caprolactam production: a survey of current technology", *Europ. Chem. News*, 24-25 (30 April 1976).
- "Toluene rivals conventional caprolactam feedstocks", *Europ. Chem. News*, 20-22 (25 June 1976).
- De Rooij, A. H., Dijkhuis, C., Van Goolen, T. T., "Caprolactame: le procédé HPO" (in French), *Inform. Chimie* (165) 121-128 (1977).
- Simons, T. J. F., "Pulsed packed columns in the production routes to caprolactam", *Chemistry and Industry*, 748-757 (7 Oct. 1978).
- "The manufacture of non-fertilizer nitrogen products. An outline of some production techniques. Caprolactam", *Nitrogen* (134) 25-32 (1981).

Chapter 13 MONOMERS FOR THE SYNTHESIS OF POLYESTERS

Terephthalic acid and dimethyl terephthalate

- Towle, P. H., Baldwin, R. H., "Make most aromatic acids using Mid Century oxidation process", *Hydrocarbon Processing*, 43 (11) 149-153 (1964).
- "Japanese process for pure terephthalic acid", *Chem. Engng*, 72 (9) 70-72 (1965).
- Sittig, M., *Dibasic Acids and Anhydrides*, Noyes Development Corporation, Park Ridge, New Jersey (1966).
- Landau, R., Saffer, A., "Development of the MC process", *Chem. Engng Progress*, 64 (10) 20-26 (1968).
- Yoshimura, T., "New process can reduce terephthalic acid costs", *Chem. Engng*, 76 (10) 78-80 (1969).
- Ichichika, Y., Yamashita, G., Tokashiki, M., Yamaji, T., "New oxidation process for production of terephthalic acid from p-xylene", *Indusr. and Engng Chem. Product Research and Develop.*, 62 (4) 38-42 (1970).
- Tani, T., Enoki, K., "Make BHET without solvents", *Hydrocarbon Processing*, 49 (11) 146-150 (1970).
- Bryant, H. S., Duval, C. A., McMakin, L. E., Savoca, J. I., "Mobil's process for TPA", *Chem. Engng Progress*, 65 (9) 69-75 (1971).
- Heinicke, K., "Novel developments of the Witten DMT process", *ACS 164th National Meeting*, New York (27 August/1 Sept. 1972).
- "Mobil improves technology for TPA production", *Europ. Chem. News*, Large Plant Survey, 72-80, 82, (13 Oct. 1972).
- Ichikawa, Y., Takeuchi, Y., "Compare pure TPA processes", *Hydrocarbon Processing*, 51 (11) 103-108 (1972).
- "Lummus offers new terephthalic acid process", *Chem. and Engng News*, 10 (2 April 1973).
- Nakaoka, K., Miyama, Y., Matsuhisa, S., Wakamatsu, S., "Preparation of terephthalic acid using paraldehyde promoter", *Industrial and Engng Chem. Product Research and Develop.*, 12 (2) 150-155 (1973).
- "Process converts p-xylene to DMT", *Oil and Gas J.*, 106-107 (16 July 1973).
- Geibin, A. P., Sze, M. C., Whitehead, R. T., "New route to terephthalic", *Hydrocarbon Processing*, 52 (9) 209-215 (1973).
- Hizikata, M., "New process for fiber-grade high-purity terephthalic acid (HTA)", *Chem. Econ. and Engng Rev.*, 9 (11, 111) 32-38 (1977).
- Ueda, T., "Hi-yield DMT by Mitsui", *Hydrocarbon Processing*, 59 (11) 143-148 (1980).

Maleic anhydride

- Merims, R., Clifton, P. V., "Catalyst selectivity key to maleic anhydride process", *Europ. Chem. News*, Large Plant Suppl., 136-138 (27 Sept. 1968).
- Sherwood, P. W., "The technology of maleic production", *World Petroleum*, 39 (11) 48-61 (1968).
- "Maleic anhydride/fumaric acid, Veba/Bayer process and Veba process", *Oil and Gas J.*, 68 (47) 60 (1970).
- Di Cio, A., Zettel, G., "How SAVA makes maleic", *Hydrocarbon Processing*, 50 (9) 167-169 (1971).
- Ushio, S., "Maleic anhydride produced from C₄ hydrocarbons", *Chem. Engng.*, 78 (21) 107-109 (1971).
- "Joint process development improves MA process yield", *Europ. Chem. News*, Large Plant Survey, 40-44 (13 Oct. 1972).
- "Mitsubishi Chemical details its C₄ based maleic process", *Europ. Chem. News*, 30 (5 April 1974).
- "Belgians tap PA wastes for maleic anhydride", *Chem. Engng.*, 81 (18) 20 b-d (1974).
- "Continuous recovery of pure maleic anhydride perfected", *Oil and Gas J.*, 72 (36) 103 (1974).
- Weyens, E., "Recover maleic anhydride", *Hydrocarbon Processing*, 53 (11) 132-134 (1974).
- "L'anhydride maléique" (in French), *Industrie du Pétrole*, 62-63 (June 1975).
- Wirth, F., "Recover MA from PA scrubber water", *Hydrocarbon Processing*, 54 (8) 107-108 (1975).
- Lenz, D., De Bouille, M., "Le procédé Bayer pour la fabrication d'anhydride maléique à partir de butènes" (in French), *Rev. Assoc. Fr. Techniciens du Pétrole* (236) 20-23 (1976).
- De Maio, D. A., "Will butane replace benzene as a feedstock for maleic anhydride?", *Chem. Engng.*, 87 (10) 104-106 (1980).
- "Nouveau procédé de récupération de l'anhydride maléique" (in French), *Chimie Actualités*, 33-34 (2 June 1976).
- Wohlfart, K., Emig, G., "Compare maleic anhydride routes", *Hydrocarbon processing*, 59 (6) 83-90 (1980).
- Malow, M., "Benzene or butane for MAN", *Hydrocarbon Processing*, 59 (11) 149-153 (1980).
- "Butane beating benzene as maleic feed", *Chem. Engng.*, 88 (22) 25 (1981).
- Budi, F., Neri, A., Stefani, G., "Future MA keys to butane", *Hydrocarbon Processing*, 61 (1) 159-161 (1982).
- Corbett, J., "Butane takes over the maleic industry", *Chem. Business*, 35-39 (3 May 1982).
- "A new maleic process awaits better times", *Chem. Week*, 131 (14) 31-32 (1982).

Phthalic anhydride

- Graham, J. J., Way, P. F., "Phthalic anhydride by fluid bed process", *Chem. Engrg Progress*, 58(1) 96-100 (1962).
- Spitz, P. H., "Phthalic anhydride revisited", *Hydrocarbon Processing*, 47 (11) 162-168 (1968).
- Jouy, Graulier, "La production d'anhydride phthalique" (in French), *Inform. Chimie, Spécial Catalyse*, 65-68 (1969).
- Allan, J. P., "Phthalic anhydride", *ECMRA 2nd International Conference*, London (27/28 March 1969).
- Ellwood, P., "New life for fixed bed phthalic anhydride route", *Chem. Engng.*, 76 (12) 80-82 (1969).
- "Phthalic anhydride Von Heyden process", *British Chem. Engng. Process SCAN* (Sept. 1969).
- Truman, A. H., "Batch distillation of phthalic anhydride", *Chem. Engineering Progress*, 66 (3) 62-65 (1970).
- Graham, J. J., "The fluidized bed phthalic anhydride process", *Chem. Engrg Progress*, 66 (9) 54-58 (1970).
- Schwab, R. F., Doyle, W. H., "Hazards in phthalic anhydride plants", *Chem. Engrg Progress*, 66 (9) 49-53 (1970).
- Koopmann, J., Burger, G., "Verfahrenstechnische Probleme bei der Grossanlage der Phthalsäureanhydrid Synthese" (in German), *Bei Ingenieursblad*, 40 (21) 637-640 (1971).
- "Von Heyden offers high space velocity PA catalyst", *Europ. Chem. News*, 40 (8 Oct. 1971).
- Morrison, J., "BASF's new phthalic anhydride process promises low cost production", *Petroleum and Petrochem. Internat.*, 11 (12) 77-80 (1971).
- "Phthalic anhydride by vapor phase oxidation", *Oil and Gas J.*, 71 (11) 82 (1973).
- Zimmer, J. C., "New phthalic anhydride process", *Hydrocarbon Processing*, 53 (2) 111-112 (1974).
- Moores, C. W., "Control PA emissions", *Hydrocarbon Processing*, 54 (10) 100-103 (1975).
- Dow, R. M., Miserlis, C. D., "Recover power from phthalic plants", *Hydrocarbon Processing*, 56 (4) 167-170 (1977).

- Wiedemann, O., Gierer, W., "Phthalic anhydride made with less energy", *Chem. Engng.*, 86 (3) 62-63 (1979).
- De Virgiliis, A., Gerunda, A., "Optimize energy usage in phthalic anhydride units", *Hydrocarbon Processing*, 61 (5) 173-175 (1982).
- Di Cio, A., Ara, R., "Phthalic anhydride. A European outlook", *ECMRA 16th International Conference*, Oslo (11/13 Oct. 1982).
- Sato, T., Nakanishi, Y., Haruna, Y., "Recycling vent gas improves phthalic anhydride process", *Hydrocarbon Processing*, 62 (10) 107-110 (1983).
- Verde, L., Neri, A., "Un nouveau catalyseur ambivalent pour la production d'anhydride phthalique" (in French), *Inform. Chimie* (247) 141-143 (1984).

Diols

- Tsutsumi, Y., "Technological trends in 1,4-butanediol", *Chem. Econ. and Engng Rev.*, 8 (5, 95) 45-50 (1976).
- Brownstein, A. M., List, H. L., "Which route to 1,4-butanediol?", *Hydrocarbon Processing*, 56 (9) 159-162 (1977).
- Tamura, M., Kumano, S., "New process for 1,4-butanediol via allyl alcohol", *Chem. Econ. and Engng Rev.*, 12 (9, 141) 32-35 (1980).
- "1,4-butanediol and THF: process details are out", *Chem. Engng.*, 88 (1) 61 (1981).

Chapter 14 MONOMERS FOR THE SYNTHESIS OF POLYURETHANES

Nitrobenzene and aniline

- Murthy, M. S., Deshpande, P. K., Kuloor, N. R., "Design of a fluidized bed reactor for the vapor phase reduction of nitrobenzene to aniline", *Chem. Age of India*, 15 (9) 981-984 (1964).
- Albright, L. F., Van Munster, F. H., Forman, J. C., "Continuous process for reducing nitroaromatics to aromatic amines", *Chemical Engineering*, 74 (23) 251-259 (1967).
- Polinski, L. M., Harvey, E. A., "Aniline production by dual function catalyst", *Industr. and Engng. Chem. Product Research and Develop.*, 10 (4) 365-369 (1971).
- Cox, P. R., Strachan, A. N., "Two-phase nitration of toluene, I", *Chem. Engng Sciences*, 27 (3) 457-463 (1972).
- Cox, P. R., Strachan, A. N., "Two-phase nitration of toluene, II", *Chem. Engng J.*, 4 (3) 253-261 (1972).
- Becker, M., Russell, J. L., "Aniline from phenol", *Chem. Engng.*, 80 (8) 42-43 (1973).
- Champman, J. W., Cox, P. R., Strachan, A. N., "Two-phase nitration of toluene", *Chem. Engng Sciences*, 29 (5) 1247-1251 (1974).
- Gans, M., "Which route to aniline?", *Hydrocarbon Processing*, 55 (11) 145-150 (1976).
- "Safe continuous production of nitro-organics", *Processing*, 45 (May 1977).
- "BOFOR offers improved process for aromatics nitration", *Europ. Chem. News*, 25 (17 Nov. 1978).
- Kanhere, J. M., Chandalia, S. B., "Elimination of the use of sulfuric acid in the nitration of aromatic compounds", *Chem. Age of India*, 30 (5) 405-409 (1979).
- McKechnie, I., Bayer, F., Drennan, J., "Aniline: phenol feed chosen", *Chem. Engng.*, 87 (26) 26-27 (1980).

Isocyanates

- "Isocyanates" (in French), *Inform. Chimie*, special issue (95) 159-170 (1971).
- Lopez, A. W., "Toluene diisocyanate", *AICHE 83rd National Meeting*, Houston, Texas (20/24 March 1977).
- Robin, J., "La chimie des isocyanates et son application aux polymères" (in French), *Inform. Chimie* (176) 203-211 (1978).
- Remirez, R., "Isocyanates on the move", *Chem. Engng.*, 86 (20) 80-84 (1979).

INDEX

(Volume 2)

- Acetaldehyde**, 31-43
Conversion
to acetic acid, 13, 44-46, 51, 145-146, 271
to acetic anhydride, 63-66
to acrylonitrile, 229
to 1-butanol, 81
to ethanol, 73, 76
to ethylidene diacetate, 149
to peracetic acid, 18
Economic data, 41-42
Initiator in synthesis
of terephthalic acid, 294
Production
by dehydrogenation of ethanol, 31-33
by hydration of acetylene, 32-35, 42
by oxidation
of ethanol, 31-33
of ethylene, 36-42, 145, 320
Reactions, 36-37
Single step process, 38-39, 42
Two step process, 40-42
of paraffins, 35-36
by splitting of ethylbenzene hydroperoxide, 116
Specifications, 42
Uses and producers, 42-43
- Acetic acid**, 43-58
Conversion
to acetic anhydride, 58-63, 66-67
to allyl acetate, 215
to ethylene glycol diacetate, 23, 150
to ethylidene diacetate, 149
to ketene, 59-61, 194
to peracetic acid, 18
to phenyl acetate, 104, 123
to propylene glycol diacetate, 26
to vinyl acetate, 141-151
Economic data, 56-57
Production
by carbonization of wood, 56
by carbonylation of methanol, 43, 52-57
High pressure process, 54, 57
Low pressure process, 54-57
Reactions, 53-54
by conversion of H₂/CO mixture, 56
by oxidation of acetaldehyde, 43-46, 57, 63-66, 145-146
Process, 44-46
Reactions, 44
by oxidation of olefins, 48, 50-52
Direct oxidation of *n*-butenes, 51
Indirect oxidation of *n*-butenes, 50-52
by oxidation of paraffins, 46-48, 57
Oxidation of butane, 47, 57
Oxidation of light gasolines, 48-49, 57
Reactant in synthesis
of 1-butanol, 81
of 1,4-diacetoxyl 2-butenes, 318, 323-325
of propylene glycol, 26
of terephthalic acid, 291-293
Specifications, 57
Uses and producers, 56, 58
- Acetic anhydride**, 58-68
Conversion
to acetic acid, 64
to diacetyl peroxide, 64
to vinyl acetate, 149
Economic data, 67
Production
by carbonylation of methylacetate, 68
by decomposition of ethylidene diacetate, 66
by oxidation of acetaldehyde, 63-67
Process, 64-66
Reactions, 63-64
by pyrolysis of acetic acid, 59-61, 67
Process, 59-61
Reactions, 59
by pyrolysis of acetone, 61-63, 67
Process, 62-63
Reactions, 61, 63
Specifications, 67
Uses and producers, 67-68
- Acetone**, 126-136
Conversion
to acetic acid, 51

- to acetic anhydride, 61-63
- to ketene, 61-63
- to methacrylates, 204-209.
- Economic data**, 135
- Production**
 - by co-oxidation of propylene and isobutane, 127
 - by dehydrogenation of isopropanol, 127-131
 - Liquid phase process, 128-129, 135
 - Reactions, 127-128
 - Vapor phase process, 128, 130-131, 135
 - by fermentation, 84, 127
 - by oxidation
 - of isopropanol, 41, 131-132
 - of paraffins, 47, 51
 - of propylene, 132-135
 - Processes, 133-134
 - Reactions, 132-134
 - by splitting of cumyl hydroperoxide, 109, 115-116, 127
- Relative importance of production ways**, 126-127
- Specifications**, 136
- Uses and producers**, 135-136
- Acetonitrile**
 - By-product in synthesis of acrylonitrile, 220-224, 226-228
 - Conversion to acrylonitrile, 222
- Acetophenone**
 - By-product in synthesis of phenol, 114-116
- Acetoxylation**
 - of benzene to phenyl acetate, 123
 - of butadiene to 1,4-diacetoxy 2-butenes, 318, 323-325, 328
 - of ethylene to glycol mono and diacetates, 23, 150
 - of propylene to propylene glycol diacetate, 26
 - of propylene to propylene glycol hydroxy acetate, 19
- Acetylene**
 - Raw material in synthesis
 - of acrylates, 195, 198-200
 - of acrylic acid, 195, 216
 - of acrylonitrile, 220, 229
 - of 1,4-butanediol, 318, 321-323, 328
 - of ethylidene diacetate, 66
 - of vinyl acetate, 141-144, 151
 - of vinyl chloride, 153-156, 163-166, 187
- Acrolein**
 - Intermediate in synthesis
 - of acetone, 131-132
 - of acrylic acid, 190-191, 193
 - of acrylonitrile, 220-221, 226, 228
 - of alkyl alcohol, 320
 - of vinyl acetate, 143
- Acrylamide**
 - Intermediate in synthesis of acrylates, 201-202
- Acrylates**, 195-203, 215-218
 - Economic data**, 215-216
 - Physical characteristics**, 195
 - Production**
 - by esterification of acrylic acid, 195-197
 - by hydrolysis of acrylonitrile, 201-202
 - by hydrolysis of ethylene cyanohydrin, 197-198
 - by transesterification, 203
 - from acetylene, 198-200
 - BASF synthesis, 199-200
 - Repte synthesis, 198
 - Rohm and Haas synthesis, 198-199
 - from ketene, 199, 201
 - Specifications**, 217
 - Uses and producers**, 215, 218
- Acrylic acid**, 189-195, 215-217
 - Conversion**
 - to acrylates by esterification, 195-197, 243
 - to higher acrylates by ethylene oxide reaction, 203
 - Economic data**, 215-216
 - Production**
 - by hydrolysis of acrylonitrile, 195
 - by hydrolysis of ethylene cyanohydrin, 190, 194, 216
 - by oxidation of propylene, 190-193, 216
 - Operating conditions, 191
 - Processes, 191-193
 - Reactions, 190-191
 - by oxidative carbonylation of ethylene, 190, 194-195
 - by polymerization of β -propiolactone, 190, 194
 - by Repte synthesis from acetylene, 195
 - Specifications**, 217
 - Uses and producers**, 215, 217
- Acrylonitrile**, 219-232
 - Conversion**
 - to acrylates, 195, 201-202
 - to acrylic acid, 195
 - to adiponitrile, 234, 246, 249-253
 - Economic data**, 230, 232
 - Production**
 - by addition of hydrogen cyanide to acetylene, 220, 229
 - by ammonoxidation of propane, 230
 - by ammonoxidation of propylene, 220-228, 230

- Catalysts, 221-222
 Operating conditions, 222
 Performances, 222-223
 Processes, 223-228
 Fixed bed, 226-228
 Fluidized bed, 224-226
 Reactions, 220
 by passage through ethylene cyanohydrin, 220, 228-229
 by passage through lactonitrile, 220, 229
 by reaction of hydrogen cyanide with ethylene, 230
 by reaction of nitric oxide with propylene, 229
 Specifications, 231
 Uses and producers, 231-232
- Adipic acid, 240-245**
- Conversion
 - to adiponitrile, 234, 246
 - to 1,6-hexanediol, 255
 - to 6-hydroxycaproic acid, 271, 274
 - to polyesters, 287
 - to polyester-polyols, 334
 - Economic data, 244
 - Production
 - by carbonylation of butadiene, 243
 - by dimerization of acrylates, 243-244
 - by hydrogenation of phenol, 240-241, 244
 - by oxidation of cyclohexane, 241-244
 - Direct, 243
 - Indirect, 241-243
 - Production schemes, 234-235
 - Specifications, 245
 - Uses and producers, 244-245
- Adiponitrile, 234, 246-253**
- Production
 - by chlorination of butadiene and cyanation of dichlorobutenes, 246-247
 - by conversion of furfural, 246
 - by dimerization of acrylonitrile, 249-253
 - Chemical dimerization, 252-253
 - Electrochemical dimerization, 249-252
 - by hydrocyanation of butadiene, 247-249
 - by reaction of ammonia with adipic acid, 246
 - Production schemes, 234
- Aldolization**
- of acetaldehyde in synthesis
 - of 1-butanol, 81
 - of butyraldehyde, 92
 - of butyraldehyde in synthesis
 - of 2-ethyl hexanol, 92
 - of higher aldehydes, 94
- Alkaline fusion of sodium benzene sulfonate to sodium phenate, 105**
- Alkylation of benzene**
- to cumene, 103, 109-112, 124
 - to 2-phenyl butane, 137
- Alkyl aluminium**
- Catalyst in oligomerization of ethylene, 95-97, 102
- Allyl alcohol**
- Intermediate in synthesis
 - of 1,4-butanediol, 320
 - of glycerin, 131-132
- Amination**
- of 11-bromoundecanoic acid to 11-aminoundecanoic acid, 275-276, 278
 - of 1,6-hexanediol to hexamethylene diamine, 255
- 11-Aminoundecanoic acid, 274-278**
- Economic data, 278
 - Production
 - by amination of 11-bromoundecanoic acid, 275-276, 278
 - by bromination of undecenoic acid, 275-278
 - by hydrolysis of methyl undecenoate, 275-277
 - by pyrolysis of methyl ricinoleate, 275-277
 - by transesterification of castor oil, 274-275
 - Production schemes, 275-276
- Ammonia**
- Reactant in synthesis
 - of acetone cyanohydrin, 208
 - of acrylonitrile, 220, 222-227, 230
 - of adiponitrile, 246
 - of 11-aminoundecanoic acid, 275-276, 278
 - of ammonium carbonate, 261
 - of aniline, 345, 349-351
 - of caprolactam, 264-270, 272
 - of cyclododecanone oxime, 262-263, 265
 - of cyclohexanone oxime, 262-263, 265
 - of cyclohexylamine, 345
 - of ethylene dichloride, 159, 171-174
 - of hexamethylene diamine, 255
 - of hydrogen cyanide, 204-207
 - of laurolactam, 282-285
 - of nitric oxide, 261-262, 266-267, 270
- Ammoniolysis**
- of cyclohexanol to cyclohexylamine, 345
 - of phenol to aniline, 345, 349-351, 356
- Ammonium carbonate**
- Reactant in synthesis of hydroxylamine sulfate, 261

- Ammonium sulfate**
 By-product in synthesis
 of acrylates, 197, 201
 of acrylic acid, 194
 of caprolactam, 262-271
 of cyclododecanone oxime, 262-263
 of cyclohexanone oxime, 262-263
 of hydroxylamine sulfate, 261
 of laurolactam, 281-283
 of methacrylates, 206, 208, 213
 of methacrylic acid, 206
 Reactant in synthesis of acrylonitrile, 225-226
- Ammonium sulfonate**
 Reactant in synthesis of adiponitrile, 250
- Ammoxidation**
 of cyclohexanone to caprolactam, 266
 of isobutene to methacrylonitrile, 213
 of propane to acrylonitrile, 230
 of propylene to acrylonitrile, 220-228
 of *p*-xylene to terephthalic nitrile, 294
- Amyl alcohols**, 90
- Aniline**, 345, 347-351, 357-358
 Conversion by condensation to polyamines, 344, 351-353
 Economic data, 356-357
 Production
 by ammoniolysis of phenol, 349-351, 356
 by reduction of nitrobenzene, 347-349, 356
 Production reactions, 345
 Uses and producers, 357-358
- Beckmann rearrangement**
 of cyclododecanone oxime to laurolactam, 282-283
 of cyclohexanone oxime to caprolactam, 263-268
- Benzene**
 Raw material in synthesis
 of benzene sulfonic acid, 103-105
 of sec.-butylbenzene, 116, 137
 of chlorobenzenes
 by chlorination, 103, 105-106
 by oxychlorination, 103, 106-109
 of cumene, 103, 109-112, 124
 of cyclohexane, 122, 235-240
 of cyclohexylbenzene, 104, 117
 of ethylbenzene, 116
 of maleic anhydride, 301-304, 306, 308
 of nitrobenzene, 345-347
 of phenol, 123
- of phenyl acetate, 123
 of 2-phenyl butane (see sec.-butyl benzene)
- Benzoic acid**
 Conversion
 to hexahydrobenzoic acid, 258, 268-270
 to phenol, 104, 118-122
 to terephthalic acid, 295-297
 Production by oxidation of toluene, 104, 117-119, 295-297, 258, 268-270
- Bis hydroxy ethyl terephthalate (biset)**
 Intermediate in synthesis of polyethylene glycol terephthalate, 288
- Boric acid**
 Reactant in synthesis
 of alcohols, 91
 of caprolactam, 266
 of cyclododecanone mixture, 281-282
 of cyclohexanol one mixture, 122, 241-242
- Brine (see Sodium chloride)**
- Bromination**
 of butadiene to 1,4-dibromobutenes, 319
 of undecenoic acid to 11-bromoundecanoic acid, 277-278
- 11-Bromoundecanoic acid**
 Intermediate in synthesis of 11-aminoundecanoic acid, 275-278
- Butadiene**
 Raw material in synthesis
 of adipic acid, 243
 of adiponitrile, 234, 246-249
 of 1,4-butanediol, 318, 323-328
 of cyclododecatriene, 279-280
 of polybutadiene-polyols, 334
- n-Butane**
 Raw material in synthesis
 of acetaldehyde, 35-36
 of acetic acid, 46-47
 of acetone, 127
 of maleic anhydride, 301, 304-306
 of methyl ethyl ketone, 137
- 1,4-Butanediol**, 287, 317-329
 Conversion to polyester-polyols, 334
 Economic data, 328
 Production
 by acetoxylation of butadiene, 318, 323-325, 328
 by bromination of butadiene, 319
 by chlorination of butadiene, 318, 325-328
 by ethynylation of formaldehyde, 318, 321-323, 328

- by hydrogenation of butyrolactone, 318
 by hydrogenolysis of diperoxide from butadiene and *t*-butyl hydroperoxide, 319
 by hydrolysis of pentosanes, 321
- Production**
 from ethylene, 320
 from propylene, 320-321
- Specifications.** 329
- Uses and producers,** 328-329
- t*-Butanol,** 81-87
 Conversion to acrylates, 197
 Economic data, 84, 86
Production
 by acetone-butanol fermentation, 81, 84
 by condensation of acetaldehyde, 81
 by hydroformylation applied to propylene, 81-84, 86
 Processes, 83-84
 Reactions, 81-83
Specifications. 86
Uses and producers, 87, 89
- 2-Butanol (sec.-butanol),** 88-89
 Conversion to methyl ethyl ketone, 128, 137
 Economic data, 88
 Production, 89
 Uses and producers, 88
- t*-Butanol,** 88-90
 Conversion
 to acrylates, 203
 to *t*-butyl hypochlorite, 12
 to methacrolein, 16, 204, 209-212
 Co-product in synthesis of propylene oxide.
 Economic data, 88
 Production by hydration of isobutene, 89
 Specifications, 90
 Uses and Producers, 89-90
- Butanols**
 Production, 81-90
- n*-Butenes**
 Raw material in synthesis
 of acetic acid, 46, 50-52
 of 2-butanol, 89, 137
 of sec.-butyl benzene, 116
 of maleic anhydride, 301, 306-308
 of methyl ethyl ketone, 133, 137
- Butyl acrylate**
 Production, 195-203
 Specifications, 217
- t*-Butyl alcohol (see *t*-Butanol)**
- t*-Butyl hydroperoxide**
 Intermediate in synthesis of *t*-butanol, 13-16, 89, 127, 209
- Reactant in synthesis of 1,4-butanediol, 319
- 1,4-Butynediol**
 Intermediate in synthesis of 1,4-butanediol, 318, 321-323
- n*-Butyraldehyde**
 Conversion to aldol, 92-94, 98
Production
 by hydroformylation of propylene, 83-84, 92
 by hydrogenation of crotonaldehyde, 92
- Calcium chloride**
 By-product in synthesis
 of ethylene oxide, 1-2
 of propylene oxide, 10
- Caprolactam,** 257-274
 Economic data, 272, 274
Production by intermediate formation
 of *o*-acetyl cyclohexanone oxime from cyclohexanone, 271
 of caprolactone from cyclohexanone, 271
 of cyclohexenyl acetate from cyclohexanone, 271
 of hexahydrobenzoic acid from toluene, 268-272
 of 6-hydroxycaproic acid from cyclohexane, 271
 of nitrocyclohexane from cyclohexane, 271
 of 1,1'-peroxydiclohexylamine from cyclohexanone, 271
 of cyclohexanone oxime, 258-266, 272
 By-production of ammonium sulfate, 264-266
 Beckmann rearrangement, 264
 Oximation, 262-263
Preparation of oxime, 261-262
 Conventional processes, 261
 New processes, 261-262
Production of cyclohexanone, 258-260
 From cyclohexane, 260
 From phenol, 258-260
Production by photonitration of cyclohexane, 266-268, 272
Production schemes, 258
Specifications, 273
Uses and producers, 273-274
- Caprolactone**
 Intermediate in synthesis of caprolactam, 271
- Carbone monoxide**
 Reactant in synthesis
 of acetic acid, 52-57

- of acetic anhydride, 149-150
- of acrylates, 195, 198-199
- of acrylic acid, 194-195
- of diurethane, 341
- of glycolic acid, 23
- of methyl adipate, 243
- of N-phenyl methylurethane, 355-356
- of phosgene, 338-340, 353-356
- of *p*-toluic aldehyde, 297-298
- Carbonylation**
 - of butadiene to methyl adipate, 243
 - of dinitrotoluenes to diurethane, 341
 - of ethylene
 - to acrylic acid, 190, 194-195
 - to methyl propionate, 215
 - to propionic acid, 215
 - of formaldehyde to glycolic acid, 23
 - of methanol to acetic acid, 43, 52-56
 - of methyl acetate to acetic anhydride, 68, 149-150
 - of nitrobenzene to N-phenyl méthylurethane, 355, 357
 - of propylene
 - to isobutyric acid, 214
 - to methylisobutyrate, 214
 - of toluene to *p*-toluic aldehyde, 297-298
- Carboxyalkylation**
 - of ethylene to methyl succinate, 320
- 4-Carboxybenzaldehyde**
 - By-product in synthesis of terephthalic acid, 293
- Castor oil**
 - Raw material in synthesis of 11-amino-undecanoic acid (RILSAN), 274-276
- Caustic soda**
 - Catalyst and reactant in synthesis
 - of acetaldehyde, 35
 - of acetone, 133
 - of acetone cyanohydrin, 205
 - of acrolein cyanohydrin, 228
 - of acrylates, 196-197
 - of acrylonitrile, 221, 227, 229
 - of 1-butanol, 81
 - of caprolactam, 267-268
 - of chlorine, 180
 - of cumyl hydroperoxide, 114
 - of cyclododecanol/one mixture, 281-282
 - of cyclohexane, 236
 - of cyclohexanol/one mixture, 242
 - of diaminodiphenylmethanes, 352-353
 - of dinitrotoluenes, 336, 338
 - of 1,4-diol 2-butenes, 327
 - of 2-ethyl hexanol, 92
 - of hexamethylene diamine, 253-254
 - of nitrobenzene, 346-347
 - of phenol, 104-106, 115
 - of polyether-polyols, 360
 - of propylene oxide, 10-12
 - of undecenoic acid, 276-277
 - of vinyl acetate, 142
 - of vinyl chloride, 155-156, 160-162
 - Co-product in synthesis of chlorine by electrolysis, 177-184
- C₄ Cut (olefinic) (see Butenes)**
 - Raw material in synthesis
 - of 1-butanol, 209
 - of cyclododecatriene, 279-280
 - of maleic anhydride, 306-307
 - of methacrolein, 214
- Chlorination**
 - of benzene to chlorobenzenes, 103, 105-106
 - of butadiene to dichlorobutenes, 234, 247, 318, 325-327
 - of ethylene to ethylene dichloride, 153, 156-160, 163-166, 175-177, 185-186
 - of tetrahydrofuran to chlorobutane, 234, 246
- Chlorine, 177-184, 188**
 - Catalyst in synthesis of vinyl chloride, 161
 - Economic data, 186, 188
 - Importance for petrochemicals, 177-178
 - Production
 - by electrolysis, 167, 178-184
 - Diaphragm cells, 178-180, 188
 - Membrane cells, 183-184, 188
 - Mercury cathode cells, 180-182, 188
 - by oxidation of hydrochloric acid, 167-169
 - Reactant in synthesis
 - of chlorobenzenes, 105-106
 - of dichlorobutane, 246
 - of dichlorobutenes, 247, 325-328
 - of ethylene chlorohydrin, 1
 - of ethylene dichloride, 153, 157-159, 163, 165-166, 175-177, 185, 187
 - of phosgene, 338-340, 354-355
 - of propylene chlorohydrin, 10-12
- Chlorobenzenes**
 - Intermediate in synthesis of phenol, 104-109
- Coal**
 - Raw material to produce benzene-carboxylic acids, 298
- Coal tars**
 - Raw material for production of phenol, 104, 123, 125
- Cooxidation**
 - of acetaldehyde and propylene, 12-13, 17-18

- of acetic acid and propylene, 18
- of ethylbenzene and propylene, 13, 16
- of isobutane and propylene, 13-16
- of isobutyraldehyde and propylene, 12
- of olefinic C₄ cut, 214
- of propionic acid and propylene, 18
- of *p*-toluic aldehyde and propylene, 18-19

- Cracking**
- of acetic acid to ketene, 59-61
- of acetone to ketene, 61-63
- of ammonium bisulfate to sulfur dioxide, 264
- of ammonium hydrogen terephthalate to terephthalic acid, 294
- of butyl acetate to acetic acid, 52
- of coal to benzene-carboxylic acids, 298
- of diurethane to tolylene diisocyanate, 341
- of ethylene dichloride to vinyl chloride, 160-166, 175-178, 187
- of ethylene glycol diacetate to vinyl acetate, 150
- of methylene diphenyl urethane to MDI, 355
- of methyl ricinoleate to heptanal and methyl undecenoate, 275-277
- of 1,1'-peroxydicyclohexylamine to 11-cyanoundecanoic acid, 284
- of tetrachloroethane and pentachloroethane to trichloroethylene and perchloroethylene, 177
- of waxes to olefins, 91

- Crude oil**
- Raw material in synthesis of vinyl chloride, 164-167, 187

- Cumene**, 109-115, 124-125
- Conversion to cumyl hydroperoxide, 112-115, 127
- Economic data, 124
- Production by alkylation of benzene, 109-112
- Specifications, 125

- Cumyl hydroperoxide**
- Intermediate in synthesis of phenol and acetone, 103, 109, 112-116, 127

- Cyanation**
- of dichlorobutane to adiponitrile, 246
- of dichlorobutenes to dicyanobutenes, 247

- 11-Cyanoundecanoic acid**
- Intermediate in synthesis of laurolactam, 284

- Cyclization**
- of 6-amino caproic acid to caprolactam, 271
- of 6-hydroxy caproic acid to caprolactone, 271, 274

- Cyclododecane**
- Intermediate in synthesis of laurolactam, 279-280

- Cyclododecanol**
- Intermediate in synthesis of laurolactam, 280-281

- Cyclododecanone**
- Intermediate in synthesis of laurolactam, 280-281

- Cyclododecanone oxime**
- Intermediate in synthesis of laurolactam, 281-283

- Cyclododecatriene**
- Intermediate in synthesis of cyclododecane, 279-280
- of cyclododecene, 284

- Cyclohexane**, 235-240
- Conversion
- to adipic acid, 241-244
- to cyclohexanol/one mixture, 103, 122, 234, 241-242, 260, 270
- to nitrocyclohexane, 271
- Economic data, 239-240
- Production
- by extractive distillation, 235
- by hydrogenation of benzene, 235-240
- Liquid phase processes, 236-240
- Reactions, 235-236
- Vapor phase processes, 239-240
- Specifications, 239
- Uses and producers, 239-240

- Cyclohexanol**
- Conversion
- to adipic acid by oxidation
- with air, 241, 243
- with nitric acid, 240-242
- to cyclohexanone, 258, 260
- to cyclohexylamine, 345
- to phenol, 122-123
- Production
- by hydrogenation of phenol, 234, 240-241, 258
- by oxidation of cyclohexane, 103, 122, 234, 241-242

- Cyclohexanone**
- Conversion
- to adipic acid, 241-243
- to caprolactam, 266
- to caprolactone, 271
- to cyclohexanone oxime, 258, 262-263, 265

- to cyclohexenyl acetate, 271
 - to peroxide, 271, 284
 - to phenol, 122-123
 - Production**
 - by cracking of 1,1'-peroxydicyclohexylamine, 271
 - by hydrogenation of phenol, 258-260
 - by oxidation of cyclohexane, 103, 122, 134, 241-242, 260, 271
 - by splitting of cyclohexylbenzene hydroperoxide, 104, 117
 - Cyclobexanone oxime**
 - Intermediate in synthesis of caprolactam, 261-266, 271
 - Cyclohexylamine**
 - By-product in synthesis of aniline, 349
 - Cyclotrimerization of butadiene to cyclododecatriene**, 279-280

 - Deacetoxylation of acetobutyric acids to acetic acid, butyrolactone and methacrylic acid, 215**
 - Dehydration**
 - Chemical dehydration
 - of adipamide and ammonium adipate to adiponitrile, 246
 - of 1,4-butanediol to tetrahydrofuran, 325
 - of *t*-butanol to isobutene, 16, 90
 - of ethylene cyanohydrin to acrylonitrile, 228
 - of higher alcohols to unsaturated aldehydes, 92-94
 - of 2-hydroxybutyraldehyde (aldol) to crotonaldehyde, 81, 92
 - of lactonitrile to acrylonitrile, 229
 - of methyl α -hydroxy isobutyrate to methyl methacrylate, 214
 - Physico-chemical dehydration
 - of acetaldehyde, 38-41
 - of acetic acid, 45-46, 48-49, 54-56
 - of acetic anhydride, 60-63, 65-66
 - of acrylates, 196-197, 201-202
 - of acrylonitrile, 226-228
 - of adiponitrile, 248
 - of aniline, 348-351
 - of benzene sulfonic acid, 105
 - of boric esters of cyclohexanol, 122
 - of butadiene, 247-248
 - of caprolactam, 270
 - of ethanol, 72-74
 - of ethylene dichloride, 158-159, 171-174
 - of ethylene glycol, 21-22

 - of ethylene oxide, 4-5, 7
 - of isopropanol, 78-79
 - of maleic anhydride, 302
 - of methanol, 289
 - of methyl methacrylate, 207-208, 211-213
 - of phenol, 107-108
 - of propylene glycol, 27
 - of vinyl acetate, 148-149
 - of vinyl chloride, 155-156
- Dehydrocyanation**
 - of methylene glutaronitrile to dicyanobutenes, 253
- Dehydrogenation**
 - of sec.-butanol to methyl ethyl ketone, 89, 137
 - of cyclododecanol/one mixture to cyclododecanone, 281-282
 - of cyclohexanol to cyclohexanone, 258
 - of cyclohexanol/one mixture to cyclohexanone, 260
 - to phenol, 122-123
 - of cyclohexylamine to aniline, 345
 - of ethanol to acetaldehyde, 31-33
 - of isobutyric acid to methacrylic acid, 214
 - of isopropanol to acetone, 126-131
 - of methyl isobutyrate to methyl methacrylate, 214
 - of *n*-paraffins to olefins, 91
- Diethyl ether**
 - By-product in synthesis of ethanol, 71
- Diethylene glycol**
 - By-product in synthesis of ethylene glycol, 21-22
- Diisocyanates**, 331-333
- Diisopropylbenzene**
 - Conversion to cumene by transalkylation with benzene, 112
- Dimerization**
 - of acrylonitrile to adiponitrile, Chemical methods, 252-253
 - Electrochemical methods, 249-252
 - of ethylene to butenes, 91
 - of light olefins to higher olefins, 91, 94
 - of methyl acrylate to dimethyl ester of 3-hexenedioic acid, 243
- Dimethyl ether**
 - By-product in synthesis
 - of acetic acid, 54
 - of methacrylates, 206, 208, 212
- 1,4-Dimethylolcyclohexane**, 287, 330
 - Production by hydrogenation of dimethyl terephthalate, 330

Dimethyl terephthalate, 287-301

Conversion

to 1,4-dimethyloxy cyclohexane, 330
to polyester-polyols, 334

Economic data, 299-301

Physical properties, 287-288

Production

by ammonoxidation of *p*-xylene, 294
by carbonylation of toluene, 297-298
by disproportionation of benzoic acid, 295-297

by isomerization of potassium salts of phthalic acids, 294-295

by nitric oxidation of *p*-xylene, 288

by oxidation and esterification of *p*-xylene, 288-291, 299

by oxidation of *p*-xylene to pure terephthalic acid, 291-294, 299

by oxidative cracking of coal, 298

Specifications, 299

Uses and producers, 300-301

Dinitrotoluenes

Intermediate in synthesis of toluene diisocyanate, 335-338, 341

Diols, 331, 333

Diphenyl ether

By-product in synthesis of phenol, 105-106, 120-121

4,4-Diphenyl methane diisocyanate, 344, 351-358

Definition, 332

Economic data, 356-357

Production

by direct carbonylation of nitrobenzene, 353-357

by phosgenation of polyamines, 351-356
Phosgenation 353-355

Synthesis of polyamines, 351-353

Production schemes, 344

Specifications, 357

Uses and producers, 357-358

Dipropylene glycol

By-product in synthesis of propylene glycol, 26-27

Dismutation (see Disproportionation)

Disproportionation

of dipotassium salt of isophthalic acid to dipotassium salt of terephthalic acid, 295
of potassium benzoate to dipotassium salt of terephthalic acid, 296-298

Divinylacetylene

By-product in synthesis of vinyl acetate, 143-144

Electrochemistry

Economic data, 188

in synthesis

of adiponitrile, 249-252

Processes, 250-252

Reactions, 249-250

of 1,4-butanediol, 320

of chlorine, 167, 177-184, 186, 188

Diaphragm cells, 178-180, 188

Membranes cells, 183-184, 188

Mercury cathode cells, 180-182, 188

Epoxidation

of ethylene to ethylene oxide, 1-9

of propylene to propylene oxide, 9-20, 89,

127

Esterification

of acrylamide sulfate to acrylates, 197-198, 201

of acrylic acid to acrylates, 195-197, 243

of adipic and co-hydroxycaprylic acids to adipate and caproate, 255

of *n*-butenes to sec.-butyl acetate, 52

of *n*-butenes to isobutyl sulfate, 89

of ethylene to ethyl sulfate, 69-71

of isobutene to *t*-butyl sulfate, 89

of methacrylamide sulfate to methacrylates, 204-208, 213

of methacrylic acid to methyl methacrylate, 209-215

of methyl hydrogen terephthalate to dimethyl terephthalate, 289

of propionic acid to methyl propionate, 215

of propylene to isopropyl sulfate, 76-77

of terephthalic acid to dimethyl terephthalate, 288-290

of *p*-toluic acid to methyl *p*-toluate, 289-290

Ethanal (see Acetaldehyde)

Ethane

Raw material in synthesis of vinyl chloride, 184-185

Ethanol, 69-76

Conversion

to acetaldehyde, 31-33

to acrylates, 195-203

Dehydration to anhydrous ethanol, 73-74

Economic data, 74

Production

by acetone-butanol fermentation, 84

by direct hydration of ethylene, 69, 71-74

by indirect hydration of ethylene, 69-71

by transformation of synthesis gas, 69

Specifications, 75

Uses and producers, 75-76

- Ethyl acrylate**
 Production, 195-203
 Specifications, 217
- Ethylbenzene**
 Intermediate in synthesis of ethylbenzene hydroperoxide, 116
- Ethylene**
 Raw material in synthesis
 of acetaldehyde, 36-41, 145
 of acrylic acid, 190, 194-195
 of acrylonitrile, 230
 of 1,4-butanediol, 320
 of ethanol, 69-74
 of ethylbenzene, 116
 of ethylene dichloride, 156-160, 168-177
 of ethylene glycol, 23
 of ethylene glycol diacetate, 23, 150
 of ethylene oxide, 1-8
 of methacrylates, 204, 215
 of methylpropionate, 215
 of propionaldehyde, 215
 of propionic acid, 215
 of vinyl acetate, 141, 143-149, 151
 of vinyl chloride, 153, 156-160, 163-165, 168-177, 186
- Ethylene dichloride**, 156-177
 Conversion to vinyl chloride, 160-166, 175-177
 Operating condition, 160-161
 Processes, 161-163
 Reactions, 160
- Production
 by chlorination of ethylene, 156-160
 Operating conditions, 157
 Processes, 157-160
 Reactions, 157
 by oxychlorination of ethylene, 168-177
 Operating conditions, 168, 170
 Processes with fixed beds, 170, 172-174
 Processes with fluidized beds, 170-172
 Reactions, 168
- Production schemes, 153, 163-164, 175-177
 Balanced, 163-164
 Integrated, 175-177
- Ethylene glycol**, 21-25
 Conversion
 to polyethylene glycol, 333
 to polyester-polymers, 334
 to polyterephthalate, 287
 Economic data, 24
- Production
 by acetylation of ethylene, 23
 by carbonylation of formaldehyde, 23
 by hydration of ethylene oxide, 21-22
 by hydrogenation of *n*-butyl oxalate, 24
- by oxidation of ethylene, 21, 23
 by passage through ethylene chlorohydrin, 23
 by transformation of synthesis gas, 23
- Specifications, 25
- Uses and producers, 24-25
- Ethylene oxide**, 1-9
 Conversion
 to acrylates, 203
 to ethylene cyanohydrin, 190, 194, 197-198, 220, 228-229
 to ethylene glycol, 21-22
 to PEG, 333, 359
 to polybutadiene-polyols, 334
- Economic data, 8
- Production
 by direct oxidation of ethylene, 2-8
 Catalysts, 3
 General scheme, 4
 Operating conditions, 3-4
 Processes with air, 6-7
 Processes with oxygen, 4-6
 Reactions, 2
 by indirect oxidation of ethylene (chlorohydrin process), 1-2
- Specifications, 8
- Uses and producers, 9
- Ethyldene diacetate**
 Intermediate in synthesis
 of acetic anhydride, 64, 66
 of vinyl acetate, 149-150
- 2-Ethyl hexanol**, 92-94, 98-100
 Conversion to acrylate, 203
 Economic data, 98
 Production, 92-94
 Specifications, 100
 Uses and producers, 99-100
- 2-Ethyl hexenal**
 Intermediate in synthesis of 2-ethyl hexanot, 92
- Ethylation**
 of formaldehyde to 1,4-butanediol, 318, 321-323
- Fermentation**
 Production
 of acetone-butanol, 84, 127
 of ethanol, 69
- Formaldehyde**
 Reactant in synthesis
 of acrylates, 195, 199-201
 of acrylic acid, 190, 194
 of 1,4-diol 2-butyne, 318, 322-323

- of methacrylates, 215
- of methylene diphenylurethane, 355
- of polyamines, 344
- of polybutadiene-polyols, 334
- Formic acid**
 - By-product in synthesis of acetic acid, 44, 47-52, 54, 56
- Fumaric acid**
 - Production by isomerization of maleic acid, 287, 310
- Furan**
 - Intermediate in synthesis of adiponitrile, 234, 246
 - of 1,4-butanediol, 321
- Furfural**
 - Intermediate in synthesis of 1,4-butanediol, 321
 - Raw material in synthesis of adiponitrile, 234, 246
- Gasoline (see Naphtha)**
- Glycerine**
 - Conversion to polyols, 333, 359-360
 - Production
 - from allyl alcohol and hydrogen peroxide, 41, 131, 137
 - from castor oil, 275-276
 - from synthesis gas, 23
- Glycolic acid**
 - Intermediate in synthesis of ethylene glycol, 23
- Glycols (see Ethylene glycol and Propylene glycol)**
- HDI (hexamethylene diisocyanate)**
 - Monomer in synthesis of polyurethanes, 332
- Heptanal (oenanthol)**
 - By-product in synthesis of methyl undecanoate, 275, 277
- Heptanoic acid**
 - Production by oxidation of heptanal, 275, 277
- Heptanol**
 - Production by hydrogenation of heptanal, 275, 277
- Hexahydrobenzoic acid (carboxylic cyclohexane)**
 - Intermediate in synthesis of caprolactam, 269-271
- Hexamethylene diamine, 253-257**
 - Economic data, 255-256
 - Production
 - by hydrogenation of adiponitrile, 234, 253-255
 - of dicyanobutenes, 253
 - by passage through 1,6-hexanediol, 255
 - Production schemes, 234
 - Specifications, 256
 - Uses and producers, 255, 257
- 1,6-Hexanediol**
 - Intermediate in synthesis of hexamethylene diamine, 253, 255
- Higher alcohols, 90-102**
 - Economic data, 98-99
 - Production
 - by hydroformylation, 91-95, 98-99
 - Aldox process, 92-94
 - 2-ethyl hexanol synthesis, 92-93, 98
 - Isodecanols synthesis, 94
 - Isooctanols synthesis, 94, 98
 - by oligomerization of ethylene, 95-97, 99, 102
 - Process, 95-97, 102
 - Reactions, 95
 - by oxidation of paraffins, 91, 99
 - Specifications, 100
 - Uses and producers, 99-101
- HMDI (Hydrogenated Diphenyl Methane 4,4'-Diisocyanate)**
 - Monomer in synthesis of polyurethanes, 332
- HXDI (Hydrogenated Xylylene Diisocyanate)**
 - Monomer in synthesis of polyurethanes, 332
- Hydration**
 - of acetylene to acetaldehyde, 31, 33-35, 42
 - of *n*-butenes to sec.-butanol, 89, 137
 - of ethylene to ethanol, 69, 71, 74
 - of ethylene oxide to ethyleneglycol, 21-22, 24
 - of isobutene to *t*-butanol, 89, 209
 - of propylene to isopropanol, 76-79, 131-132
 - of propylene oxide to propylene glycol, 26-28
- Hydroalkylation**
 - of benzene to phenylcyclohexane, 104, 117
- Hydrobromic acid**
 - Reactant in synthesis of 11-bromoundecanoic acid, 275-278
 - of terephthalic acid, 291, 293
- Hydrochloric acid**
 - By-product in synthesis of vinyl chloride, 160-166, 175-177

Conversion to chlorine by oxychlorination.
167-176
Reactant in synthesis
of acetaldehyde, 36-39
of acetone, 132-134
of acrylates, 198
of acrylic acid, 194
of acrylonitrile, 229-230
of adiponitrile, 247-249
of aniline, 347
of chlorine, 178-183
of diaminodiphenylmethanes, 351-353
of dichloroethane, 167-175
of ethylene glycol, 23
of fumaric acid, 310
of methyl ethyl ketone, 137
of methylene diphenyl urethane, 357
of nitrosyl chloride, 266-268, 283
of phenol, 105-108
of vinyl acetate, 145-146
of vinyl chloride, 153-156, 163-166

Hydrochlorination
of acetylene to vinyl chloride, 153-156,
163-166, 187

Hydrocyanation
of butadiene to adiponitrile, 246-249
of methylene glutaronitrile to dicyanobutenes, 252-253

Hydroformylation
of acetalized acrolein to acetal, 321
of alkyl *t*-butyl ether to *t*-butyl butanediol ether, 320
alkyl acetate to acetoxybutyraldehyde, 215
of alkyl alcohol to aldehyde/alcohol, 320
of *n*-butenes and isobutene to amyl aldehydes, 90
of cyclododecene to aldehyde, 284
of ethylene to propionaldehyde, 215
of heptenes and octenes to corresponding higher aldehydes, 94-95
of higher olefins to aldehyde, 91-95, 99, 101-102
of propylene to *n* and isobutyraldehydes, 81-84, 92, 214

Hydrogen

Reactant in synthesis
of adiponitrile, 247-248
of aniline, 345, 347-349, 356
of 1,4-butanediol, 318-320, 322-323, 326-327
of 1-butanol, 81, 83-85
of caprolactam, 267-268
of cyclododecane, 279-280
of cyclohexane, 235-239

of cyclohexanone, 259, 260
of 1,4-diacetoxypentane, 318, 324-325
of dimethyl hexahydroterephthalate, 330
of dimethylol cyclohexane, 330
of ethylene glycol, 23-24
of 2-ethyl hexanol, 92, 98
of hexahydrobenzoic acid, 269-270
of hexamethylene diamine, 253-255
of higher alcohols, 92-94, 99
of hydroxylamine, 262
of hydroxylamine sulfate, 261
of methyl adipate, 243
of pure terephthalic acid, 292-293
of tetrahydrofuran, 246, 321
of tolylene diamine, 337-338

Hydrogenation

of acetaldehyde to ethanol, 73
of acrokin to allyl alcohol, 320
of acrylonitrile to adiponitrile, 249-251
of acrylonitrile to propionitrile, 249-250
of adipic acid to 6-hydroxycaproic acid, 271
of adiponitrile to hexamethylene diamine, 253-255
of ammonium salt of C₁₂ unsaturated α , ω -aldehyde acid to aminododecanoic acid, 284
of amyl aldehydes to amyl alcohols, 90
of benzene to cyclohexane, 122, 235-239
of benzoic acid to hexahydrobenzoic acids, 269-270
of 1,4-butanediol to 1,4-butanediol, 318, 322-323
of *n* and iso butyraldehydes to *n* and iso butanols, 81, 83-84, 92
of C₄ aldehyde alcohol to 1,4-butanediol, 320
of 4-carboxybenzaldehyde to *p*-toluic alcohol, 292-293
of crotonaldehyde to 1-butanol, 81
of 11-cyanoundecanoic acid to 12-amino dodecanoic acid, 284
of cyciododecatriene to cyclododecane, 279-280
of cyclododecatriene to cyclododecene, 284
of 1,4-diacetoxypentane to 1,4-diacetoxypentane, 318, 324-325
of dicyanobutenes to adiponitrile, 247, 253
of dimethylterephthalate to dimethyl hexahydroterephthalate, 330
of dimrotulene to tolylene diamine, 335, 337-338
of 1,4-diol 2-butene to 1,4-butanediol, 318, 326-327
of 2-ethyl hexenal to 2-ethyl hexanol, 92, 93
of furan to tetrahydrofuran, 234, 246
of heptanal to heptanol, 273, 277

- of 3-hexene dioic acid to methyl adipate, 243
 of higher aldehydes to corresponding alcohols, 91-94
 of isobutene to isobutane, 16
 of maleic anhydride to 1,4-butanediol, 318
 of methyl glycolate to ethylene glycol, 23
 of α -methyl succinate to 1,4-butanediol, 320
 of nitrales ions to hydroxylamine ions, 262
 of nitrobenzene to aniline, 345, 347-349
 of 6-nitrocaproic acid to 6-aminocaproic acid, 271
 of nitrocyclohexane to cyclohexanone oxime, 271
 of phenol to cyclohexanol, 240, 258
 of phenol to cyclohexanone, 259-260
- Hydrogen cyanide**
 By-product in synthesis of acrylonitrile, 220, 223, 226-228
 Production, 204-207
 Reactant in synthesis
 of acetone cyanohydrin, 205, 207-208
 of acrylates, 197
 of acrylic acid, 194
 of acrylonitrile, 220, 228-230
 of adiponitrile, 247-249
 of dicyanobutenes, 247
 of ethylene cyanohydrin, 194, 197
 of methacrylates, 204-208
- Hydrogenolysis**
 of adipic and co-hydroxycaproic acids esters to 1,6-hexanediol, 255
 of butadiene polyperoxide to 1,4-butanediol, 319
 of dimethyl hexahydroterephthalate to 1,4-dimethylcyclohexane, 330
 of diperoxide from butadiene and *t*-butylhydroperoxide to 1,4-butanediol, 319
- Hydrogen peroxide**
 Co-product in oxidation
 of sec.-butanol to methyl ethyl ketone, 137
 of isopropanol to acetone, 127, 131-132
 Reactant in synthesis
 of acetone, 131-132
 of caprolactam, 271
 of laurolactam, 284
 of propylene oxide, 18
 of polybutadiene-polyols, 334
- Hydrolysis**
 of acetic anhydride to acetic acid, 64
 of acetone cyanohydrin to methacrylamide sulfate, 204-205.
- of acrylonitrile to acrylamide sulfate, 195-201
 of allyl acetate to allyl alcohol, 320
 of boric esters
 of cyclododecanol, 281-282
 of cyclohexanol, 122, 241-242
 of chlorobenzenes to phenol, 103-109
 of 1,4-diacetoxymethane to 1,4-butanediol and acetic acid, 318, 323-325
 of 1,4-dibromo 2-butenes to 1,4-diol 2-butenes, 319
 of 1,4-dichloro 2-butenes to 1,4-diol 2-butenes, 319, 326-327
 of ethylene chlorohydrin to ethylene glycol, 23
 of ethylene cyanohydrin
 to acrylamide sulfate, 195, 197-198
 to acrylic acid, 190, 194
 of ethylene glycol diacetate to ethylene glycol, 23
 of hydroxylamine disulfonate to hydroxylamine sulfate, 261
 of linear higher olefins aluminates to alcohols, 95-97
 of methacrylonitrile to methacrylamide sulfate, 213
 of methyl adipate to adipic acid, 243
 of methyl undecenoate to undecenoic acid, 275-277
 of methyl vinyl ether to methanol and acetaldehyde, 35
 of 6-nitro cyclohexanone to 6-nitro caproic acid, 271
 of phenyl acetate to phenol, 104, 123
 of phenyl benzoate to phenol, 120-121
 of propylene glycol diacetate to propylene glycol, 26-27
 of residue of tolylene diamine phosgenation to tolylene diamine, 340
 of sulfates of acrylamide to acrylic acid, 201
 of sulfates of *t*-butyl to *t*-butanol, 89
 of sulfates of ethyl to ethanol, 69-71
 of sulfates of isobutyl to 2-butanol, 76-77
 of sulfates of isopropyl to isopropanol, 89
 of sulfates of methacrylamide to methacrylic acid, 204-208
 of terephthalic nitrile to ammonium hydrogen terephthalate, 294
 of vinyl acetate to acetaldehyde, 145
- Hydroquinone**
 Inhibitor in synthesis
 of acrylates, 196-197, 199-202
 of acrylic acid, 192-193

- of methacrylates, 210-211, 213
- of vinyl acetate, 143
- Hydroxylamine**
 - Intermediate in synthesis of caprolactam, 261-262, 264
- Hydroxylamine sulfate**
 - Intermediate in synthesis
 - of caprolactam, 261-263
 - of laurolactam, 281-282
- Hypochlorous acid**
 - Intermediate in synthesis
 - of ethylene glycol, 23
 - of ethylene oxide, 1-2
 - of propylene oxide, 10-12
- Iodine (methyl iodide)**
 - Catalyst or reactant in synthesis
 - of acetic acid, 52-56
 - of acetic anhydride, 68
 - of 1,4-butanediol, 320
 - of isobutyric acid, 214
 - of vinyl acetate, 150
 - of vinyl chloride, 161, 186
- Ion exchange resins**
 - Catalyst or separating agent in synthesis
 - of acetic acid, 52, 54
 - of acrylates, 197, 203
 - of 1,4-butanediol, 325
 - of *t*-butanol, 89, 209
 - of caprolactam, 264-265, 268
 - of chlorine, 180, 182, 184
 - of isopropanol, 77-78
 - of methacrylates, 210
 - of phenol, 115
 - of propylene glycol, 26
- Isobutane**
 - Raw material in synthesis
 - of acetone, 127
 - of *t*-butanol, 14-16, 89, 127, 209
 - of methacrylates, 204
- Isobutanol, 81-87**
 - By-product in synthesis of 2-ethyl hexanol, 93
 - Production by hydroformylation of propylene, 81-85
 - Processes, 81, 83-85
 - Reactions, 81-82
 - Specifications, 86
 - Uses and producers, 87, 89
- Isobutene**
 - Co-product in synthesis of propylene oxide, 16
- Raw material in synthesis**
 - of 1,4-butanediol, 320
 - of *t*-butanol, 89, 209
 - of methacrylates, 204, 213-214
- Isobutyraldehyde**
 - Conversion to isobutyric acid, 214
 - Production by hydroformylation of propylene, 82-85, 92, 214
- Isododecanol**
 - Production by oxo synthesis, 94
- Isomerization**
 - of maleic acid to fumaric acid, 310
 - of methylcyclopentane to cyclohexane, 235
 - of potassium salts of phthalic acids, 294-295, 298
 - of propylene oxide to allyl alcohol, 320
- Isononanol**
 - Production by oxo synthesis, 94
- Isooctanol**
 - Production by oxo synthesis, 94
- Isophthalic acid**
 - Raw material in synthesis of terephthalic acid, 295
- Isopropanol, 76-80**
 - Conversion to acetone
 - by dehydrogenation, 127-131, 135
 - by oxidation, 127, 131-132
 - by reaction with acrolein, 131-132
 - Co-product in acetone-butanol fermentation, 84
 - Economic data, 79
 - Production
 - by esterification of propylene and hydrolysis, 76-77, 79
 - by hydration of propylene, 77-79
 - Specifications, 80
 - Uses and producers, 80
- Isopropyl benzene (see cumene)**
- Isotridecanol**
 - Production by oxo synthesis, 94
- Ketene**
 - Intermediate in synthesis
 - of acetic anhydride, 59-63
 - of acrylates, 195, 199, 201
 - of acrylic acid, 190, 194
 - of cyclohexenyl acetate, 271
- Laurolactam, 279-285**
 - Economic data, 285

- Intermediates synthesis**
- cyclododecane, 279, 280
 - cyclododecatriene, 279-280
- Production**
- by oximation of cyclododecanone, 281-283, 285
 - by ozonization of cyclododecatriene, 283-284
 - by passage through cyclododecane, 284
 - by photomitroization of cyclododecane, 283, 285
 - by pyrolysis of 1,1'-peroxydicyclohexylamine, 284-285
- Lime**
- Reactant in synthesis
 - of anhydrous ethanol, 73
 - of ethylene oxide, 1
 - of phenol, 115
 - of propylene oxide, 12
- Maleic acid (see Maleic anhydride)**
- Maleic anhydride, 301-310**
- Conversion
 - to 1,4-butanediol, 318
 - to fumaric acid, 310
 - Co-product in synthesis of phthalic anhydride, 301, 308, 312, 315
 - Economic data, 308, 310
 - Production by oxidation
 - of benzene, 302-304, 308
 - of *n*-butane, 304-306, 308
 - of *n*-butenes, 306-308
 - Specifications, 309
 - Uses and producers, 309-310
- MDI (see Diphenylmethane 4,4-diisocyanate)**
- Membranes**
- in synthesis
 - of adiponitrile, 248-249, 250-252
 - of chlorine, 183-184
- Metathesis**
- of benzoic acid and dipotassium terephthalate to benzoate and acid, 297
- Methacrolein**
- Intermediate in synthesis of methacrylates, 209-214
- Methacrylates, 203-219**
- Economic data, 215-216
 - Production
 - from acetone and hydrogen cyanide, 204-209
 - Operating conditions, 116, 204-206
 - Processes, 206-209
 - Reactions, 204-206
- from *t*-butyl alcohol, 90, 209-213
 - Operating conditions, 209-210
 - Processes, 210-213
 - Reactions, 209
 - from ethylene, 215
 - from isobutene, 213
 - from olefinic C₄ cuts, 213-214
 - from propylene, 214
 - Specifications, 217
 - Uses and producers, 215, 218-219
- Methacrylic acid**
- Intermediate in synthesis of methacrylates, 203, 206, 209-215
- Methanation**
- CO removing, 236
- Methane**
- Raw material in synthesis
 - of acrylonitrile, 222
 - of hydrogen cyanide, 204-205
- Methanol**
- Conversion
 - to acetic acid, 52-56
 - to acrylates, 195-203, 243
 - to dimethyl terephthalate, 289
 - to diurethane, 341
 - to methyl adipate, 243
 - to methyl glycolate, 23
 - to methyl hydrogen terephthalate, 289
 - to methyl isobutyrate, 214
 - to methyl methacrylate, 206-212
 - to methyl propionate, 215
 - to methyl ricinoleate, 275-276
 - to methyl succinate, 320
 - to methyl *p*-toluate, 289-290
 - to N-phenyl methylurethane, 355
 - Co-product in synthesis of acetaldehyde, 85
- Methyl acetate**
- Intermediate in synthesis
 - of acetic acid, 44-46, 54, 56
 - of acetic anhydride, 68
 - of vinyl acetate, 149-150
 - Production from synthesis gas, 149-150
- Methyl acrylate**
- Production, 195-203, 243
 - Specifications, 217
- Methylal**
- Reactant in synthesis of methacrylates, 215
- Methylchloroform**
- Production by hydrochlorination of vinylidene chloride, 177
- Methyl ethyl ketone, 137-139**
- Economic data, 138

- Initiator in synthesis of terephthalic acid, 294
- Production**
 - by dehydrogenation of sec.-butanol, 137
 - by oxidation
 - of *n*-butane, 47, 137
 - of sec.-butanol, 131-132, 137
 - of *n*-butenes, 133, 137
 - by splitting of 2-phenyl butane hydroperoxide, 116, 137
- Specifications, 139
- Uses and producers, 139
- α -Methylstyrene**
 - By-product in synthesis of phenol, 18, 115-116
- Metiloil**
 - By-product in synthesis of methyl undenoate, 277
- Naphtha**
 - Raw material in synthesis
 - of acetaldehyde, 35
 - of acetic acid, 48-49
 - of acetone, 127
 - of vinyl chloride, 164
- Naphthalene**
 - Raw material in synthesis of phthalic anhydride, 310-312, 314-316
- NDI (Naphthalene Diisocyanate)**
 - Monomer in synthesis of polyurethanes, 333
- Nitration**
 - of benzene nitrobenzene, 345-347
 - of cyclohexane to nitrocyclohexane, 271
 - of cyclohexenyl acetate to 2-nitrocyclohexanone, 271
 - of toluene to dinitrotoluenes, 335-336, 338
- Nitric acid**
 - Reactant in synthesis
 - of adipic acid, 240-244
 - of chlorobenzenes, 107
 - of 1,4-diacetoxy 2-butenes, 323
 - of dinitrotoluenes, 335-336, 338
 - of methacrylates, 204
 - of nitrobenzene, 345-347
 - of terephthalic acid, 288
- Nitrobenzene, 345-347**
 - Conversion
 - to aniline, 347-349
 - to MDI, 355-357
 - Economic data, 356-357
 - Production by nitration of benzene, 345-347
- Nitrogen oxides**
 - Reactants in synthesis
 - of acrylonitrile, 229
 - of adipic acid, 241
 - of ammonium nitrite, 261
 - of chlorine, 167-168
 - of hydroxylamine, 262
 - of hydroxylamine sulfate, 261
 - of methacrylates, 204
 - of nitrosyl sulfuric acid, 266-267, 270-27
- Nitrosyl chloride**
 - Reactant in synthesis
 - of caprolactam by photonitration, 266-268
 - of laurolactam by photonitration, 28
- Nitrosyl sulfuric acid**
 - Intermediate in synthesis
 - of caprolactam, 269-270
 - of laurolactam, 283-284
 - of nitrosyl chloride, 266-268
- Nylon, 233-235**
- Oenanthal (see Heptanol)**
- Oligomerization**
 - of butenes to octenes, 91
 - of ethylene to higher *o*-olefins, 91, 95-97
 - of propylene to hexenes, 91
- Orthophthalic acid (see phthalic anhydride)**
- Oxidation**
 - of acetaldehyde
 - to acetic acid, 43-46, 57, 145-146, 271
 - to acetic anhydride, 63-67
 - to peracetic acid, 18
 - of acetoxybutyraldehydes to corresponding acids, 215
 - of acrolein to acrylic acid, 190-193
 - of ammonia to nitrogen oxides, 261
 - of benzene
 - to maleic anhydride, 301-304, 306, 308
 - to phenol, 123
 - of benzoic acid to phenol, 117-122
 - of bituminous coal to benzene carboxylic acids, 298
 - of *n*-butane
 - to acetic acid, 47, 57
 - to acetone, 127
 - to butanol, 81
 - to maleic anhydride, 137
 - of sec.-butanol to methyl ethyl ketone, 137
 - of *n*-butenes
 - to acetic acid, 50-52

- Production by oxidation**, 294, 308, 311-316
Liquid phase process, 315
Vapor phase processes, 311-316
 Processes, 312-316
 Reactions, 311
 Separation, 312
 Specifications, 316
 Uses and producers, 316-317
- Polyamides (see Nylons)**
 Monomers for polyamides, 233-285
- Polybutadiene-polyols**
 Monomers in synthesis of polyurethanes, 334
- Polybutylene terephthalate**, 287
- Polyesters**
 Monomers for polyesters, 287-330
- Polyester-polyols**
 Monomers in synthesis of polyurethanes, 334
- Polyether-polyols**, 359-361
 Definition, 333, 359
 Economic data, 360-361
 Production, 359-360
 Uses and producers, 361
- Polyethylene terephthalate**, 287
- Polymeric MDI (see Diphenyl methane 4,4-diisocyanate)**
 Definition, 332
- Polyols**
 Monomers in synthesis of polyurethanes, 331, 333-334, 359-361
 Other polyols, 334
 Polyester-polyols, 334
 Polyether-polyols, 333, 359-361
- Polyperoxydation**
 of butadiene, 319
- Polyurethanes**
 Monomers for polyurethanes, 331-361
- Potash**
 Catalyst and reactant in synthesis
 of acetone cyanohydrin, 205
 of methacrolein, 215
 of methacrylic acid, 215
 of methyl methacrylate, 215
 of potassium benzoate, 296
- Potassium carbonate**
 Reactant in synthesis
 of acetone cyanohydrin, 205
 of ethylene oxide, 6
 of terephthalic acid, 298
- PPG (polypropylene glycol)**
 Monomer in synthesis of polyurethanes, 333, 359
- Propane**
 Raw material in synthesis
 of acetic acid, 46
 of acetone, 127
 of acrylonitrile, 230
 of hydrogen cyanide, 205
- 1,2-Propanediol**
 Co-production in synthesis of ethylene glycol, 23
- Propionaldehyde**
 Intermediate in synthesis of methacrylates, 215
- Propylene**
 Raw material in synthesis
 of acetone, 127, 131-134, 145
 of acrylic acid, 190-193, 243
 of acrylonitrile, 219-229
 of 1,4-butanediol, 319-320
 of 1-butanol, 81-84
 of cumene, 103, 109-112
 of 2-ethyl hexanol, 92-93
 of higher olefins, 94
 of isopropanol, 76-79
 of methacrylates, 204, 214
 of propylene glycol, 26
 of propylene oxide, 10-19
- Propylene glycol**, 26-29
 By-product in synthesis of propylene oxide, 16
 Conversion to PPG, 333, 359
 Economic data, 28
 Production
 by acetoxylation of propylene, 26
 by hydration of propylene oxide, 26-28
 Specifications, 28
 Uses and producers, 29
- Propylene oxide**, 9-20
 Conversion
 to allyl alcohol, 320
 to PPG, 333, 359-360
 to propylene glycol, 26-28
 Economic data, 19-20
 Production
 by acetoxylation of propylene, 19
 by direct oxidation of propylene, 12-13
 by electrochemistry, 12
 by enzymatic conversion of D-glucose, 19
 by indirect oxidation of propylene (chlorohydrin process), 10-12, 19
 by oxidation of propylene with peroxide compounds, 13-19

- Hydrocarbon hydroperoxides. 14-16
 Peroxids or hydrogen peroxide. 17-19
 Reactions, 13
 Specifications, 20
 Uses and producers, 20
- PTMG (Polytetra methylene glycol)**
 Monomer in synthesis of polyurethane, 333
- Pyrolysis (see Cracking)**
- Reduction (see hydrogenation)**
- Reverse osmosis (see Membranes)**
- Sodium bicarbonate**
 Reactant in synthesis
 of ethylene glycol, 23
 of vinyl chloride, 186
- Sodium carbonate**
 Reactant in synthesis
 of acrylates, 198
 of chlorine, 180
 of cumyl hydroperoxide, 112, 114
 of phenol, 115
- Sodium chloride**
 Raw material in synthesis
 of chlorine, 117-184
 of vinyl chloride, 185-186
- Sodium formate**
 Reactant in synthesis of 1,4-diol 2-butenes, 327
- Sodium hypochlorite**
 Reactant in synthesis of chlorine, 182
- Sodium sulfate**
 Reactant in synthesis of adiponitrile, 248-249
- Sodium sulfite**
 Reactant in synthesis of phenol, 104-105
- Splitting**
 of cumyl hydroperoxide, 103, 109, 113-115, 127
 of cyclohexylbenzene hydroperoxide, 104, 117
 of ethylbenzene hydroperoxide, 116
 of 2-phenyl butane, hydroperoxide, 116, 137
- Styrene**
 Co-product in synthesis of propylene oxide, 16
- Succinic acid**
 By-product in synthesis of acetic acid, 47-48
- Sugars**
 Raw material in synthesis
 of acetone, 84
 of 1-butanol, 84
 of ethanol, 69, 84
 of polyether-polyols, 359
- Sulfonation**
 of benzene to benzene sulfonic acid, 103-105
- Sulfur**
 Impurity in synthesis of cyclohexane, 236-237
 Inhibitor in synthesis of methacrylamide sulfate, 205
- Sulfur dioxide**
 Reactant in synthesis
 of hydroxylamine disulfonate, 261
 of phenol, 104-105
 of sulfuric acid, 264, 266, 271
- Sulfuric acid**
 Catalyst or reactant in synthesis
 of acetaldehyde, 33, 35
 of acetone cyanohydrin, 208
 of acrolein cyanohydrin, 228
 of acrylates, 196-197, 201-203
 of acrylic acid, 194
 of acrylonitrile, 222, 224-227
 of adiponitrile, 250-252
 of 2-butanol, 89, 137
 of *t*-butanol, 89, 209
 of caprolactam, 263-272
 of chlorine, 169
 of cyclododecane oxime, 281-282
 of cyclohexanone oxime, 262-263
 of dimethyl terephthalate, 288, 296
 of dinitrotoluenes, 335-336, 338
 of ethanol, 69-71
 of higher alcohols, 97
 of hydrogen cyanide, 206
 of hydroxylamine sulfate, 261
 of isopropanol, 76-77
 of laurolactam, 282-283
 of methacrylamide sulfate, 208
 of nitrobenzene, 345-347
 of nitrosyl sulfuric acid, 266-267, 269-270
 of phenol, 104-105, 115
 of propylene oxide, 18
 of vinyl chloride, 155, 169
- Synthesis gas**
 Reactant in synthesis of
 of acetaldehyde, 41
 of acetic acid, 56

- of amylic aldehydes, 91
t-butyl and 1,4-butanediol ether, 310
 of C_4 aldehyde/alcohol, 320
 of ethylene glycol, 23-24
 of *n* and isobutylaldehydes, 81-85
 of methyl acetate, 149-150
 of vinyl acetate, 150
- TDI (see Toluene diisocyanate)**
- Terephthalic acid (see Dimethyl terephthalate)**
- Tetrachloroethane**
 Conversion by pyrolysis, 177
- Tetrahydrofuran**
 Conversion to PTMG, 333, 359
 Intermediate in synthesis
 of adiponitrile, 234
 of 1,4-butanediol, 321
 Production by dehydration of 1,4-butanediol, 325
- Toluene**
 Raw material in synthesis
 of benzoic acid, 117-119, 268-269
 of caprolactam, 268-271, 284
 of dinitrotoluenes, 335-336, 338
 of phenol, 104, 117-122
 of paracetamol, 18
 of terephthalic acid and dimethyl terephthalate, 288, 295-297, 299
- o*-Tolnic acid**
 By-product in synthesis of terephthalic acid, 293
- p*-Tolnic acid**
 By-product in synthesis of terephthalic acid, 293
 Intermediate in synthesis of dimethyl terephthalate, 288-289
- Tolylene diamine**
 Intermediate in synthesis of toluene diisocyanate, 335, 337-340
- Toluene diisocyanate, 335-343**
 Definition, 331
 Economic data, 341-342
 Production by
 by direct carbonylation of toluene, 341
 by nitration of toluene, 335-340, 342
 Nitration to dinitrotoluene, 335-336, 338
 Reduction of dinitrotoluene to toluene diamine, 337-338
 Specifications, 343
 Uses and producers, 342-343
- Transalkylation**
 of isopropylbenzene to cumene, 112
- Transesterification**
 of acrylates, 203
 of castor oil to methyl ricinoleate, 274-276
- Triethyleneglycol**
 By-product in synthesis of ethylene glycol, 21-22
- Tripropylene glycol**
 By-product in synthesis of propylene glycol, 26
- Undecenoic acid**
 Intermediate in synthesis of 11-aminoundecanoic acid, 275, 277
- Vinyl acetate, 141-152**
 Economic data, 150-151
 Production
 from acetaldehyde and acetic anhydride, 149-150
 from acetylene, 141-144, 151
 from ethylene, 141, 143, 145-149, 151
 Liquid phase processes, 145-146, 151
 Vapor phase processes, 145-149, 151
 from ethylene glycol diacetate, 149
 from methyl acetate, 149-150
 Specifications, 151
 Uses and producers, 150, 152
- Vinyl chloride, 152-177, 184-189**
 Economic data, 186-187
 Production
 by chlorination of ethylene and cracking of ethylene dichloride, 156-166, 175-178, 187
 Chlorination, 156-160, 163-166, 175-178, 187
 Cracking, 160-166, 175-178, 187
 by chlorination of ethylene by chlorine obtained chemically, 185-186
 by crude oil cracking (Kureha process), 164-167
 by hydrochlorination of acetylene, 153-156, 163-166, 187
 by oxychlorination of ethane, 184-185
 by oxychlorination of ethylene, 167-177, 187
 In situ oxidation, 168-174, 187
 Operating conditions, 168

Processes with fixed beds, 170, 172-174,, 187
Processes with fluidized beds, 170-172, 187
Oxidation of hydrochloric acid to chlorine, 167-169, 187
Production schemes, 153, 163-164, 175-177
 Balanced schemes, 153, 163-164, 175-177
 Integrated schemes, 175-177
Specifications, 188
Uses and producers, 186, 189

Vinylidene chloride
Production by dehydrochlorination of trichloroethane, 177

XDI (Xylylene DIisocyanate)
Monomer in synthesis of polyurethanes, 332

***o*-Xylene**
Raw material in synthesis
 of phthalic anhydride, 294, 310-313, 315-316
 of teraphthalic acid and dimethyl terephthalate, 288, 294-295

***p*-Xylene**
Raw material in synthesis of terephthalic acid and dimethyl terephthalate, 288-294, 299