

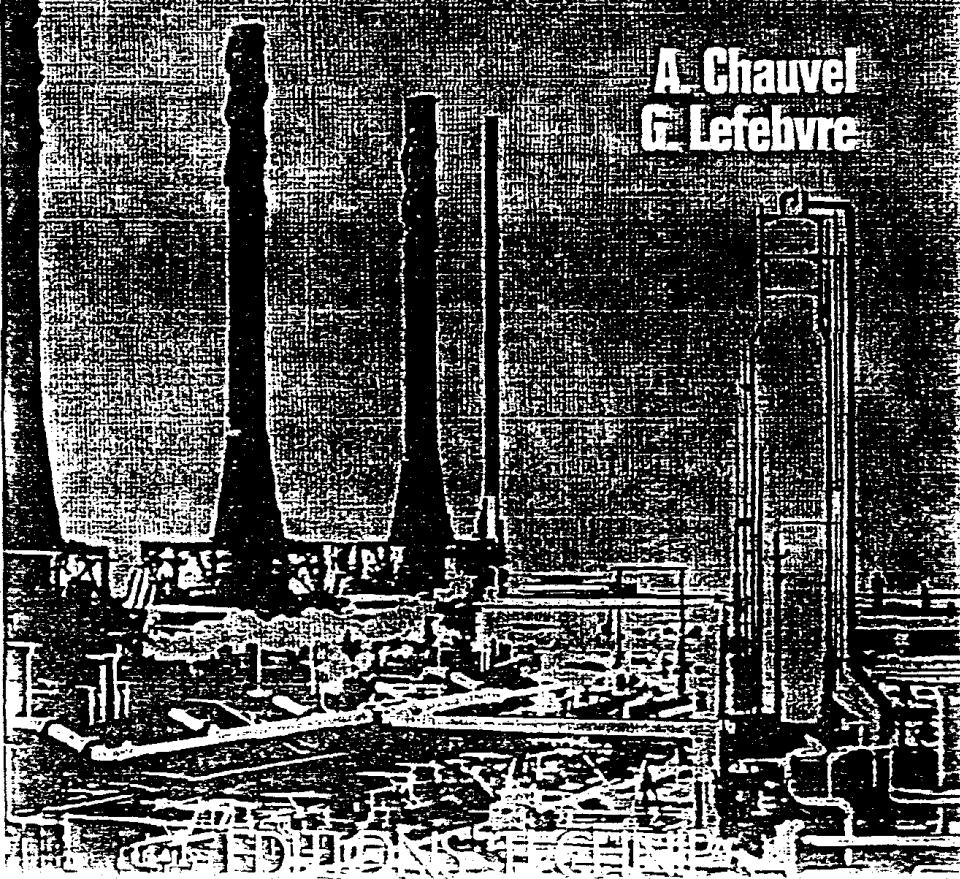
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PETROCHEMICAL PROCESSES

1

SYNTHESIS-GAS DERIVATIVES
AND MAJOR HYDROCARBONS

A. Chauvel
G. Lefebvre



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PETROCHEMICAL PROCESSES

TECHNICAL AND ECONOMIC CHARACTERISTICS

1

**SYNTHESIS-GAS DERIVATIVES
AND MAJOR HYDROCARBONS**

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FOREWORD

Since 1971, 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, Toray) 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 dimethylocyclohexane 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

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INTRODUCTION

The development of modern chemistry in the past thirty years clearly demonstrates that oil and natural gas are the ideal raw materials for the synthesis of most mass-consumption chemicals. In addition to the fact that they have been and still are very widely available, they are formed; especially in the case of oil, of a wide variety of compounds providing access to a multitude of possible hydrocarbon structures. The biological and physicochemical processes that contributed to their formation have furnished, apart from a certain quantity of aromatic hydrocarbons, a large proportion of saturated hydrocarbons (paraffins and naphthenes). In fact, these compounds generally display low reactivity, so that it is not easy to obtain the desired finished products. This is why the production of these derivatives entails a sequence of chemical operations which, in practice, require the combination of the facilities in which they take place within giant petrochemical complexes.

PETROCHEMICAL COMPLEXES

The initial objective is to manufacture various types of high chemical reactivity product from petroleum hydrocarbons. These products are the first generation intermediates :

- (a) Hydrogen, ammonia, methanol.
- (b) Olefinic and dienic hydrocarbons : ethylene, propylene, butadiene, isoprene etc.
- (c) Aromatic hydrocarbons : benzene, toluene, styrene, xylenes etc.
- (d) Acetylene.

In a second stage, a new series of chemical operations is conducted to introduce various hetero-atoms into the final molecule, including oxygen, nitrogen, chlorine and sulfur. This leads to the formation of so-called second generation intermediates.

A final operation is needed to obtain the target product by determining its formulation, so that its properties correspond to its intended uses. These products include plastics, synthetic fibers, fertilizers, solvents, elastomers, insecticides, detergents etc. Figure 1 illustrates the links existing between petroleum raw materials and mass-consumption finished products, and stresses the main processes employed.

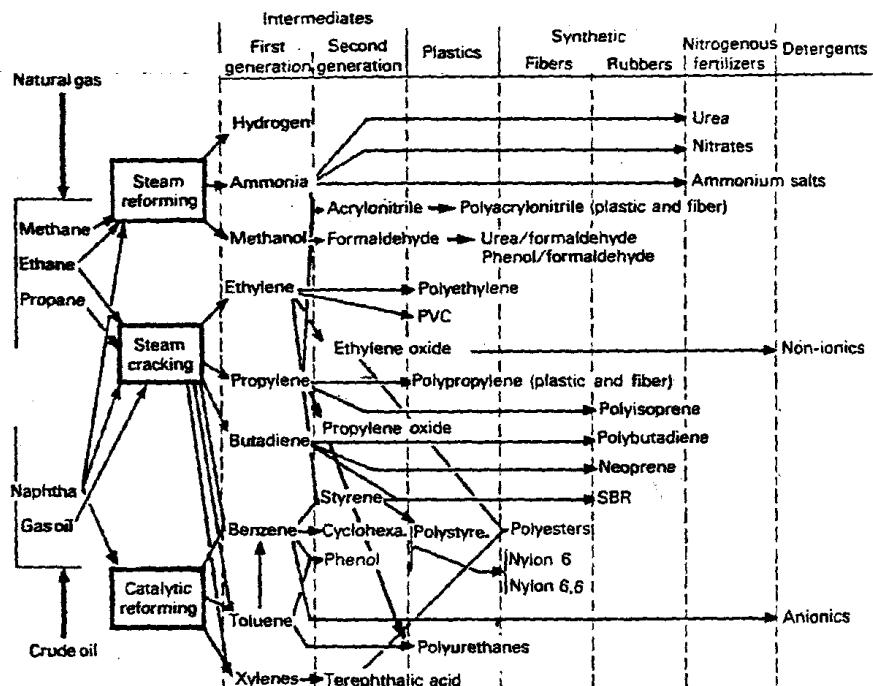


Fig. 1. Overall view of petrochemical intermediates manufacture.

This three-step classification shows many exceptions, and, indeed, various trends emerge to reduce the number of sequences in the formation of a given finished product.

Thus, ethylene, obtained from petroleum or natural gas hydrocarbons, is also a monomer for the direct formation of a plastic such as polyethylene, or of an elastomer such as Ethylene-Propylene-Termonomer (EPT) rubber. Acetic acid, produced in several steps from acetylene or ethylene, is also produced directly by the oxidation of a mixture of saturated hydrocarbons (naphtha).

On the other hand, a large number of operations is sometimes necessary to complete one step or another: one example is the synthesis of formal. It is necessary to oxidize the hydrocarbons to a mixture of CO and H₂, whose composition must be adjusted by secondary conversions, then recombine this mixture to form methanol, and finally proceed with a new controlled oxidation of methanol to formal.

Furthermore, the basic reactants must also be used in suitable form. Hence oxygen may be derived from water or air: in a number of cases, the air must be enriched with oxygen to avoid uselessly transporting, heating, and finally eliminating, large amounts of nitrogen. The latter, which is too unreactive with hydrocarbons, must usually be converted first to ammonia or nitric acid, or even to hydrogen cyanide. As for chlorine, it

is obtained by the electrolysis of alkaline chlorides. But hydrochloric acid can also be used in combination with oxygen. This reaction, oxychlorination, is extremely valuable, especially for the synthesis of vinyl chloride. It also offers a solution to the problem of surplus HCl resulting from many hydrocarbon chlorination reactions. The other halogens (fluorine, bromine and iodine) and sulfur play a more modest role: sulfur usually occurs in the form of sulfates and sulfonates, especially in detergents.

Despite these exceptions, the foregoing classification nevertheless retains its validity; by emphasizing the step involving the production of first generation intermediates, it has the merit of also identifying three major types of petrochemical complexes. In accordance with the desired first generation products, it is hence possible to distinguish the following industrial sites:

- (a) **Complexes based on synthesis gas chemistry** and culminating in the production of fertilizers and resins. Their processes are centered on **steam reforming**, which is sometimes supplanted by **partial oxidation** if the raw materials, instead of being light hydrocarbons (methane, ethane etc), or naphtha, become heavier (gas oils, residues etc). In this case, a CO/H₂ mixture is first produced which, after adaptation, leads to the production of hydrogen, to the synthesis of ammonia or methanol, followed by that of formal, acetic acid etc. To a certain degree, synthesis gas chemistry offers a promising answer, capable of providing a relay for current methods, in the event that tensions surrounding the availabilities and prices of petroleum raw materials are felt anew.
- (b) **Olefinic and diolefinic complexes**, of which the basic installation consists of **steam cracking**. This can proceed with ethane, propane, naphtha, as well as gas oil, or even crude oil. It was originally designed to produce essentially ethylene, but, depending on the feedstock employed, it also constitutes an ideal operation to obtain propylene, butadiene and aromatics (especially benzene) as co-products.
- (c) **Aromatic complexes**, more specific to the refining industry for the production of high octane motor fuels, centered around **catalytic reforming**. With respect to petrochemicals, they are mainly intended to obtain benzene, ethylbenzene, ortho- and paraxylene, and employ naphtha as the essential raw material.

Figures 2, 3 and 4 offer an illustration of typical petrochemical complexes associated with industrial units based in the first case on synthesis gas chemistry, intended in the second to manufacture chiefly olefins and diolefins, and in the third to produce aromatic hydrocarbons.

CONTENT AND LIMITS OF THE BOOK

Objectives

The objective is to gather together the information likely to facilitate what can be called "petrochemical process evaluation", by analogy with the refining and treatment of crude oil. In fact, based on a demand for various organic compounds identified by a

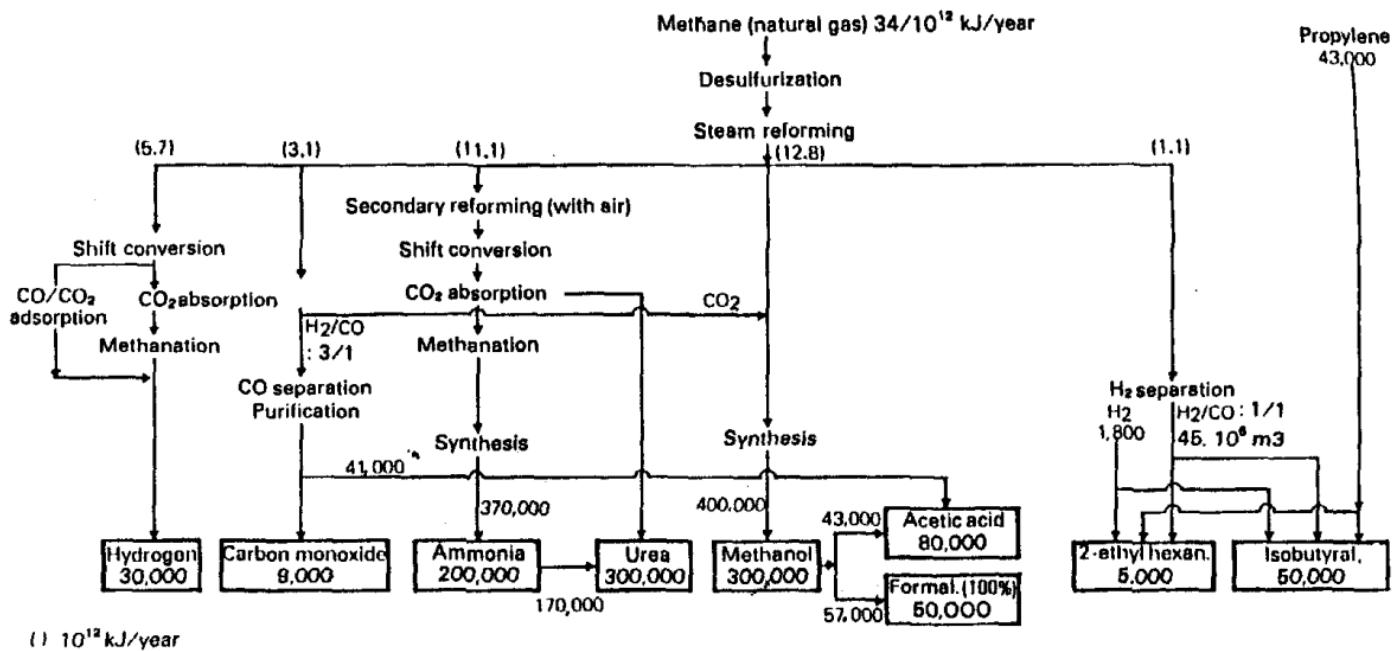


Fig. 2. Typical complex for the manufacture of synthesis gas (H₂/CO). Balance (t and kJ/year).

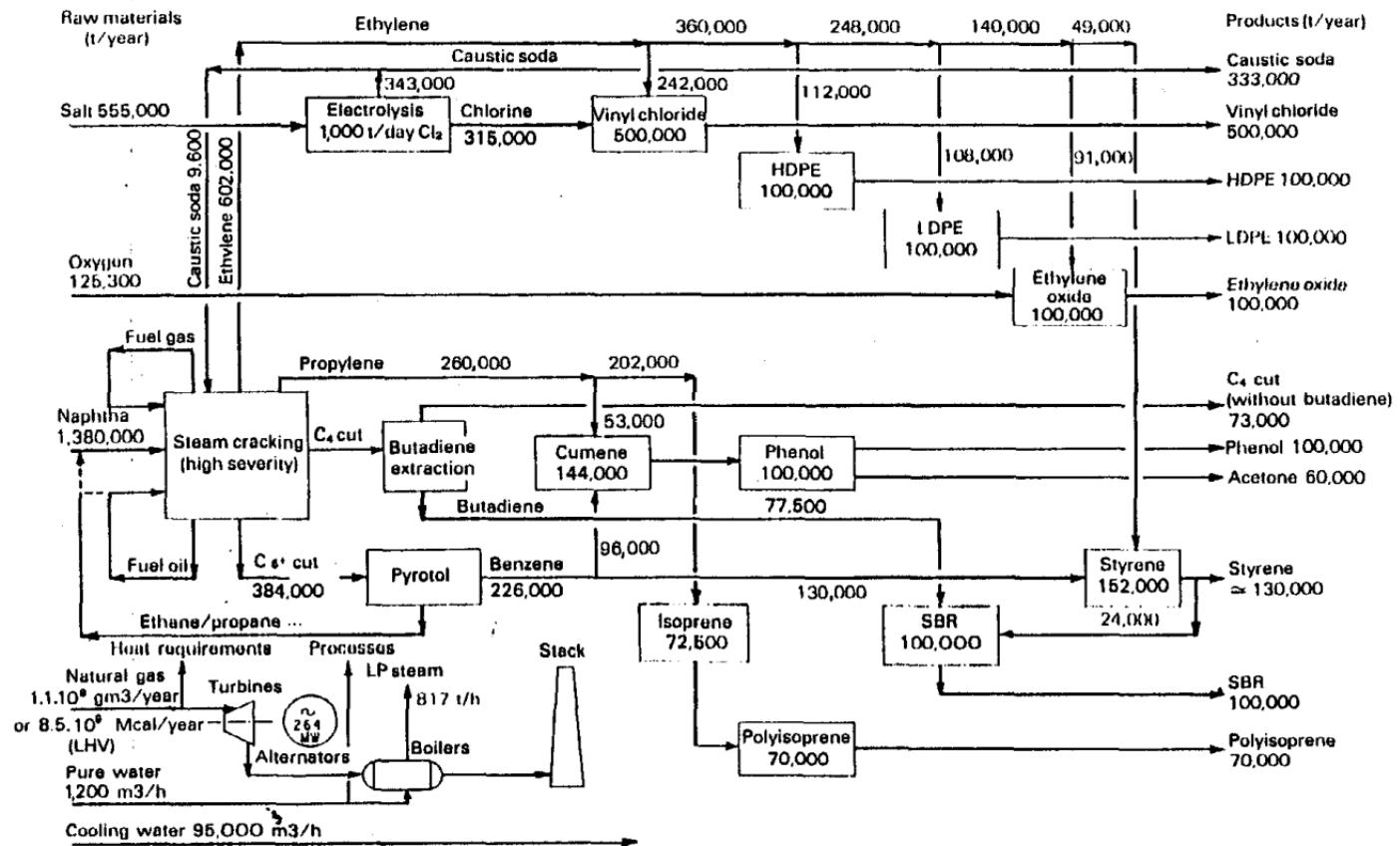
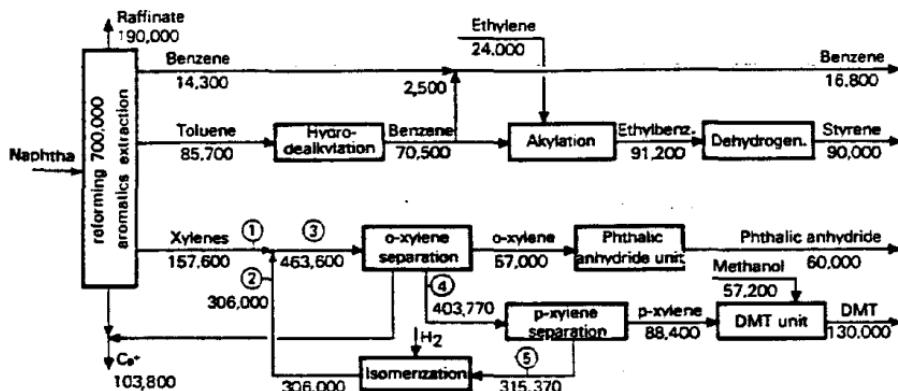


Fig. 3. Typical olefinic complex. Balance (t/year).



	1		2		3		4		5	
	T	%	T	%	T	%	T	%	T	%
Ethylbenzene	23,170	14.7	15,000	4.9	38,170	8.3	38,170	9.4	38,170	12.1
Orthoxylene	26,800	17.0	64,000	20.9	90,800	19.6	33,800	8.4	33,800	10.7
Paraxylene	31,200	19.8	64,000	20.9	95,200	20.5	95,200	23.6	6,800	2.2
Metaxylylene	73,600	46.7	163,000	53.3	236,600	51.0	236,600	58.6	236,000	75.0
C ₉ ,	2,830	1.8	—	—	2,830	0.6	—	—	—	—
Total	157,600	100	306,000	100	463,600	100	403,770	100	315,370	100

Fig. 4. Typical aromatics complex. Balance (t/year).

market survey, and in accordance with the availabilities of raw materials that are also determined, the procedure consists in devising a series of operating sequences to provide an answer to the desired conversions, in line with the initial requirements.

In practice, within the framework of this book, this petrochemical process evaluation is limited to the production of second generation intermediates. Moreover, it does not lead to the identification of a single solution, but to the consideration of several different schemes, in as much as each offers a technologically viable answer. It also consists in emphasizing the technical requirements of the conversion operations planned, as well as potential unfeasibilities related to the inherent facts of the problem: this means the need to propose alternative solutions, requiring a minimum of adaptation of the basic data.

To be capable of making a valid choice among the various alternatives, or to compile a classification in terms of overall flow sheets or operating sequences, if several processes are in competition, petrochemical process evaluation must be supplemented by an economic study.

Accordingly, without claiming to offer a complete answer in terms of technology, or hoping to suggest a fully satisfactory solution from the economic standpoint, this book proposes to provide details which, within the framework of a teaching activity or preliminary design, will help to sketch out an outline of what a petrochemical complex comprises, to calculate an overall budget envelope, to evaluate the energy expenditures etc. In short, this setting could provide the basis for a more thorough job, carried out by specialists (consultants) and comprising, for example, bid invitations to process licensors, in accordance with the sequences planned, as well as the interpretation and detailed analysis of the results of such a survey.

Technico-economic factors

Chapters 1, 2, 3 and 4 describe the basic operations and auxiliary treatments which serve to obtain first generation intermediates. They essentially include the following conversions:

- (a) Steam reforming or partial oxidation.
- (b) Steam cracking or thermal cracking.
- (c) Catalytic reforming.

The following chapters, arranged in a order which recalls the development of the petrochemical industry, offer details concerning the most important second generation intermediates. The compounds examined constitute the essential steps of a branch which provides the link between petroleum refining, the production of major reactants such as chlorine, sulfuric acid, caustic soda etc, and the main industries consuming organic chemicals, foremost among them plastics, synthetic fibers, elastomers and detergents.

Compounds which are themselves finished products, such as solvents (perchloro and trichloroethylene, ethanolamines, carbon tetrachloride) or which are only involved in small amounts in the chemical industry (glycerin, oxalic acid) are not covered by specific studies.

For each product examined, these chapters⁽¹⁾ give the description of the main industrial methods of production, and their principal technical and economic characteristics: battery limits investments at a given date, material balance, utilities consumption, shift labor. To derive an opinion of the scale of the markets, the most important uses are also discussed, usually with details about production, capacity and consumption in different countries or groups of countries at a given date.

(1) Given the size of the book, it became necessary to group these chapters into two complementary volumes which could be consulted and used independently of each other. Volume 1, which focuses more on major first generation intermediates, deals with the production of synthesis gas and its derivatives, and of hydrocarbons. Volume 2 deals more specifically with oxygenated, chlorinated and nitrogenated second generation compounds.

Use of economic data

Battery limits investments

The investment figures given in the different chapters represent the cost of the facilities at the so-called battery limits, of which the following are:

- (a) Imported:
 - . Raw materials.
 - . Standard utilities: electricity, steam, water (cooling, process etc), fuels, refrigeration.
 - . Chemicals, catalysts and solvents.
- (b) Exported:
 - . Products manufactured in the unit.
 - . By-products, including combustible gases, residues and tars, and wastes, if any.
 - . Utilities to be treated: condensates, cooling water etc.

They correspond to mid-1986 for an installation with a given production capacity, located in France.

These investments are average values which may deviate by 10 to 20 per cent, or even more, from those pertaining to real cases, for which the specific circumstances of establishment are taken into consideration. This means that, although they, as well as the other economic characteristics quoted, result from a critical statistical compilation based on data from various sources (proposals, evaluations, publications) and hence offer a correct assessment of the economic value of the processes at a given time, for typical service conditions, the comparisons between technologies which may be inferred should not be used to discard any given industrial application, but merely to spotlight certain trends.

Indeed, an apparently disadvantaged technique could benefit from specific considerations (adaptation to available feedstock, product quality, financial conditions of a project) to offset an economic inferiority in relation to the competition.

Available for a given production capacity, date and location, the investment values thus mentioned must be adapted to the conditions of the study in most cases. This normally involves extrapolating these figures, bringing them up to date, and accounting for location factors:

(1) To make the capacity extrapolation, the simplest solution is to use the following formula:

$$I_B = I_A \left(\frac{C_B}{C_A} \right)^f \quad \text{generally with } f \cong 0.65 \text{ to } 0.70$$

where I_A is known and I_B is to be determined, representing the battery limits investments corresponding to capacity C_A and C_B . f is an extrapolation exponent, incorrectly called "extrapolation factor": it is only constant in a limited capacity interval. In practice, three cases of values of f are distinguished:

- (a) Extrapolation of plants of standard design: main facilities consisting essentially of columns, tanks, heat exchangers, furnaces etc. In this case, f can be taken as 0.65

over a relatively wide range of capacities (for example, ranging by a factor of 1 to 5 towards higher and lower tonnages).

- (b) Extrapolation to higher capacities of more complex plants or those located beyond the range of validity of the factor 0.65: main equipment chiefly comprising reaction furnaces, tubular reactors, rotating machines such as centrifuges, rotary filters, extractors, grinders etc, and whose maximum output, in the current state of the art, cannot exceed certain limits. Beyond this, the equipment must be duplicated to deal with the possible doubling of certain units: this requires using higher values for f , ranging from 0.8 to 0.9.
- (c) Extrapolation to lower capacities, located beyond the range of validity of the factor 0.65. At low capacities, the relative share of secondary equipment (piping, civil works, metals structures, instrumentation, electricity, thermal insulation, building, painting etc), and of erection and indirect field costs (craning equipment, temporary buildings etc), increases in relation to that of the main equipment. To account for this fact, i.e. higher investments, a lower extrapolation factor of about 0.5 to 0.55 should be adopted.

(2) Investments are kept current by normally using indexes that are regularly calculated and possibly published.

If A_n is the value of the index related to year n , the ratio of the battery limits investments of plants I of the same installation between two years 1 and 2 will be equal to the ratio of the corresponding indexes A :

$$\frac{I_1}{I_2} = \frac{A_1}{A_2}$$

A very large number of updating indexes is available. In practice, each manufacturer has his own or makes use of price escalation formulas which obey the same principle. Some of them are published: in the United States, for example, these include the Nelson Cost Index published in the periodical The Oil and Gas Journal, which is specific to refining-related processes, the CE Cost Index and the Marshall and Stevens Cost Index, published by the periodical Chemical Engineering, more relevant to chemicals in general. They are distinguished by the year used as the base year (100), but also, and above all, by the reference elements or partial indexes which govern their establishment and the weighting carried out to determine the overall index. Since this weighting itself evolves with time, a number of adaptations are periodically required if the values calculated using an index deviate too far from reality. In the absence of such revisions, it is therefore important to avoid any updating covering an overlong period, especially since, in the meantime, the process itself may have evolved and improved, while retaining its initial principles.

This situation can be illustrated by Fig. 5, which relates to the same base of 100 in 1958 the changes in the Nelson, Chemical Engineering and Marshall/Stevens indexes in the United States, by comparing the observed increase in the average costs of petrochemical plants over the 1960/1985 period. Hence this is the curve that should be used to make the earlier data current.

(3) It is extremely problematic and difficult to account for location factors which, in a comparison between different countries, appear in three main aspects:

- (a) Currency parity.
- (b) State of technological and industrial progress.
- (c) Relative level of wages and social charges.

As in the case of updating, one may tend to use composite indexes to take account of the two latter parameters in particular, using a location factor which introduces variable weightings of the components as a function of the country concerned. This type of work was carried out by J. Cran, who picked the same basis of 100 in 1970 for all countries. However, it is also necessary to make a differentiation pertaining to the reference year. Many authors have tried to solve this problem in recent years. Among the latest studies is that by N. Boyd, whose main results are given in Tables 1 and 2: the values indicated serve to account for the location factor for a number of industrial countries, in order to compare the costs, expressed in United States dollars, of plants which are absolutely identical, each being assumed to be entirely designed, dimensioned,

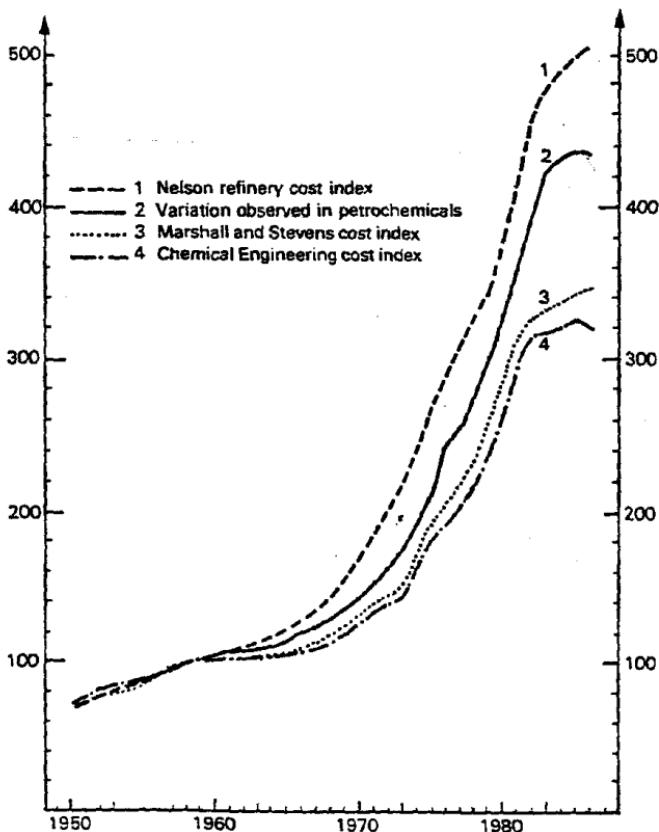


Fig. 5. Comparative variation in cost indexes in the United States.
Base 1958 = 100.

TABLE I

COMPARISON OF ERECTED COSTS OF INSTALLATIONS IN DIFFERENT INDUSTRIALIZED COUNTRIES

On 1 January	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Australia	0.55	0.59	0.66	0.69	0.78	1.00	1.15	1.33	1.46	1.57	1.71	1.93	2.15	2.58	2.77	2.91	3.15	3.36
Belgium	0.49	0.61	0.61	0.68	0.79	1.00	1.09	1.16	1.27	1.29	1.40	1.50	1.64	1.89	1.99	2.01	2.06	2.07
Canada	0.65	0.70	0.73	0.77	0.86	1.00	1.20	1.33	1.46	1.56	1.76	1.95	2.24	2.46	2.42	2.47	2.52	2.57
Denmark	0.48	0.59	0.59	0.67	0.76	1.00	1.02	1.06	1.16	1.27	1.38	1.54	1.64	1.99	2.14	2.19	2.32	2.41
France	0.49	0.59	0.64	0.70	0.79	1.00	1.13	1.25	1.34	1.46	1.59	1.82	2.05	2.50	2.73	2.84	2.97	3.10
Italy	0.43	0.50	0.54	0.57	0.74	1.00	1.19	1.43	1.67	1.92	2.27	2.67	3.15	3.89	4.38	4.71	5.12	5.31
Japan	0.55	0.62	0.63	0.69	0.78	1.00	1.11	1.26	1.39	1.50	1.58	1.70	1.79	1.84	1.84	1.84	1.89	1.87
Netherlands	0.51	0.60	0.67	0.70	0.78	1.00	1.09	1.14	1.22	1.18	1.24	1.31	1.42	1.54	1.54	1.57	1.59	1.63
Norway	0.53	0.63	0.69	0.74	0.83	1.00	1.10	1.22	1.35	1.45	1.53	1.69	1.78	2.07	2.18	2.28	2.43	2.73
Sweden	0.55	0.59	0.65	0.69	0.81	1.00	1.05	1.16	1.24	1.37	1.49	1.67	1.81	2.05	2.26	2.37	2.57	2.77
United Kingdom ..	0.48	0.56	0.64	0.71	0.78	1.00	1.30	1.45	1.61	1.76	2.04	2.35	2.56	2.78	2.92	3.10	3.34	3.56
West Germany	0.59	0.68	0.75	0.80	0.88	1.00	1.03	1.07	1.11	1.14	1.21	1.29	1.38	1.53	1.52	1.56	1.60	1.60
United States	0.66	0.71	0.77	0.82	0.87	1.00	1.11	1.18	1.27	1.39	1.53	1.68	1.85	1.96	2.09	2.13	2.19	2.10

TABLE 2
ERECTED COSTS OF INSTALLATIONS IN DIFFERENT INDUSTRIALIZED COUNTRIES
COMPARED WITH THOSE IN THE UNITED STATES

On 1 January	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Australia	0.62	0.62	0.66	0.67	0.87	0.92	0.89	0.94	0.85	0.87	0.84	0.90	0.89	0.86	0.80	0.76	0.67	0.68
Belgium	0.58	0.68	0.65	0.73	0.94	1.07	1.00	1.01	1.10	1.18	1.36	1.21	0.92	0.81	0.72	0.60	0.68	0.92
Canada	0.83	0.87	0.86	0.82	0.90	0.92	0.95	1.05	0.98	0.87	0.90	0.90	0.92	0.92	0.86	0.81	0.76	0.80
Denmark	0.64	0.73	0.71	0.76	0.97	1.06	1.01	0.98	0.98	1.10	1.13	1.05	0.80	0.76	0.72	0.62	0.71	0.98
France	0.57	0.61	0.61	0.68	0.83	0.85	0.93	0.89	0.87	0.96	1.02	1.04	0.82	0.75	0.68	0.58	0.67	0.90
Italy	0.58	0.63	0.63	0.66	0.78	0.86	0.88	0.81	0.82	0.91	1.01	1.01	0.78	0.79	0.74	0.65	0.72	1.00
Japan	0.38	0.40	0.39	0.45	0.54	0.58	0.55	0.59	0.65	0.82	0.79	0.77	0.73	0.60	0.62	0.58	0.65	0.94
Netherlands	0.60	0.66	0.72	0.75	0.97	1.04	1.05	1.05	1.12	1.13	1.18	1.12	0.82	0.82	0.73	0.61	0.69	0.96
Norway	0.72	0.79	0.83	0.87	1.09	1.16	1.16	1.28	1.25	1.29	1.31	1.32	1.07	1.00	0.92	0.82	0.89	1.15
Sweden	0.86	0.87	0.90	0.95	1.17	1.24	1.18	1.24	1.13	1.19	1.26	1.29	0.99	0.90	0.76	0.70	0.79	1.03
United Kingdom ..	0.58	0.62	0.66	0.69	0.72	0.77	0.81	0.70	0.72	0.80	0.94	1.08	0.86	0.79	0.68	0.59	0.70	0.81
West Germany	0.62	0.71	0.77	0.81	1.08	1.02	0.98	0.99	1.02	1.12	1.20	1.13	0.88	0.85	0.76	0.64	0.73	1.01
United States	←																	→

supplied with equipment, and built in the same geographic area. Table 3 gives the currency parities to be used as of 1 January 1975 to apply the procedure proposed by Boyd, if the investments are given in or are to be converted into local currency.

TABLE 3
CURRENCY PARITIES ON 1 JANUARY 1975
IN RELATION TO THE UNITED STATES DOLLAR

Country	Currency
Australia	0.76
Belgium	39.20
Canada	0.99
Denmark	6.12
France	4.73
Italy	660.00
Japan	298.00
Netherlands	2.70
Norway	5.53
Sweden	4.44
United Kingdom	0.43
West Germany	2.65

Capital costs

Battery limits investments account for only a fraction of the total amount required for the operation of an industrial installation. An evaluation calculation based on the use of an economic criterion, designed to allow an economic comparison between several processes or flow sheets, hence requires the consideration of all the capital costs.

Although they can be determined accurately, these other fixed assets can, as a first approximation and for most of them, be determined from the knowledge of the battery limits investments amounts, using percentages. Thus, a typical breakdown of these costs would be as follows (Fig. 6):

Battery limits investments	I_1
Off sites	$I_2 = 0.4 I_1$
Total units	$I_1 + I_2$
Engineering	$I_3 = 0.12 (I_1 + I_2)$
Spare parts	$I_4 = 0$ (for highly industrialized countries)
Fees (royalties, process book)	$I_5 = 0.05 \text{ to } 0.10 (I_1 + I_2)$
Fixed capital	$CF = \Sigma I_1 \text{ to } I_5$
Initial load of catalysts ⁽²⁾ , solvents, molecular sieves etc	I_6 (problem data: hourly space velocity)

(2) In heterogeneous catalysis only. Knowledge of the space velocity helps to determine the quantity of catalyst required and the price of this catalyst for the initial load. If metals can be recovered, I_1 includes only the price of the support, impregnation, promoters etc. The cost of the metals itself is included in Working Capital (WC). The initial loads are extrapolated in proportion to capacity.

Interest on construction loan	$I_1 = 0.09 \text{ CF}$ (for a construction period of two years)
Start-up costs	$I_2 = 3$ months of exploitation costs, not including materials cost
Depreciable capital	$DC = \sum I_1$ to I_3
Working capital	$WC = \text{Current provision } 2 \times I_3$ - precious metals

Operating cost (Fig. 7)

Every economic calculation requires the prior determination of an operating cost (FF/year) or a cost price (FF/t of product or feed). It also presumes the prior fixing of the stream factor (theoretical operating time of a unit in a year, 8000 h/year in general) and the utilization factor, which is the ratio of actual output to production capacity (100 per cent in a preliminary calculation).

Operating cost includes:

- (a) Variable costs.
- (b) Labor.
- (c) Fixed costs.

Variable costs incorporate:

- (a) Material cost: raw materials, less by-products.
- (b) Chemicals, solvents and catalysts: in heterogeneous catalysis, knowledge of catalyst life helps to calculate the catalyst expenditure: if it contains recoverable metals, only the cost of the support, impregnation, promoters etc, and losses of these metals, are taken into account.
- (c) Utilities: steam, electricity, fuel, cooling and process water etc.

Labor is normally expressed by a number of operators per shift, which is merely multiplied by an annual cost, and which includes the number of workers needed to guarantee continuous operation of the facilities (5 to 6 shifts per day considering holidays, absenteeism etc.), social charges and supervision (20 per cent of operator wages). Tables 4 and 5 provide an idea of the different transaction prices of chemicals, utilities and labor conditions prevailing in France and in the United States in 1986.

Fixed costs reflect the influence of investments in operating cost. They include maintenance, taxes and insurance and overheads which amount on the whole to about 7 per cent of the cost of the units ($I_1 + I_2$), a provision for depreciation (10 per cent of depreciable capital for linear depreciation of the facilities over ten years), and, depending on the economic calculation method adopted, financial charges (7 per cent depreciable capital on the average, and 9 per cent of working capital).

Exploitation costs represent the aggregate of variable costs and labor. Manufacturing costs include the above as well as maintenance, taxes and insurance and overheads.

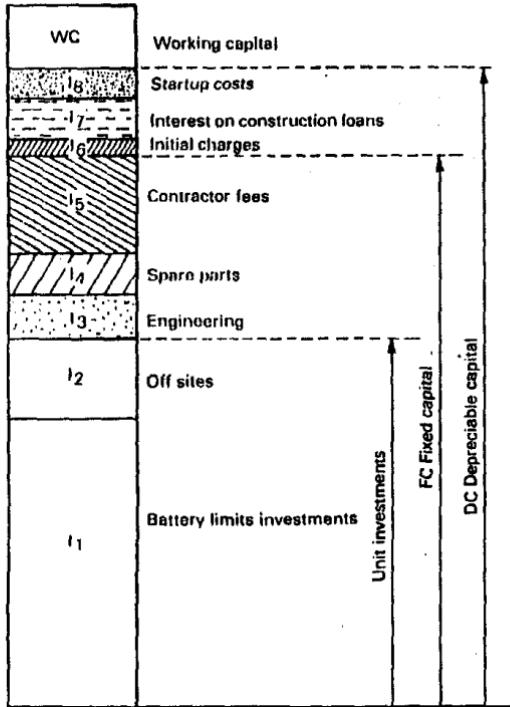


Fig. 6. Investment costs.

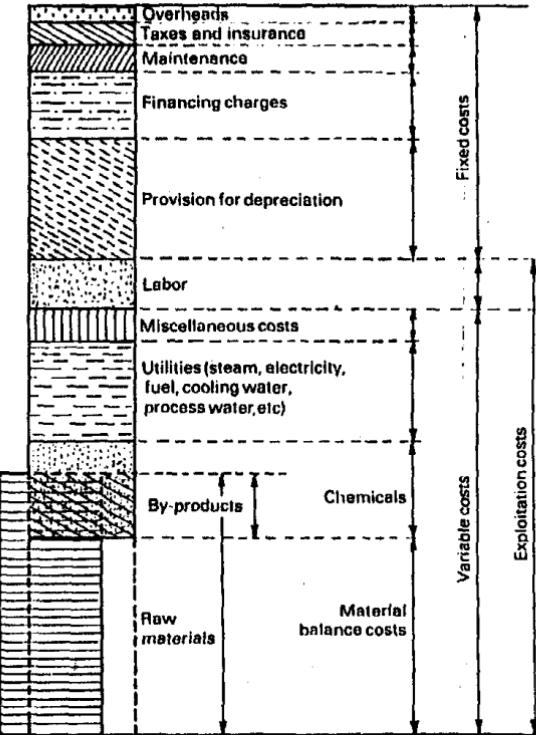


Fig. 7. Operating cost items.

AVERAGE TRANSACTION PRICES OF CHEMICALS (US\$/t)
 France and Gulf Coast Conditions (January 1986)

Product	France	Gulf Coast	Product	France	Gulf Coast
Acetic acid	585	550	Hydrogen (Catalytic reforming)	430	-
Acetone	510	550	Hydrogen (Steam reforming)	1,140	-
Acetylene	2,150	2,120	Hydrogen cyanide	1,160	1,100
Acrylonitrile	920	930	Hydrogen peroxide (35%)	560	515
Adipic acid	1,270	1,260	Isobutene (Pure)	745	705
Ammonia	165	145	Isopropanol	520	620
Benzene	320	390	Maleic anhydride	750	1,170
Butadiene	620	660	Methanol	150	200
Butane	220	220	Methyl ethyl ketone	745	795
Butane-Butenes (C ₄ cut)	205	240	Naphtha	205	215
1-butene	605	575	Nitric acid (36°B-100% basis)	160	190
Butyl alcohol Sec.	830	795	Nitrogen	57	-
Butyl alcohol Tert.	-	1,550	Oxygen	50	-
Capro lactam	1,990	1,920	Phenol	660	840
Caustic soda	250	180	Phthalic acid	715	695
Chlorine (Liq.)	180	195	Polyethylene (HDPE)	1,040	970
Cyclohexane	420	440	Polyethylene (LDPE)	900	795
Dimethylterephthalate	700	650	Polyethylene (LLDPE)	1,010	830
Ethanol (95%)	870	620	Polypropylene	1,020	1,015
Ethanolamine (Mono-and Di-)	1,020	970	Polystyrene (Normal)	1,120	1,060
Ethylbenzene	515	485	Polystyrene (Impact)	1,165	1,125
Ethylene	490	480	Polyvinyl chloride	750	730
Ethylene glycol (Mono-and Di-)	690	685	Propane	220	220
Ethylene oxide	850	815	Propylene	455	440
2-ethyl hexyl alcohol	885	835	Propylene oxide	1,110	1,050
Formaldehyde (37% wt)	545	525	Styrene	585	595
Fuel gas	185	145	Sulfuric acid (65.5° Ord.)	86	48
Fuel oil (3 to 5% S)	175	135	Terephthalic acid	730	705
Fuel oil (1 to 2% S)	185	145	Toluene	280	370
Fuel oil (0.5 to 1% S)	195	165	Urea	140	110
Gas oil	315	250	Vinyl acetate	915	860
Gasoline (Regular)	310	250	Vinyl chloride	650	620
Gasoline (Premium)	295	265	o-xylene	400	395
Hexamethylenediamine	2,140	-	p-xylene	540	530
Hydrochloric acid (20-21° B)	76	64	Xylenes (Mixed)	325	350

TABLE 5
LABOR AND UTILITY COSTS
(France and United States Conditions, mid-1986)

Conditions		France	United States
Labor (shift operator, including supervision) (US\$·year)		170,000	185,000
Fuels			
Fuel oil ⁽¹⁾ ⁽²⁾ (US ¢/kWh)		1.2	0.75 ⁽⁴⁾ -0.9
Gas ⁽³⁾ (US ¢/kWh)		1.2	0.8 ⁽⁴⁾ -1.0
Coal ⁽²⁾ (US ¢/kWh)		0.6	0.55 ⁽⁴⁾
Steam			
IP (US \$/t)		11	9
MP/HP (US \$/t)		12	10 ⁽⁵⁾
Electricity			
For $10 < P \leq 40$ MW (US ¢/kWh)		3.4	5.0
For $P > 40$ MW (US ¢/kWh)		2.9	4.8 ⁽⁶⁾
Cooling water (US ¢/m ³)		1.8	2.0 ⁽⁷⁾
Process water (US ¢/m ³)		50	20
Refrigeration (US ¢/kWh)			(8)
°C			
0		4.8	5.6
10		5.2	6.1
20		5.7	6.8
30		6.3	7.6
50		7.7	9.5
80		10.8	12.6

(1) No. 2 in France, No. 6 in the United States.

(2) LHV basis (1 kWh = 3,413 BTU).

(3) HHV basis.

(4) Steam-electricity utility plants.

(5) Average value (min. 8, max. 12).

(6) 3.6 Gulf Coast - 7.6 West Coast.

(7) 1.7 Gulf Coast - 2.8 West Coast.

(8) Based on power at 5.0 US ¢/kWh.

Economic comparison

The economic comparison can be made by means of operating cost or cost price which, by themselves, help to assess the profitability of one or more processes or schemes. In economic practice, however, the large number of criteria employed proves how imperfect they are, and how it is difficult, even here, to assess the value of a project accurately. Among the methods employed are those based on experience and which, for the sake of simplicity, look like genuine cooking recipes, as opposed to those that result from a really economic procedure involving the discounting concept. Among the former are the following:

- (a) Pay out time (POT) : ratio of depreciable capital to the cash flow, i.e. the aggre-

gate of gross profit (difference between sales and operating cost), less taxes, plus depreciation, as follows:

$$POT = \frac{DC}{(V - C)(1 - a) + A}$$

where

DC = depreciable capital,

V = volume of income or sales,

C = operating cost,

a = tax rate.

A = provision for depreciation.

- (b) **Return on investment (ROI)** : ratio of the difference between income and manufacturing costs to depreciable capital, as follows :

$$ROI = \frac{V - D}{DC}$$

where

DC = depreciable capital,

V = volume of income or sales,

D = manufacturing costs (variable costs, labor, maintenance, taxes and insurance, and overheads).

The latter include the discounted cash flow, internal rate of return, discounted pay-out time, economic cost price etc.

A convenient basis for comparison consists in determining the minimum profitable selling prices by setting a value of the POT (five years for example) or of the internal rate of return. In the latter case, an approximate method for linear depreciation of the facilities over ten years and an internal rate of return of 15 per cent, consists in applying the following expression :

$$V = \left(\frac{DC + zWC}{\beta \times \text{capacity}} - A \right) \frac{1}{1 - a} + D + A$$

where

DC = depreciable capital.

z = 0.7528.

β = 5.019.

WC = working capital.

D = manufacturing costs.

A = provision for depreciation.

a = tax rate.

It is impossible within the scope of this introduction to describe these methods, which are also discussed in considerable detail in the *Manual of Economic Analysis of Chemical Processes*, published by McGraw Hill, N.Y., 1981 and in the *Manuel d'évaluation économique des procédés*, published by Editions Technip, Paris, 1976. The same applies to all the details of the economic calculation, which is treated only briefly to reveal the manner in which they are used.

Chapter 1

HYDROGEN SYNTHESIS GASES AND THEIR DERIVATIVES

The growing importance of hydrogen is the outcome of the development of catalytic refining processes, especially desulfurization and hydrocracking, and of the rise in the production of ammonia, methanol and certain intermediates (cyclohexane by benzene hydrogenation) in chemical synthesis.

Table 1.1 gives the hydrogen consumption figures for a number of important reactions.

TABLE 1.1
HYDROGEN CONSUMPTION
(m^3/m^3 of liquid feedstock or per ton of product)

Process or product	Unit	Consumption
Refining		
Desulfurization		
Gasoline	m^3/m^3	12
Gas oil	m^3/m^3	50
Heavy distillate	m^3/m^3	100
Cracking	m^3/m^3	240 to 700
Ammonia	m^3/t	2,000
Methanol	m^3/t	1,600
Benzene (Hydrodealkylation)	m^3/t	350
Naphthalene (Hydrodealkylation)	m^3/t	500
Cyclohexane	m^3/t	1,000

1.1 HYDROGEN

Hydrogen ($bp_{1.013} = -249.4^\circ\text{C}$, d at boiling point 0.0697) can be prepared by one of the following methods:

- (a) The treatment of certain gas mixtures, by-products of the manufacture of coke, of olefins by steam cracking, and, above all, of gasolines by catalytic reforming. The raw hydrogen produced by these operations is often diluted with chemical compounds, of which the light hydrocarbons (methane, ethane) account for the largest share. Since most industrial uses demand a purity of 80 to 95 per cent volume, hydrogen is primarily prepared from catalytic reforming effluents which usually display suitable purity, while hydrogen from steam cracking, of which only part is recovered (by Joule Thomson expansion) at a sufficient degree of purity, is reserved for the treatment of other products turned out by the same facility. Higher recovery of hydrogen available at lower purity requires the installation of purification units (cryogenics, adsorption on solid), which are only viable if the effluents from various processes (steam cracking, benzene dealkylation with hydrogen, xylenes isomerization purge, miscellaneous hydrogenations, hydro-cracking etc.) can be combined in the same installation.
- (b) The decomposition of hydrocarbons and other organic raw materials (coal, lignite, wood etc.) by three methods:
 - . Decomposition into carbon and hydrogen.
 - . Partial oxidation.
 - . Steam treatment.
- (c) Water decomposition, which can be carried out by:
 - . Electrolysis, which can benefit from cheap electricity (nuclear and hydropower plants etc.).
 - . Thermochemical cycles.
 - . The use of iron oxides in the presence of CO, a very old method for obtaining hydrogen, used during the Second World War to inflate captive anti-aircraft balloons.

1.1.1 Purification processes

These processes involve physical and physicochemical separation techniques aimed to remove impurities from hydrogen-containing gaseous mixtures, by-products from various refining and petrochemical operations, as well as effluents from the decomposition of organic raw materials. The specific applications in which these methods participate in the latter case will be examined below with the study of the synthesis of derivatives such as ammonia and methanol. For the time being, they are discussed in general terms, together with their use to eliminate hydrocarbons, and possibly low contents of oxygenated compounds, from certain hydrogen-rich gases.

They are divided into four main groups.

1.1.1.1 Absorption

Absorption is by far the most widespread industrially, but applies chiefly to the separation of oxygen and sulfur compounds which occur in large amounts in effluents from partial oxidation and from the steam treatment of organic raw materials. Two typical and vastly different situations thus exist:

- (a) **Effective purification of industrial waste gases.** from which the hydrocarbon impurities must be removed. These impurities are dissolved by scrubbing, using a heavier hydrocarbon (gas oil, aromatic oil) for example. However, an operation of this type is not widely practised industrially owing to its lack of selectivity and the low purification rate achieved. It is inapplicable for obtaining hydrogen in a purity greater than 85 per cent volume.
- (b) **Specific removal or even recovery in the pure state.** of components present in high contents in the gases to be treated. In this situation, where each case demands an appropriate solvent or complexant for the substance to be removed, the following main applications are encountered :
 - Separation of acid gases (H_2S , CO_2 , etc.) by means of amines, alkaline carbonates and methanol (see Section 1.1.2.6).
 - Purification and production of carbon monoxide by scrubbing with liquid nitrogen (see Section 1.3.1.1) or complexation by copper/aluminum tetrachloride (see Section 1.2).

1.1.1.2 Adsorption

Gas phase adsorption on solids (silica gels, activated charcoal, synthetic zeolites, molecular sieves) is also practised industrially. It is more suitable for the purification of effluents that display some complexity of composition. Its effectiveness depends on many parameters, particularly the volatility and polarity of the feedstock components.

Hydrogen, which is highly volatile and non-polar or polarizable, is, when mixed with various impurities, practically unadsorbable, and is hence easy to purify by this method. The regeneration of adsorbent beds which have fixed the other components is usually carried out by raising the temperature obtained by a stream of hot gas which also acts as the desorbent: the restoration of adsorption conditions then requires the beds to be cooled. These heat transfers are slow, making the process inapplicable to rapid cycles, and restricts it to the separation of small amounts of impurities.

Instead of operating by temperature variations (Temperature Swing Adsorption: TSA cycle), if the content of secondary components is high, it is preferable to regenerate the adsorbent by pressure variations (Pressure Swing Adsorption: PSA cycle). This method, which helps to obtain high-purity hydrogen (99.9 per cent volume) from effluents containing 80 to 85 per cent volume, was developed in particular by *Union Carbide* with its Hysiv PSA process, and by *Linde*.

In principle, a PSA cycle comprises four successive phases: adsorption, depressurization, low pressure purge, and recompression. Theoretically, the operation can be made continuous by the use of two adsorbent beds only, operating alternately, one on the first phase and the second on the last three. In practice, this arrangement leads to large hydrogen losses during purge and depressurization. It is therefore preferable to increase the number of beds, using at least four, and currently ten in *Union Carbide's "Polybed"* integrated variant. In the initial simplified version, alternate operation takes place as follows (Fig. 1.1):

- (a) One of the beds, for example the first, supplied with the feed gas, available between 1 and $4 \cdot 10^5$ Pa absolute, is in the adsorption phase at an optimal temperature of about 10 to 15°C, and produces pure hydrogen under pressure ($\Delta P = 0.06 \cdot 10^6$ Pa).

- (b) The second bed is in the depressurization stage, which releases gas to purge the third bed and to pressurize the fourth, whose final pressurization level is subsequently obtained by purified hydrogen available at high pressure.
- (c) This purge of the third bed takes place at low pressure (between 0.1 and $1 \cdot 10^6$ Pa absolute) to guarantee the most complete possible removal of impurities. As a rule, the ratio of the inlet to exit pressures must be at least 4 : 1.
- (d) The final bed is recompressed using gas from the second bed and by a fraction of purified hydrogen from the first bed.

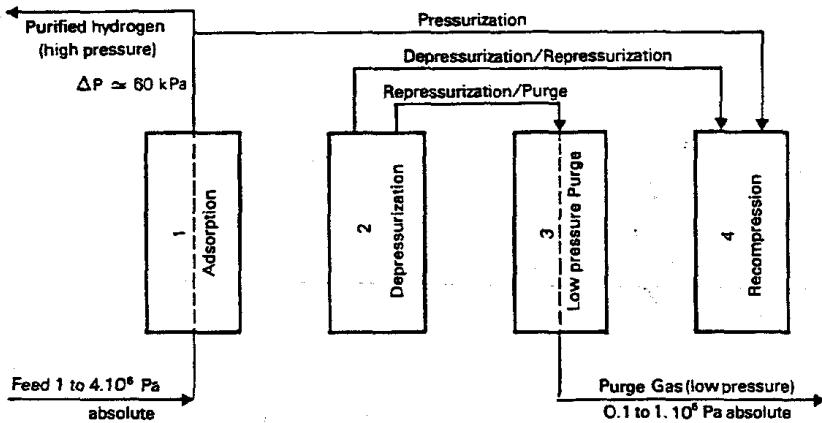


Fig. 1.1. Base scheme of the PSA four-bed process.

The separation yield depends on the feed and purge pressures: it is a maximum when the former reaches 1.5 to $2 \cdot 10^6 \text{ Pa}$ absolute and the second $0.1 \cdot 10^6 \text{ Pa}$ absolute. It also depends on the hydrogen content of the feedstock. In this case, it peaks at 85 per cent if the hydrogen content exceeds 80 per cent volume. The process is economically unprofitable for a hydrogen concentration lower than 30 per cent volume. Optimal conditions prevail at 75 to 80 per cent volume.

In the "Polybed" version with ten adsorbent beds, three of them are in the adsorption phase at all times. Pressurization takes place in two steps, with an intermediate countercurrent purge by purified hydrogen, and a final cocurrent purge. Recompression also takes place in steps. The different sequences are programmed and automatically monitored. The yield in this case may reach 85 to 88 per cent for a feedstock containing 65 to 75 per cent volume hydrogen.

Before introducing the feed, a number of precautions must be observed to eliminate various impurities, such as ammonia, by prior washing with water. The process does not tolerate the presence of high contents of acetylene, H_2S , methanol, moisture, C_3 -hydrocarbons etc. However, it allows unlimited quantities of nitrogen, carbon monoxide, argon, methane, ethylene, ethane and carbon dioxide.

1.1.1.3 Permeation

The use of membranes for liquid separation was developed industrially over twenty years ago (osmosis, dialysis, ultrafiltration etc.). Gaseous permeation through palladium, alloyed or unalloyed, although limited to the production of low unit capacities, has also been marketed for many years (1965). On the other hand, the industrial use of organic membranes is of much more recent date (1981). This development is associated with that of specialty polymers, and, above all, with the generalization of a special process to manufacture reverse osmosis systems. This technique, proposed by Loeb, serves to deposit a fine layer of polymer on a porous structure consisting of the same material and designed to guarantee overall mechanical strength of the system. This achieves a substantial gain in the maximum unit treatment capacity of membrane separators, by reducing unit size and increasing total diffusion surface area.

The quantity of gas treated depends on the permeation rate, which is given by the expression :

$$Q = k \frac{S \cdot \Delta P}{e}$$

where k is the permeability of the membrane, S its surface area, e its thickness, and ΔP the difference in partial pressure for the same product on each side.

This explains why, in comparison with systems featuring porous supports, dense inorganic or organic membranes, which lead to very low permeation rates, are of limited value for the treatment of high gas flow rates (up to 100,000 m³/h).

As a rule, this type of operation is subject to pressure requirements of the gas to be treated (between 1 and 15 . 10⁶ Pa absolute) or, more specifically, differences in pressure (between 0.7 and 7 . 10⁶ Pa) and, in the case of organic systems, to temperature requirements (between 0 and 60, or even 100°C).

A. Palladium membranes, alloyed and unalloyed

Their operating principle is based on the special feature displayed by molecular hydrogen of dissociating into atomic hydrogen, around 300 to 400°C, in contact with a palladium surface, and diffusing across this wall and then recombining at the outlet. This makes it possible to separate the other components of the hydrogen-containing gas, provided they are not poisons to the membrane (heavy hydrocarbons, H₂S, olefins etc.). Otherwise, it is necessary to pretreat the feedstock gas. Moreover, the presence of hydrogen in the vicinity of palladium at a temperature incompatible with dissociation conditions, i.e. lower than 260°C, damages the structure of the extremely thin metallic film (about 0.01 mm), which is deposited on a support. Consequently, the gases cannot be heated and cooled in the immediate vicinity of the membrane. As a rule, palladium is used alone or alloyed with 5 per cent weight silver.

To give one example, using a feed of electrolytic origin available at 1.5 to 4 . 10⁶ Pa absolute, hydrogen is obtained at 0.5 to 0.7 . 10⁶ Pa absolute with a purity of 99.98 to 99.99 per cent.

B. Organic membranes

In the field of gas separation a large number of materials can be used (polyolefins, polyamides (polyaramids), polyesters, polysulfones and, more specifically, polyvinyl-

trimethylsilane, polytetrafluoroethylene etc., cellulose acetate, cellulose and silver nitrate etc.) for the manufacture of membranes, researched and developed chiefly in the United States, Western Europe and Japan, mainly by *Allied-Signal, AKZO, Dow Chemical, Du Pont, Monsanto, Rhône-Poulenc, Ube, Union Carbide, W.R. Grace*, etc. The separators, which can be grouped in series or in parallel, use these membranes in various configurations:

- (a) In the form of hollow fibers grouped in tube bundles of 10,000 to 100,000 elements: *AKZO-Air Product, Dow-BOC (British Oxygen Corp.), Du Pont-Air Liquide, Monsanto-Permea, Ube, Union Carbide-Linde*, etc.
- (b) In an arrangement of spiral-wound sheets around a collector, which provides for the alternate and successive flow of the feedstock and the treated gas, that of the isolated constituents, and the separation function (*Delta Engineering's Delsep process, Gosep by Envirogenics, W.R. Grace-Separex* etc.).

In hollow fiber systems, the shells are 0.10 to 0.20 m in diameter and 3 to 6 m long. The inside and outside diameters of each of the diffuser elements range from 0.4 to 0.8 mm. In sheet systems, which normally have six membrane windings in series alternating with gas flow systems, the shells are approximately 10, 20 and 25 cm in diameter.

The applications involved essentially pertain to adjustments of the composition of certain gases, the separation of impurities (acid gases H₂S and CO₂); and the recovery or purification of certain gaseous components (H₂, CO₂, O₂, natural gas etc.).

For the hydrogen enrichment of effluents from hydrotreating units, Monsanto's Prism TM process, using gas containing 60 to 75 per cent H₂ ($\cong 15,000 \text{ m}^3/\text{h}$) available at 3.5 to $5.5 \cdot 10^6 \text{ Pa}$ absolute, furnishes a product with a purity of 92 to 98 per cent volume, with a yield of 80 to 90 per cent at $2 \cdot 10^6 \text{ Pa}$ absolute.

1.1.1.4 Cryogenics

Like absorption, cryogenic purification takes place differently depending on whether it is necessary to enrich with hydrogen an effluent whose main impurities are hydrocarbons, or to remove, and then to produce at a high degree of purity, a specific compound such as carbon monoxide.

In the former case, which is discussed in this study, only partial condensation is performed industrially. In the latter, scrubbing can also be carried out with liquid methane or nitrogen (see Section 1.2). However, this means that the residual hydrogen gas is polluted by one or the other of these two compounds, and this could restrict its field of application or, on the contrary, facilitate its use. Hence the use of liquid nitrogen offers an interesting solution for ammonia synthesis from an effluent produced by partial oxidation of organic feedstocks (see Section 1.3.1.1) in so far as, introduced with hydrogen at the rate of 2 to 8 per cent volume, this represents the use of one of the reactants for the production of ammonia, whereas methane, on the contrary, is a diluent.

On the whole, partial condensation takes place on effluents available at high pressure and previously dried. After low-temperature liquefaction of the impurities, it consists in revaporizing them at low pressure to recover the energy expended for cooling.

If the treatment aims only to remove the heaviest hydrocarbons, condensation occurs from -40°C . It can be carried out using an external refrigeration system which requires low energy consumption. On the other hand, if it is necessary to remove compounds such

as ethane, methane and carbon monoxide, the temperatures required are in the range of -155°C . Thus, to minimize energy consumption, use is made of the Joule Thomson expansion of the liquefied fraction, or of hydrogen expansion in a cryogenic turbine at the lowest temperature of the installation, an operation therefore conducted at the cost of a substantial lowering of the availability pressure.

If carbon monoxide is initially present (case of synthesis gases produced by partial oxidation or steam reforming, for example), a residual content is inevitable in the purified gas. This can at best be reduced to 2.5 per cent volume, a maximum purity corresponding to the value given by the liquid/vapor equilibria of the H_2/CO mixture at the service pressure (3 to $4 \cdot 10^6$ Pa absolute), and at the maximum cooling temperature ($\geq -155^{\circ}\text{C}$). A methane/carbon monoxide column can finally be used to separate the CO.

Figure 1.2 shows a steam-cracked hydrogen recovery and purification flow sheet by Joule Thomson expansion and heat transfer by means of plate-type heat exchangers. The hydrogen recovery rate, at a purity of 98 per cent volume, is thus more than 98.5 per cent from an effluent whose initial content is 70 per cent volume.

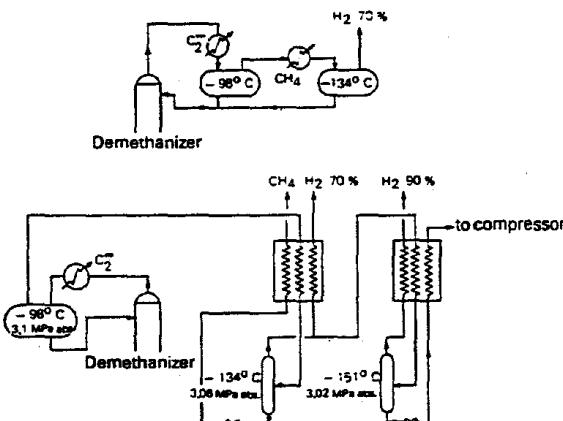
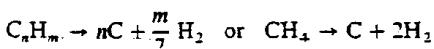


Fig. 1.2. Circuit for the recovery and purification of hydrogen by Joule-Thomson expansion.

1.1.1.5 Chemical processes of hydrogen purification

In principle, the chemical processes used are those that selectively convert the hydrocarbon compounds polluting the hydrogen.

One example is the thermal decomposition of these hydrocarbon into carbon and hydrogen according to the general reaction:



($\Delta H_{298}^0 = 75 \cdot 10^6 \text{ kJ mol}$) in the case of methane.

This reaction, which must be conducted at high temperature (Fig. 1.3), has not been exploited industrially on account of the operating conditions, which are not readily compatible with economical equipment, and also because of the difficulties encountered in the separation of hydrogen and carbon black.

1.1.1.6 Economic data

Table 1.2 lists miscellaneous economic data pertaining to the purification of hydrogen by adsorption, cryogenics and permeation.

TABLE 1.2
-HYDROGEN PURIFICATION. SEPARATION OF HYDROCARBONS AND OTHER
NON-OXYGENATED IMPURITIES. ECONOMIC DATA
(France conditions, mid-1986)

Process	Adsorption	Cryogenics (condensation)	Organic membranes		
Technology	PSA Hysiv Union Carbide	Petrocarbon Development	Prism Monsanto		
H ₂ yield (%)	75	94.5	95	95.7	95
H ₂ purity (%)	99.5	92.5	95.2	87.8	95
Material balance (m ³ /h)					
Feedstock	30.000 ⁽¹⁾	30.000 ⁽²⁾	30.000 ⁽¹⁾	30.000 ⁽³⁾	30.000 ⁽¹⁾
Product	19.000	18,700	25,300	19,900	25,200
Purge	11.000	11,300	4,700	4,700	5,800
Battery limits investments (10 ⁶ US\$)	2.4	3.0	2.5	2.8	5.1
Consumption per 1,000 m ³ of pure hydrogen					
Utilities					
HP steam (t)	—	0.08	0.06	0.07	—
Electricity (kWh)	—	10	35	45	70
Cooling water (m ³)	—	6	6	4	—
Instrument air (m ³)	3	5	5	5	5
Miscellaneous (adsorbent, membranes) (US\$)	0.5	0.9	0.9	0.5	0.5
Labor (Operators per shift) ..	0.5	0.5	0.5	0.5	0.5

(1) Composition (% vol.) : H₂ = 84 ; C₁ = 6.2 ; C₂ = 3.1 ; C₃₊ = 6.7; Pressure = 2.35 . 10⁶ Pa absolute.

(2) Composition (% vol.) : H₂ = 60.8; N₂ = 20.0; CH₄ = 12.2; Ar = 3.1; NH₃ = 3.9; Pressure = 7.0 . 10⁶ Pa absolute.

(3) Composition (% vol.) : H₂ = 60.8; N₂ = 20.0; CH₄ = 12.1; Ar = 3.2; NH₃ = 3.9; Pressure = 14.0 . 10⁶ Pa absolute.

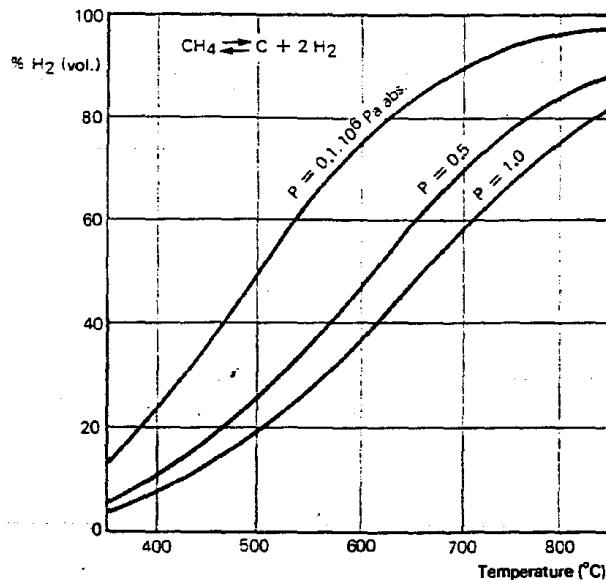


Fig. 1.3. Equilibrium of methane decomposition.

1.1.2 Techniques for producing hydrogen from hydrocarbons and organic raw materials

1.1.2.1 Main schemes

As discussed above, the thermal decomposition of hydrocarbons is employed neither as an industrial method for producing hydrogen, nor for the purification of certain effluents. On the other hand, it appears as a side reaction in processes of controlled oxidation with oxygen and water reforming, the only ones commercialized at present.

Many different feedstocks are employed: natural gas (methane, ethane, propane etc.), petroleum cuts (Liquefied Petroleum Gas: LPG, naphtha, fuel oil, vacuum residues, asphalts etc.), coal, biomass (lignocellulose wastes, wood etc.).

Depending on the specific case (catalytic or other process), the previous removal of certain impurities may or may not be necessary: sulfur derivatives, mercury, other metals. Furthermore, they yield effluents of variable compositions which must be treated to improve the total yield of the operation and to extract the hydrogen.

Figure 1.4 provides a glance at the succession of treatments which accompany the implementation of the two basic industrial processes used for the manufacture of hydrogen:

- (a) Partial oxidation.
- (b) Steam reforming.

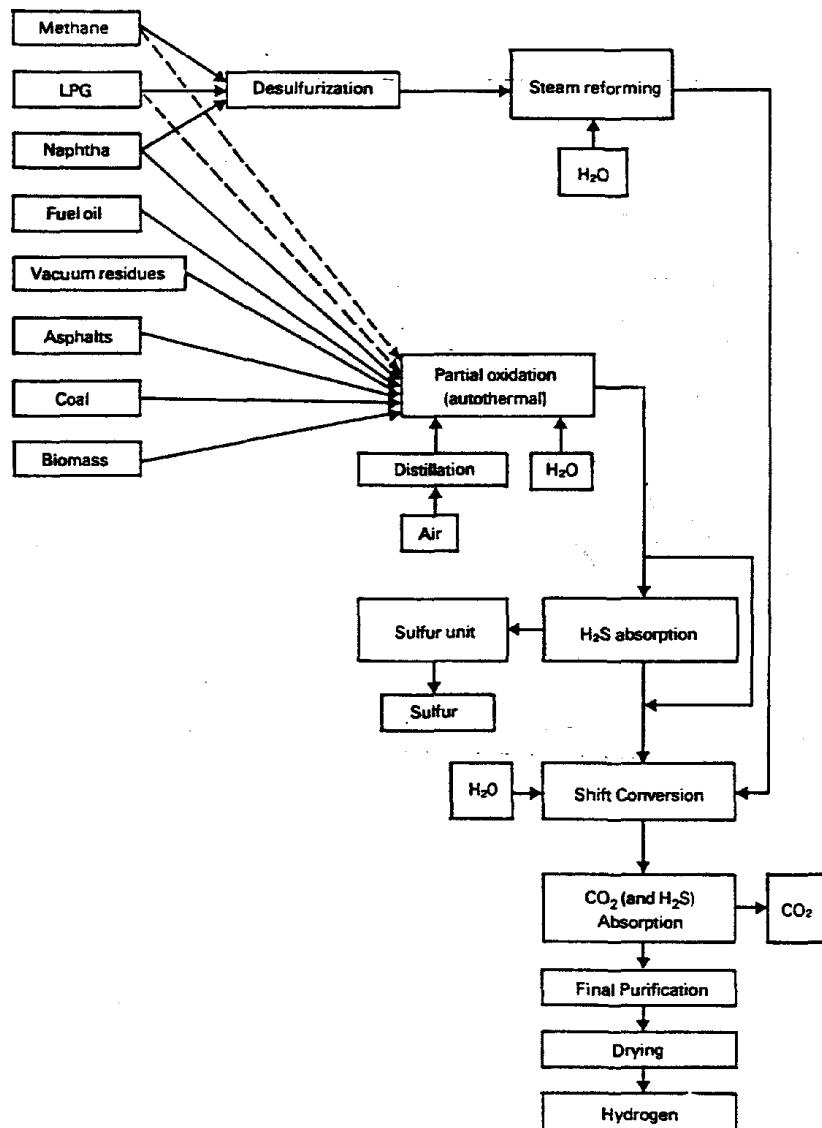


Fig. 1.4. Processing of carbonaceous feedstocks to produce hydrogen.

The following operations are carried out:

- Conversion of CO with steam (shift conversion).
- Extraction of acid gases CO_2 and H_2S , supplemented in the case of sulfur-containing effluents by a Claus unit designed to prevent pollutant releases into the atmosphere.
- Final purification designed to eliminate the last traces of CO.

Depending on the flow sheet concerned, pretreatments comprise:

- For steam reforming: desulfurization, essentially intended to protect the catalyst.
- For partial oxidation with oxygen: air distillation.

1.1.2.2 Partial oxidation

This type of process can theoretically be used to treat any gaseous, liquid or solid feed. In practice, however, it is reserved for the conversion of the cheapest raw materials such as heavy hydrocarbons (especially fuel oil), and possibly, in the future, petroleum residues (asphalts), coal and biomass (wood). In this case, moreover, the conversion is usually called "gasification".

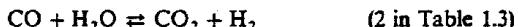
A. Thermodynamic and kinetic aspects of the reactions

The chemical mechanisms involved in the controlled oxidation of hydrocarbons are extremely complex. A simplified interpretation can nevertheless be provided by considering methane. The following transformations are considered in this case:

- Combustion reaction: since it takes place at elevated temperature, at which carbon monoxide is one of the main products formed, it is convenient ⁽¹⁾ for thermodynamic calculations to assume the following overall representation:



- For carbon monoxide, the following equilibrium reaction must be added:



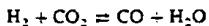
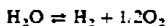
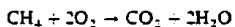
due to the presence of the water formed during combustion or added by steam injection.

- A hydrocarbon decomposition reaction:



The first conversion is exothermic and exentropic: it is virtually complete and also serves to reach the temperature required for the operation which, with the exception of preheating at a low temperature level, takes place adiabatically.

(1) Another thermodynamic pathway yielding the same products can be employed:



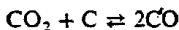
The second reaction depends on an equilibrium which shifts in the desired direction at low temperature. From a thermodynamic standpoint, to obtain high hydrogen contents in the effluent produced (raw synthesis gas), the operating conditions must guarantee the lowest possible service temperatures. In practice, this consideration is incompatible with the partial oxidation operation which, due to its exothermicity, creates a high reaction temperature (950 to 1250°C).

TABLE 1.3
ENTHALPY AND ENTROPY VARIATIONS IN REACTIONS
ASSOCIATED WITH THE PARTIAL OXIDATION OF METHANE

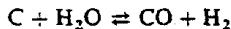
Reaction	ΔH_{298}^0 (kJ/mol)	ΔS_{298}^0 u.e.
1. $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	206.225	214.83
2. $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-41.178	42.42
3. $\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2$	165.047	172.41
Reactions (1 + 2)		
4. $\text{CH}_4 \rightleftharpoons \text{C}_{(\text{s})} + 2\text{H}_2$	74.874	75.01
5. $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	-172.528	-176.54
Reactions (4 + 2 - 1)		
6. $\text{C}_{(\text{s})} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	131.350	134.10
Reactions (1 - 4)		
7. $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247.402	257.25
8. $\text{CH}_4 + 3/2\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2\text{O}$	-519.515	81.62

This effect must therefore be corrected by a supplementary catalytic conversion of CO, after having cooled the gas obtained. Thus, by excess water injection and by lowering the temperature, the conditions reached cause the equilibrium to shift towards the production of hydrogen.

The third conversion, the decomposition of methane into its elements, favored by the high temperature, is the main side reaction (Fig. 1.3). To a certain degree, the presence of CO_2 and water helps to offset these harmful effects, due to the formation of powdery carbon by means of the following equilibria :



(Boudouard's equilibrium, 5 in Table 1.3)



(6 in Table 1.3)

The results of a thermodynamic analysis, which takes account of these three reactions, can be transposed, for a system operating adiabatically, to a graph where the following are plotted as a function of the ratio of the amounts of oxygen and methane employed (Fig. 1.5) :

- (a) The carbon black production zone.
- (b) Curves giving the CO, CH_4 and H_2O content and the H_2/CO ratio.
- (c) The final temperature of the operation.

The scale of the upper x-axis gives the CO and H_2 content of the gaseous effluent in per cent volume.

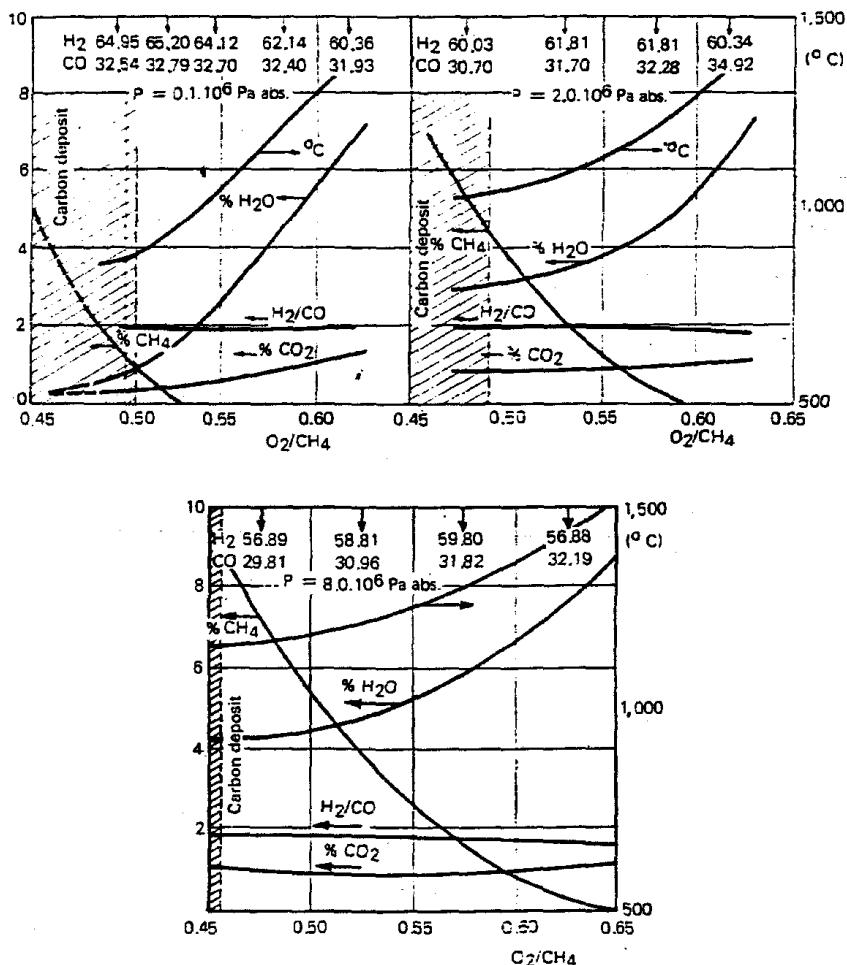
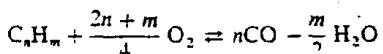


Fig. 1.5. Preheating of reactants at 593°C. Partial oxidation of the mixture. Equilibrium composition (From C. Raimbault, IFP).

These curves show that avoiding the production of carbon black can yield a low methane content in the final gas, which can be adapted by adjusting the initial O₂/CH₄ ratio.

In the case of the heavier hydrocarbons, the basic conversion is the following:



As the H/C ratio in the feed decreases, the tendency to favor the production of carbon increases. Since the amount of water formed by combustion becomes insufficient, it is therefore necessary to operate in the presence of steam, even at elevated temperature. The thermodynamic calculation shows that, at identical temperatures, an increase in pressure results in larger water requirements and a decrease in oxygen requirements. Simultaneously, the residual methane content increases, and this can be offset by raising the temperature. The highest carbon content feedstocks (residues, coal, biomass) constitute the limit case.

B. Technological aspects

Depending on the raw material employed, the following three main groups of technologies can be distinguished:

- Techniques of partial oxidation of petroleum cuts, which are generally thermal and use burners (*Texaco, Shell*). Some of them use contact masses whose catalytic effect is claimed by the process licensors (*ONIA-GEGI: Office National des Industries de l'Azote, Montecatini, Koppers-Totzek*). However, the high temperatures employed and the danger of carbon deposits on the contact mass do not favor the spread of these technologies.

The flow sheet of these partial oxidation processes comprises:

- (a) A burner in which oxygen and preheated steam are injected with the hydrocarbon.
- (b) A section which recovers heat contained in the off-gas, either by direct contact or in a boiler.
- (c) A section to remove carbon black by washing or filtration.

Figures 1.6 and 1.7 offer a schematic representation of units of the Texaco and Shell type, whose special feature is to recover the carbon formed by washing with water, and then to extract the sludge obtained with naphtha. The extract can then be homogenized with the feed and thus sent directly to the partial oxidation reactor (Shell version), or previously treated by stripping by reboiling in the presence of heavier hydrocarbons, such as fuel oil or crude oil, in order to separate and recycle the naphtha (Texaco version).

- Coal gasification which, after drying, crushing and grinding of the feed, is carried out in three main types of installation:

- (a) Moving (incorrectly called fixed) bed reactors (*Lurgi*).
- (b) Fluidized bed reactor (*Winkler*).
- (c) Entrained-bed reactor (*Koppers, Texaco*).

These different technologies yield different hydrocarbon contents of the raw gas, as shown by Table 1.4.

Thus, in the case of the entrained-bed (dual flow) reactor, the methane content is very low and does not require specific fractionation. In the fluidized bed reactor, hydrocarbons other than methane are not formed. With the moving bed technique, operating in countercurrent flow, the hydrocarbon content ($\text{CH}_4, \text{C}_2\text{H}_6$) is sometimes high enough to require their separation from the gas produced, and possibly their conversion by supplementary steam reforming. A more detailed analysis of the main gasification processes under development or already industrialized is given in Table 1.5.

On the whole, the removal of ash and soot plays a vital role in the treatments directly surrounding coal gasification.

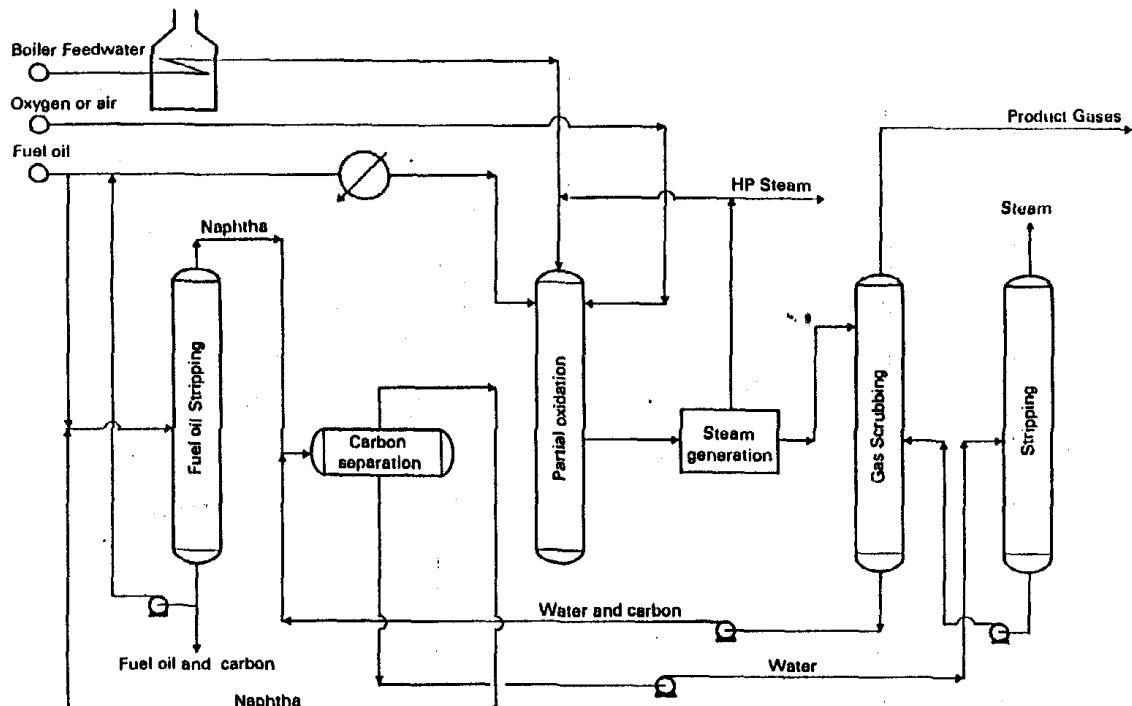


Fig. 1.6. Hydrogen manufacture by partial oxidation. Texaco process.

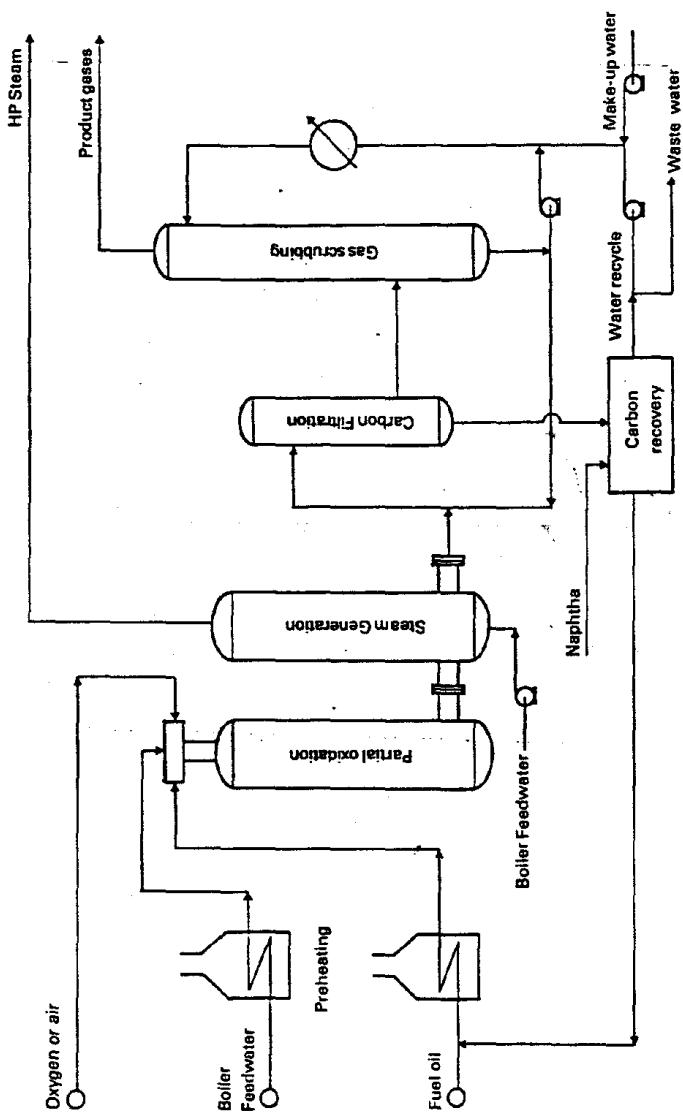


Fig. 1.7. Hydrogen manufacture by partial oxidation. Shell process.

TABLE 1.4
TYPICAL COMPOSITION OF A DRY CRUDE GAS PRODUCED
BY PARTIAL OXIDATION (% VOL)

Feedstock	Fuel oil	Coal		
		Burner	Entrained bed	Moving bed
Components :				
H ₂	47.3	34.7	38.1	40.0
CO	46.7	52.4	21.0	35.0
N ₂ + A	0.2	0.9	0.8	1.6
CO ₂	4.4	10.3	29.0	21.0
CH ₄ , C ₂ H ₆	0.6	0.1	9.0	2.0
H ₂ S + COS	0.8	1.6	1.4	0.4
NH ₃	—	—	0.7	—

• The conversion of lignocellulose wastes, or more generally of dry biomass ⁽²⁾, can be achieved after reducing the feedstock to a suitable particle size distribution by grinding, by partial oxidation using a technology similar to that employed for coal, or by flash pyrolysis. These two techniques differ in the method of using the oxygen, and possibly air, which is direct in the former case and indirect in the latter, inasmuch as the heat necessary for the operation is then obtained by the separate combustion of the pyrolysis residues (tar).

(a) The gasification of wood, or, more generally, biomass, takes place by a complex process in which three stages can be distinguished:

- Drying between 100 and 300°C.
- Pyrolysis between 200 and 500°C or higher.
- Reduction and oxidation which occur between oxygen, moisture, carbon dioxide, carbon monoxide and carbon, at a temperature below 1000°C for wood.

As to coal, the gasifiers may be of three types, featuring a "fixed", entrained or fluid bed. In the first, the bed is moving rather than fixed, the fuel flows by gravity, and ash is removed at the bottom of the reactor by a mobile grid system or in batches. The gases flow in parallel, co- or countercurrent contact, or even perpendicular to each other.

This is a well-established technology, and has been replaced today by the fluidization of fine particles (grains of sand, carbonization products, ash) using a controlled flow rate gas stream. As for entrained-bed reactors, they have not yet been employed to treat lignocellulose wastes.

Industrial gasification achievements by themselves have succeeded in upgrading municipal wastes. Union Carbide's Purox process represents a typical technology in the field. Many developments have occurred with wood : Table 1.6 provides an idea of the dry gas compositions obtained, which vary with the type of gasifier and the feedstock.

(2) Biomass with a dry matter content over 70 to 80 per cent weight, as opposed to "wet" agricultural wastes which are used for fermentation.

TABLE I.5
GENERAL CHARACTERISTICS OF THE MAIN GASIFICATION PROCESSES FOR BITUMINOUS COALS

Process	Lurgi Dry ash	Winkler	Koppers/ Totzek	Lurgi Slagging ash	Shell/ Koppers	Saarberg Otto	Texaco	U. Gas
Pressure (10^6 Pa absolute)	Commercialized	Commercialized	Commercialized	4.0 to 10.0	3.0	2.5	3.0 to 10.0	2.0
Reactor type	Fixed bed	Fluidized bed	Entrained bed	Fixed bed	Entrained bed	Turbulent bed	Entrained bed	Fluidized bed
Typical composition (% vol.)								
H ₂	38	35 ⁽²⁾ , 35 ^(1,2)	32-29 ⁽²⁾	28	29-30 ⁽²⁾	31	34-36	50
CO	21	48-52	55-56	54	64-62	58	44-51	37
CO ₂	29	19-9	11-12	4	4-7	9	13-19	9
CH ₄	8	2-3	-	7	-	-	6	3
By-products	Phenols tars			Phenols tars				
H ₂ /CO ratio	1.81	0.73-0.67	0.58-0.52	0.52	0.45-0.48	0.53	0.77-0.71	1.35

(1) Winkler high-temperature variant.

(2) Sub-bituminous coal/lignite.

TABLE I.6
TYPICAL COMPOSITIONS OF DRY GASES
PRODUCED BY WOOD GASIFICATION (% vol.)

Process	Partial oxidation	Flash pyrolysis
N ₂	0.3	—
H ₂	28.4	15.5
CO	47.5	32.5
CO ₂	17.2	38.0
CH ₄	6.6	11.5
Heavy		2.5
Total ...	100.0	100.0

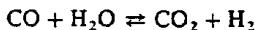
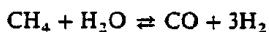
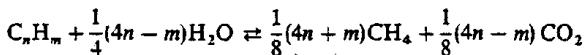
- (b) Flash pyrolysis was developed in particular by *Garrett Energy Research and Engineering*, a subsidiary of *Occidental Petroleum*, and by *Battelle Columbus*. In both processes, systems featuring equipment sections that are isolated from each other in terms of gas transfers, are used to dry the wood, and then for pyrolysis around 800 to 900°C using the flue gases obtained by the combustion of the residues formed. This produces effluents with a higher heating value. Heat exchanges occur on the biomass itself, which advances by gravity from one section to the next, or by means of a solid heat transfer medium which retains tars and is then cleaned by combustion and recycled.

1.1.2.3 Steam treatment (steam reforming)

This type of process, which operates in the presence of catalysts, serves to treat feeds ranging from methane to cuts with an end boiling point of 200°C, although the latter are little used today⁽³⁾.

A. Thermodynamic and kinetic aspects of the reactions

Steam reforming is based essentially on the controlled oxidation, by water, of methane or, more generally, hydrocarbons. The main reactions are as follows:



The first conversion, which is exothermic, is practically complete between 400 and 600°C. At these temperatures the second, which is endothermic and exentropic and hence favored by low pressures, is still limited by an equilibrium, as shown by Table 1.7, where the calculation was made for an initial stoichiometric mixture of steam and methane at atmospheric pressure.

(3) Pilot developments are under way for the steam reforming treatment of heavy residues by the Japanese company *Toyo Engineering Co.*

TABLE 1.7
EQUILIBRIUM CONCENTRATIONS $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$

(°C)	CH_4 (mole %)	H_2O (mole %)	CO (mole %)	H_2 (mole %)
427	42.6	42.6	3.7	11.1
527	30.0	30.0	10.0	30.0
627	14.50	14.50	17.5	52.5
727	5.55	5.55	22.2	66.7
827	1.80	1.80	24.1	72.3
927	0.50	0.50	24.5	74.5

Even by raising the proportion of steam in the mixture, methane cannot be totally converted. This is achieved by a conversion operation in the presence of oxygen or air, called **secondary reforming** or **post-combustion**. This resembles partial oxidation in the presence of catalysts, and is mainly used for the preparation of gas intended for ammonia synthesis (see Section 1.3.1.2).

Moreover, since the temperature is too high for the CO equilibrium to shift towards hydrogen production, a separate operation is required to convert the carbon monoxide by low-temperature steam.

Finally, the theoretical amount of steam is determined not only by the foregoing reactions, but by the need to prevent the conversion:



which must be replaced by the action of steam on CO:



B. The catalyst and its conditions of use

For the main or primary reforming, the catalyst employed in the presence of methane is usually **nickel** on alumina. To slow down carbon formation, a potassium promoter is added to facilitate the action of steam on carbon monoxide.

For a naphtha feedstock, the catalyst is based on nickel deposited on calcium or magnesium silico-aluminate incorporating potassium, or nickel on an alumina support with uranium promoter. Nickel on calcium aluminate is generally used for post-combustion.

These catalysts operate in relatively severe conditions of temperature, pressure and steam-to-hydrocarbon ratio. Thus, they operate between 850 and 940°C at the outlet of the reaction zone, under average pressures of 1.5 to $2.5 \cdot 10^6$ Pa absolute, reaching up to $4 \cdot 10^6$ Pa absolute in the most modern processes. This is because, although thermodynamic considerations encourage the use of low pressures, it is economically interesting to employ the highest possible pressures, in order to reduce the costs of purification and compression before use. In most of the installations, the steam-to-hydrocarbon ratios at the reactor inlets normally range from 2 to 4, representing two to three times the necessary stoichiometry.

This means that the accidental presence of liquid water and elevated temperatures favor the sintering of both the metal and the support, which must therefore be as stable as

possible and have a large surface area. The presence of nickel also makes the systems employed sensitive to impurities such as sulfur compounds, halogens and arsenic, which are liable to give rise to reactions only reversible with difficulty. To avoid excessive deactivation, it is therefore necessary to desulfurize the feeds first to residual contents of 0.05 to 0.1 ppm. The potential sulfur is thus converted at around 350 to 450°C and at $5 \cdot 10^6$ Pa absolute, in the presence of cobalt and molybdenum base catalysts, to hydrogen sulfide, which is then adsorbed on masses of zinc oxide. The migration of potash at high temperature causes basic corrosion of the equipment and faster coking of the fractions of catalytic bed where potash is absent.

The volume hourly space velocity, in comparison with the vaporized hydrocarbon feedstock, is normally around 1600 to 2000 h^{-1} for primary reforming. In high-pressure treatment (2.5 to $3 \cdot 10^6$ Pa absolute), they reach 5000 h^{-1} . In post-combustion, which serves to reduce the quantities of residual methane in the dry gas to 0.1 to 0.3 per cent, the volume hourly space velocities range from about 2500 to 3000 h^{-1} .

As a rule, the operating conditions must be adapted to the type of feedstock available and the desired product. Table 1.8 gives the results of various primary steam reforming operations in different conditions of feed, temperature, pressure, quantity of water etc.

TABLE 1.8
STEAM REFORMING (FIRST REACTOR)

Feedstock	Methane 99.5%	Methane ⁽¹⁾ 96%	Propane 98%	Naphtha $\text{CH}_{2.10}$	Naphtha $\text{CH}_{2.12}$	Naphtha $\text{CH}_{2.3}$
Furnace exit temperature (°C).....	790	820	790	760	685	800
Furnace exit pressure (10^6 Pa absolute)	2.1	3.2	2.1	1.6	3.1	0.3
Mole of steam per carbon feed- stock	4	3.5	4	2.4	2	5.7
Dry gas produced (% vol.)						
H ₂	77.45	69.30	73.73	63.70	43.40	74.00
CO	12.40	9.70	13.30	12.90	6.20	8.90
CO ₂	10.05	10.40	12.82	14.70	18.10	17.00
CH ₄	0.10	10.60	0.15	8.70	32.30	0.10
Furnace exit steam dry gas ..	0.579	0.768	0.660	0.447	0.710	1.04

(1) C₂H₆ = 3%; C₃H₈ = 1%.

C. Technological aspects

The reactors employed display many similarities to those used for steam cracking (Section 2.1.4.1). These reactors are tubular furnaces, which can be divided today into four main types:

- (a) Vertical (or up-fired) furnaces with inspiring floor burners, consuming the purge gas of the installation.
- (b) Twin-cell furnaces, with side heating by means of rows of inspiring gas burners (KTI : Kinetics Technology International ex Selas for example).

- (c) Vertical (or down-fired) furnaces with roof burners, generally short-flame and forced-draft, allowing the combustion of liquids (*Topsoe* for example).
- (d) Terrace wall furnaces equipped with natural-draft burners or combination burners capable of accepting a wide variety of gaseous and liquid fuels (*Foster Wheeler* for example). Although these are more expensive, they display greater operating flexibility and achieve more homogeneous heating.

In each of these reactor types, the combustion chamber operates in negative pressure by means of a draft blower. Two main sections can be distinguished:

- A convection zone, in which the heat recovered from the flue gas provides various services, by means of tube bundles normally laid out horizontally: two-step preheating of the reforming feedstock, heating of the steam/hydrocarbon blend to a temperature of 450 to 570°C, but always below the cracking temperature, superheating of the steam to one or more temperature levels, steam generation, boiler feedwater heating, and, if required, heating of combustion air. In these conditions, the thermal efficiencies approach 90 per cent with flue gas sent to the stack at 180 to 200°C.
- A radiation zone with radiation by the combustion gases and the refractories, particularly in terrace wall furnaces. It features a tube bundle, filled with catalyst, comprising 500 tubes in the largest units, with an inside diameter of between 8.3 and 12.6 cm, a maximum length of 10 to 15 m, thickness less than 18 to 20 mm, which achieve heat transfer of an average of 225 to 250 . 10^6 J/h . m² related to the inside surface area. These tubes are laid out vertically in one or more rows separated by burners depending on the type of furnace, suspended from counterweight or spring devices designed to prevent creep due to expansion (250 mm for a length of 15 m), connected at the top and bottom to inlet and outlet distributors and collectors. Their cold filling must be carefully performed so that the pressure drop from one tube to the next, which may be as high as 0.5 . 10^6 Pa gauge, does not undergo variations of more than 5 per cent about the average value. Otherwise, the resulting changes in flow rates may cause substantial local overheating. The tubes are of alloyed steel, usually 25/20 chromium/nickel, capable of withstanding skin temperatures of about 900 to 950°C, and a maximum of 1000°C. 25/35 chromium/nickel steels can actually exceed this limit and operate at reaction pressures above 2 . 10^6 Pa absolute.

The outlet collectors, of Incoloy 800 or Manaurite 900, must be followed by expansion loops (pigtails) to offset the mechanical forces due to rapid temperature variations. They lead to waste heat boilers that are normally of two types:

- (a) Fire tube boilers, which are compact and inexpensive, but are limited to the production of steam at 7 . 10^6 Pa absolute.
- (b) Vertical water tube boilers, about 10 m in height, much more efficient but more difficult to maintain.

The recovery of heat from the reformed gas is completed by an economizer, and the gas is sent to subsequent treatment at a temperature of about 130 to 150°C.

Figure 1.8 gives a simplified representation of the steam reforming section for natural gas, using a terrace wall furnace equipped with peripheral facilities (desulfurization, waste heat boilers, steam drum etc.).

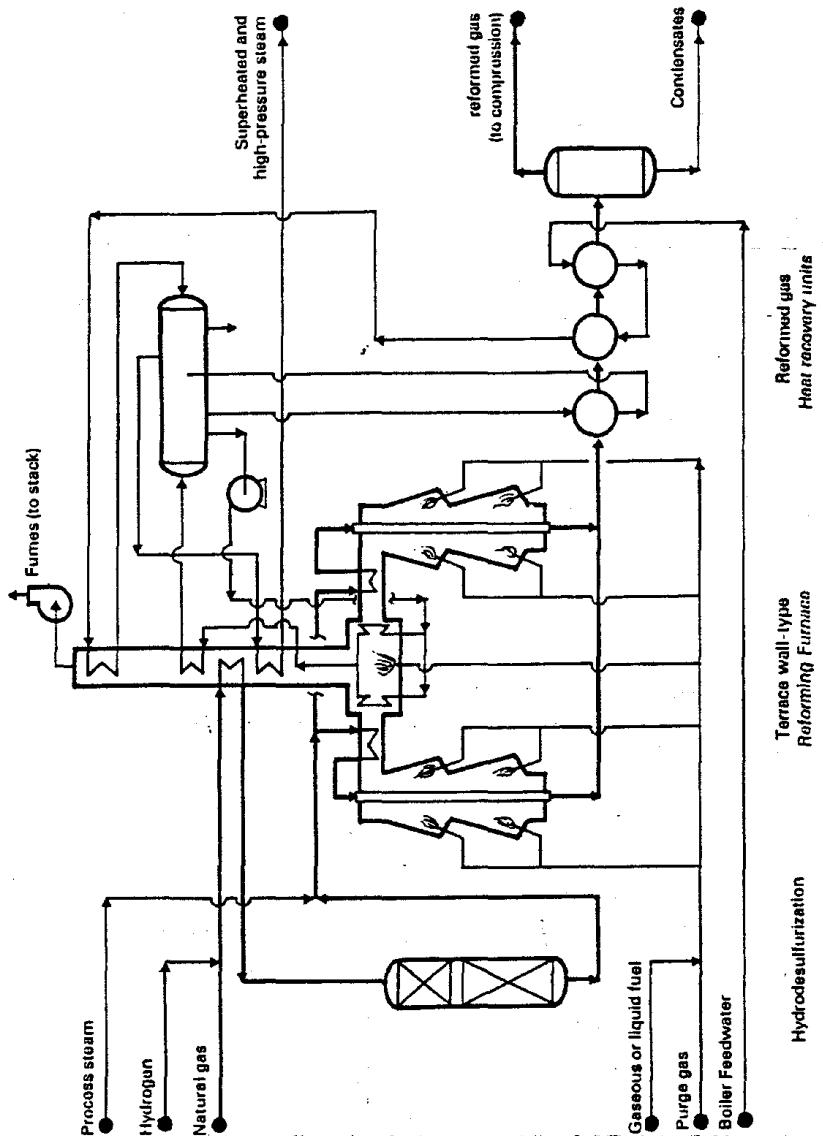


Fig. 1.8. Steam reforming furnace section.

1.1.2.4 Autothermal treatment

A number of processes combine both the above techniques in order to compensate for the endothermicity of steam treatment by combustion with oxygen or air. These include the technology developed jointly in the 1950s by SBA (*Société Belge de l'Azote*) and *Haldor Topsoe*, and the low-pressure techniques subsequently proposed by ONIA, BASF (*Badische Anilin und Soda Fabrik*) etc.

In principle, the SBA/Topsoe process consists in mixing the burner exit gases with steam and sending the mixture to a fixed-bed reactor on a nickel base catalyst, at about $2 \cdot 10^6$ Pa absolute and about 950°C. This technique, sometimes called partial catalytic oxidation, is only applied to the conversion of natural gas, LPG and naphthas, particularly because, if heavier feeds are used, problems arise in the prior separation of sulfur derivatives that cannot be tolerated by the catalyst, as well as excessive deposits of tars and coke. Table 1.9 gives a number of typical gas compositions obtained in this type of process.

Using this technique, it is therefore possible to produce a low-methane content gas directly. To obtain pure hydrogen, however, the method requires the use of oxygen for combustion. This drawback disappears if the gas produced is intended for ammonia synthesis, in which, on the contrary, nitrogen is indispensable and is supplied by the air used for the conversion.

TABLE I.9
TYPICAL GAS COMPOSITIONS OBTAINED IN THE SBA/TOPSOE PROCESS (% vol.)

Type of combustion	With oxygen		With air (for NH ₃)	
Feedstock	Natural gas	Naphtha	Natural gas	Naphtha
Components :				
H ₂	68.3	62.6	52.9	48.0
CO	20.3	16.4	14.6	15.0
CO ₂	10.5	20.6	9.8	16.0
CH ₄	0.4	0.1	0.3	0.1
N ₂	0.2	0.1	22.0	20.3
A	0.3	0.2	0.4	0.6
Total	100.0	100.0	100.0	100.0

1.1.2.5 Hydrogen enrichment of the gas obtained by partial oxidation or steam reforming

As shown by Table 1.10, the effluents produced by partial oxidation and steam reforming exhibit high carbon monoxide contents. To produce hydrogen or ammonia, in order to raise the productivity of the installation, it is necessary to convert the CO with steam, still called the "shift conversion", by the reaction already discussed:



From the thermodynamic standpoint, the production of hydrogen is an exothermic

Conversion (item 2 of Table 1.3), which is favored at low temperature and in the presence of excess steam. Hence, even with an H_2/CO ratio of 3, it is necessary to operate above $250^\circ C$ for the conversion of carbon monoxide to be practically total.

TABLE 1.10
COMPOSITION OF EFFLUENTS PRODUCED
BY PARTIAL OXIDATION AND STEAM TREATMENT (% vol.)

Process	Partial oxidation				Steam reforming ⁽¹⁾ Natural gas
	Natural gas	Naphtha	Fuel oil	Coal ⁽²⁾	
Feedstock					
Components					
H_2	61	51	47	40	55-57
CO	35	45	47	35	12-15
CO_2	2-3	2-3	4	21	7-12
CH_4	—	—	1	2	—
N_2	0-1	0-1	—	2	22-24
Miscellaneous	2-0	2-0	1	—	4-2

(1) Fluidized bed.

(2) With post-combustion with air: gas for ammonia synthesis.

At these temperature levels, however, and especially with low H_2/CO ratios, the side reactions producing methane and carbon also develop substantially. To minimize their effects, the catalysts employed must be both active and selective. This double requirement raises a number of difficulties, which are circumvented in practice by carrying out the conversion of carbon monoxide in two steps, with intermediate cooling and possibly the injection of additional water at the inlet to the second stage:

- (a) The first reaction, at high temperature, prevents the production of coke.
- (b) The second, at low temperature, serves to intensify the conversion of CO and to reduce its content in the final dry gas to 0.05 to 0.1 per cent volume.

High-temperature conversion employs catalysts based on iron oxides (80 to 95 per cent weight) and chromium (5 to 10 per cent weight) which can withstand the presence of small amounts of sulfur products without an excessive loss of activity. They operate between 300 and $450^\circ C$, and as high as $550^\circ C$, with volume hourly space velocities of 300 to 3000 h^{-1} , and lead to residual CO contents of 1 to 2 per cent volume.

Certain catalytic systems based on the use of cobalt and molybdenum offer good resistance to sulfur. On the other hand, they cannot guarantee advanced conversion of carbon monoxide, of which a few per cent remain in the effluent obtained. Their value resides in the simplification of the purification schemes for effluents produced by the partial oxidation of sulfur-containing feeds. This is because they do not require prior removal of hydrogen sulfide, which can be removed subsequently in a single acid gas separation.

The exothermicity of the reaction results in a temperature increase of about $3^\circ C$ per cent CO converted, for $H_2O/$ feed gas ratios of 2 to 4, at pressures of 2 to $2.5 \cdot 10^6\text{ Pa}$ absolute. Since a given catalyst bed cannot withstand total temperature increases of

more than 100°C without the risk of reversing the equilibrium and rapid catalyst deterioration, multi-stage reactors must be provided if the initial CO content is high. Reactors in which the advance is limited, with intermediate cooling by water injection.

Low-temperature conversion takes place in the presence of catalysts consisting of oxides of copper (15 or 30 per cent weight) and zinc (30 per cent weight), deposited on alumina, operating around 200 to 250°C, with VHSV (Volume Hourly Space Velocity) of 2000 to 5000 h⁻¹. These catalyst systems, whose activity is proportional to the copper content, are highly sensitive to impurities, especially sulfur and halogenated compounds. Hence they cannot be used as a relay for cobalt and molybdenum based high-temperature conversion catalysts. Moreover, they are often preceded by protective masses of supported zinc oxide. After use, they are in a reduced, very pyrophoric form, which requires special precautions in handling. Low-temperature conversion is unnecessary if final purification is carried out by a PSA cycle (see Section 1.1.1.2).

Table 1.11 gives data on two cases of operation for the conversion of CO with steam.

TABLE 1.11
CATALYTIC CONVERSION OF CARBON MONOXIDE WITH STEAM

Composition and conditions	Case 1		Case 2	
	First stage	Second stage	First stage	Second stage
Feedstock (% vol.)				
CO	17.0	2.0	11.70	2.00
CO ₂	6.3	18.3	10.90	18.15
H ₂	72.4	75.9	76.15	78.75
CH ₄	4.3	3.8	1.25	1.10
H ₂ O/dry gas	0.55	0.35	1.6	—
Inlet temperature (°C)	290	290	375	300
Outlet temperature (°C)	390	300	—	310
Pressure (10 ⁶ Pa absolute)	0.2	0.2	1.1	1.1
Products (% vol.)				
CO	2.0	0.8	2.00	0.3
CO ₂	48.3	18.4	18.15	19.5
H ₂	75.9	76.9	78.75	79.1
CH ₄	3.8	3.9	1.10	1.1
H ₂ O dry gas	0.35	0.33	—	—

1.1.2.6 Hydrogen purification

In a conventional flow sheet, at the exit of low-temperature conversion, hydrogen meeting the standard commercial specifications (average 97 per cent volume) can only be obtained by means of supplementary purification treatments, including the successive removal of the following products:

- (a) Moisture, by condensation, passage on a molecular sieve, or quenching.
- (b) Acid gases, particularly carbon dioxide, whose content in the effluent reaches 15

to 20 per cent volume, and possibly hydrogen sulfide evolved by the partial oxidation of non-desulfurized liquid feeds or coal gasification, and present in about 1 to 2 per cent volume in conventional conversion schemes only.

- (c) Carbon monoxide, normally present in small amounts, less than 1 per cent.
- (d) Methane and nitrogen: from traces to a few per cent.

A. Acid gas elimination

Depending on the raw material concerned and the controlled oxidation method employed, and also according to the type of catalyst used for the conversion of CO with steam, acid gas elimination exhibits three different aspects:

- (a) Separation of carbon dioxide only: this concerns steam reforming effluents.
- (b) Two-step separation, before and after CO conversion with steam, beginning with the separation of hydrogen sulfide and all or part of the CO₂, and followed by that of carbon dioxide alone: this case applies to partial oxidation or gasification, and steam conversion catalysts based on iron and chromium oxides.
- (c) Joint separation of hydrogen sulfide and CO₂, after conversion with steam on cobalt and molybdenum catalysts: this concerns partial oxidation and gasification.

The combined presence of H₂S and CO₂ in a given effluent usually leads to a joint removal operation. This type of treatment stems from the fact that, among the most economical alternatives available, the liquid absorption of acid constituents is the most widespread, and also because, at the technical level, the type of product to be extracted, apart from its acidic character, has little effect on the behavior of the solvent employed. Hence, although, as a rule, hydrogen sulfide is absorbed faster than CO₂, the separation of the different acid gases is more or less simultaneous. For reasons of environmental protection, this scheme must also be supplemented by the direct conversion of hydrogen sulfide to sulfur.

a. Conventional industrial methods of acid gas separation and treatment

The main techniques developed or industrialized in this area chiefly concern absorption by means of solvents.

Reversible chemical absorption

The acid gases extracted are released by raising the temperature and lowering the pressure. The basic solutions employed to achieve this include the following:

- (a) Alkanolamines: monoethanolamine with or without corrosion inhibitor (MEA, Union Carbide Ucar process), diethanolamine (DEA, SNEA/DEA process), triethanolamine (TEA), methyldiethanolamine (MDEA, Dow, Shell and BASF processes), diisopropylamine (DIPA, Shell process), and diglycolamine (DGA, Econamine Fluor process).
- (b) Alkaline salts: potassium or sodium carbonates, with or without amines, Hot-Pot, modified Benfield and Hipure processes. Catacarb (Eikmeyer), Giammarco-Vetrocote (CO₂), Alkacid-M and Alkacid-Dik (BASF), Carsol (Carbochimie), Seaboard, Vacuum Carbonate, etc., tripotassium phosphate.
- (c) Ammonia: aqueous solutions, Collin, Diamox processes, etc.

Physical absorption by means of solvents

Physical absorption can be achieved by solvents whose effectiveness depends on the partial pressure of the acid gases. The absorption of these feedstock components varies directly with their partial pressure. They are then liberated, and the solvent regenerated by expansion. The systems employed make use of the following main solvents: dimethyl ether of polyethylene glycol (Norton Selexol process), methanol (Lurgi Rectisol process), N-methylpyrrolidone (Purisol process), propylene carbonate (Fluor-Solvent process), polyethylene glycol/methylisopropyl ether (Estasolvant process), and Catasol technology (Eikmeyer).

Combined absorption

The use of solvent mixtures helps to combine the chemical and physical effects of absorption. This mainly involves the following systems: methanol and ethanolamines (Lurgi Amisol processes), sulfolane and diisopropylamine (Shell Sulfinol process).

The other methods that can be employed for acid gas separation are those already discussed for the purification of hydrogenated effluents, but applied to the removal of compounds often present in high contents:

- (a) Adsorption on solid beds: these techniques include the use of boxes containing iron sponge (wood chips impregnated with ferric oxide), zinc oxide, activated charcoal, and especially molecular sieves initially developed by Haines, and now by Union Carbide (Hysiv-PSA processes, see Section 1.1.1.2), which proposes a flow sheet in which its technology substitutes for both low-temperature conversion and chemical absorption.
- (b) Permeation (see Section 1.1.1.3).
- (c) Cryogenic separation (see Section 1.1.1.4).

The conversion of hydrogen sulfide to elemental sulfur is essentially designed to minimize atmospheric pollution. Several processes are available, and the main ones belong to one of the following two categories:

- (a) Liquid phase H_2S conversion techniques, in the presence of redox systems: these include the Stretford process, which employs an alkaline solvent containing sodium carbonate, anthraquinone disulfonic acid as redox agent, and sodium metavanadate as activator. The Takahax process, industrialized in Japan, operates with an aqueous solution of sodium carbonate containing naphthoquinone sodium sulfonate. The Thylox process, formerly widely used in the United States, but currently abandoned due to the toxicity of the redox agents concerned, operates in the presence of sodium carbonate and sodium thioarsenite as activator. Finally, the Giammarco-Vetrocoke sulfur process, which is closely comparable to the previous technique, employs solutions of arsenites and arseniates.
- (b) The wet method Claus process: this essentially involves two technologies that have not yet been industrialized: the Townsend process, which uses triethylene glycol as the reaction medium, and the Fugapol process, developed by IFP (*Institut Français du Pétrole*) and implementing the Claus reaction of sulfur dioxide, obtained by the combustion of part of the sulfur produced, with hydrogen

sulfide, in the liquid phase around 130°C, in the presence of polyethylene glycol as solvent and a catalyst.

Various other techniques have also been developed, particularly the Ferrox, Manchester, Perox, Lacy-Keller, Lo-Cat, Freeport sulfur processes, etc.

b. Technological aspects of acid gas separation by absorption

The most widespread processes in chemical absorption are the following:

Processes using alkanolamines

Techniques of this type guarantee rapid, nearly complete absorption, not only of hydrogen sulfide, but also of CO₂, alone or mixed with H₂S. They are unaffected by variations in partial pressure of the acid components, and are accordingly better adapted to installations operating at low pressure and requiring the separation of carbon dioxide up to very low contents.

The presence of sulfur oxides and of CS₂, COS, HCN, organic acids, nitrogen-containing bases, etc., is detrimental to the economical use of absorption by alkanolamines. This is because, in the same way as carbon dioxide and hydrogen sulfide, the solvent also reacts with the impurities. However, whereas the complexes obtained with H₂S or CO₂ are decomposed by simple heating followed by stripping, an additional chemical treatment is required in the latter case. This reclaiming operation is carried out with a compound such as sodium carbonate (Na₂CO₃). Other problems also affect this type of treatment, chiefly corrosion, foaming, solvent losses and, at the design level, high flow rates, large steam requirements, heat exchanges, etc.

Figure 1.9 shows a flow sheet using MEA.

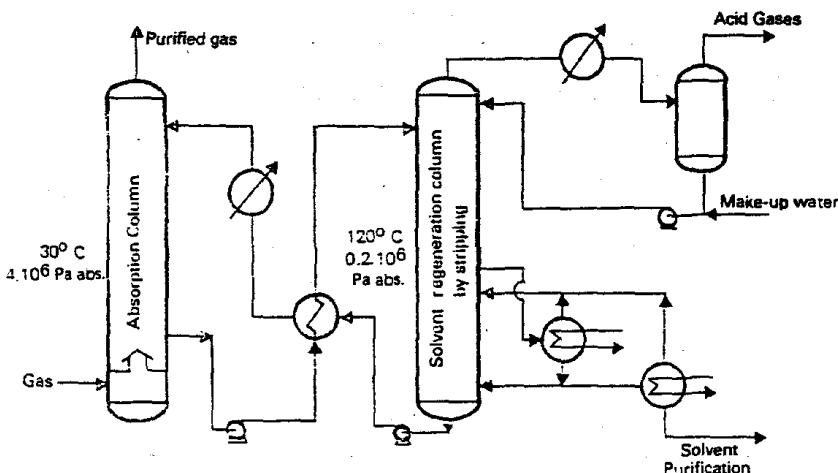


Fig. 1.9. Base scheme of an absorption unit (ethanolamine).

Processes employing alkaline salts

These normally operate with an aqueous solution of a potassium or sodium salt buffered to pH from 9 to 11. Two categories of processes can be distinguished, depending on the operating conditions:

- Some processes operate only at ambient temperature, 20 to 40°C, and serve to separate hydrogen sulfide from the CO₂, which is only partly absorbed.
- Others can withstand temperatures close to those required for thermal reclaiming of the solvents (105 to 115°C, 2 . 10⁶ Pa absolute): these techniques are suitable for treating effluents under pressure.

Processes employing alkaline salts, especially potassium carbonate solutions, are strongly influenced in their operation and their performance by the partial pressure of the acid gases. Hence they are unsuitable at low or high pressures for the absorption of a low-content feedstock component. It is preferable to combine high pressure with a sufficient CO₂ concentration.

Techniques based on the use of alkaline salts, carbonate solution in particular, offer the following advantages:

- Limited solvent degradation.
- Low losses.
- Moderate steam requirements.

The presence of impurities such as COS and CS₂ does not affect the absorbent medium. On the other hand, corrosion (especially electrolytic, or by certain by-products), erosion, due to solid particles, and foaming may occur.

In principle, physical absorption is inapplicable to feedstocks available at very low pressures, because the amount of gas absorbed is proportional to the partial pressure of the gas. For the same reason, it is also necessary for the concentration of the component to be separated to be high, to make the operation economically interesting.

These operating conditions constitute a decisive advantage due to the reduction in the rate of solvent, and hence of its recirculation, and accordingly of capital investment and operating costs.

On the whole, corrosion and foaming tend to be absent. Solvent losses are also usually low because of their normally high boiling points and their resistance to impurities such as COS, CS₂ and mercaptans. Care is taken to avoid the presence of heavy components such as hydrocarbons, which are liable to build up in recycle streams. Solvent reclaiming by simple expansion also helps to minimize energy expenditures. If the applicable specifications are very stringent, this operation must be performed by stripping (reboiling, steam or inert gas).

Figure 1.10 shows the flow sheet of a Selexol type installation.

c. Choice of acid gas separation method

To remove the acid gases from an effluent, the different potential situations can be summarized by four cases, depending on the final goal:

- Separation of carbon dioxide.
- Separation of hydrogen sulfide.

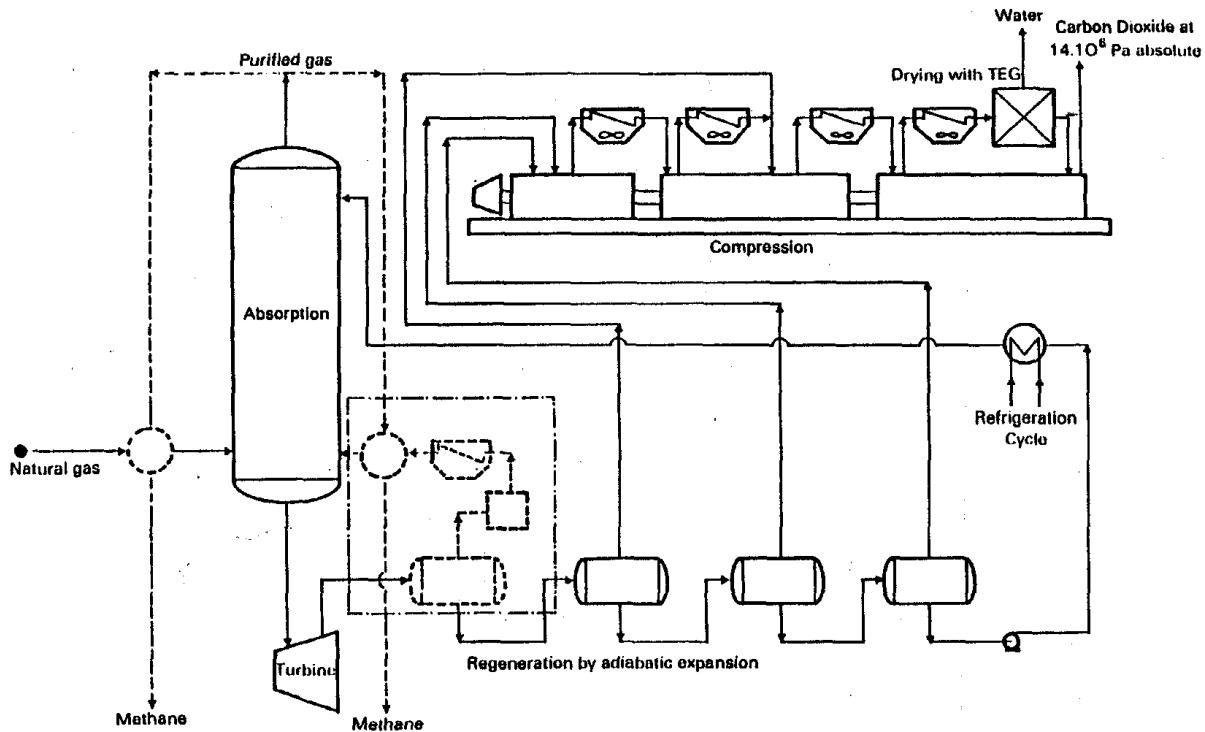


Fig. 1.10. Base scheme for the absorption of CO₂ by a physical method (Selexol process) and its compression, from a natural gas (content > 10% vol).

- (c) Simultaneous separation of carbon dioxide and hydrogen sulfide.
- (d) Selective separation of hydrogen sulfide.

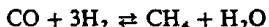
The first and third alternatives are the ones that appear most frequently in hydrogen purification schemes.

In both situations, the procedure to be followed in selecting the ideal separation process first consists in referring to the graphs in (a) and (b) of Fig. 1.11, which offer a preliminary selection according to the partial pressure of the acid gases in the feed, and the residual content of these gases desired in the effluent. A final selection can then be made on the basis of the feedstock composition, solvent circulation rate, and steam consumption during reclaiming.

B. Final purification

The foregoing treatments do not totally remove traces of CO, which can be removed by one of the following operations:

- (a) Absorption in a cuprous liquor (cuprous ammonium acetate or cuprous ammonium formate) or in cold methanol. The Tenneco Cosorb process uses copper aluminum tetrachloride (see Section 1.2).
- (b) Methanation, which achieves the following conversion:



This is practically total above 300°C and, even at atmospheric pressure, lowers the residual CO content to less than 20 ppm and to a few ppm under pressure. It takes place in the presence of nickel base catalysts deposited on alumina and doped with chromium oxide. The exothermicity of the reaction (Δr from 70 to 80°C/per cent CO converted) requires operation with two catalyst beds and intermediate effluent cooling.

- (c) Catalytic oxidation of CO to CO₂: this method, which lacks selectivity, is not widely used.

1.1.2.7 Economic data

Tables 1.12a and 1.12b offer a variety of economic data concerning the production of hydrogen from different feedstocks, as well as that of synthesis gas in an H₂/CO molar ratio ranging from 1:1 to 3:1. In fact, the techniques employed to produce pure hydrogen can be exploited to adapt the composition of H₂/CO gas mixtures, so as to use them in specific conversions like those giving rise to certain alcohols (see Sections 9.3 and 9.4) by olefin hydroformylation. Table 1.12c gives details about processes for the elimination of acid gases obtained starting with natural gas and coal.

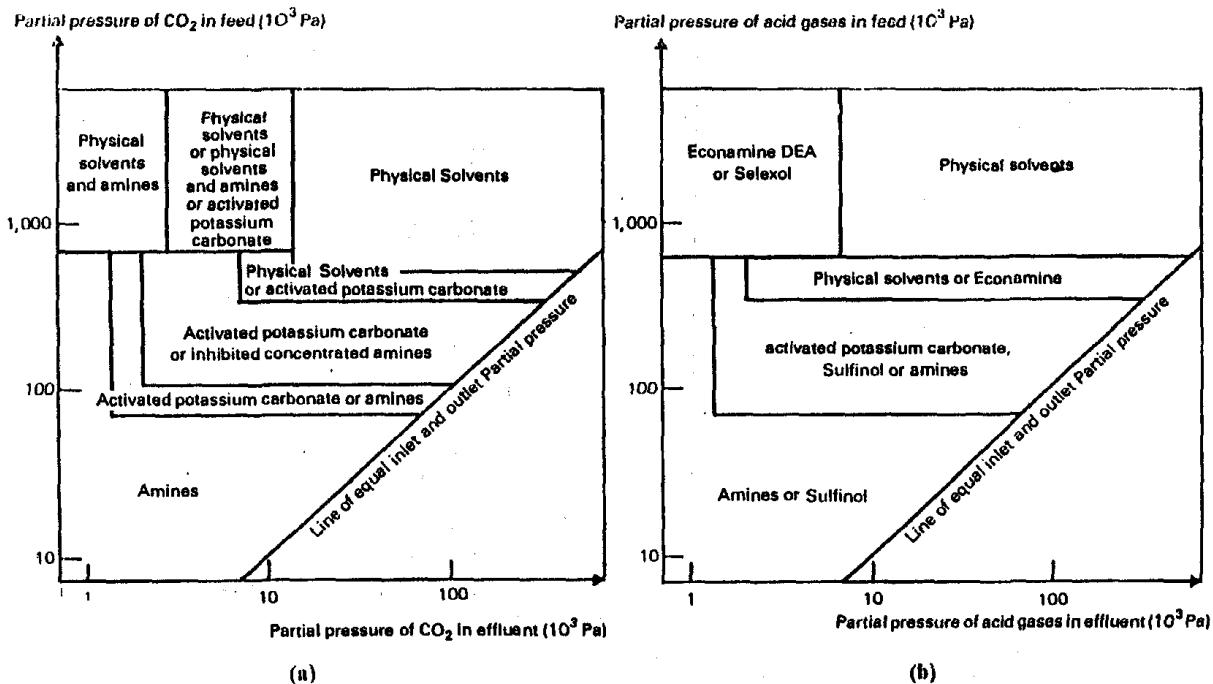


Fig. 1.11. Choice of acid gas separation techniques.

- Separation of carbon dioxide.
- Simultaneous separation of hydrogen sulfide and carbon dioxide (without other impurities).

TABLE I.12a
HYDROGEN PRODUCTION AT 97 TO 98 % VOLUME, ECONOMIC DATA
(France conditions mid-1986)

Raw material	Natural gas		Naphtha	Vacuum residue		Coal
Process	Steam reforming		Steam reforming	Partial oxidation		Gasification ⁽¹⁾
Capacity (10 ³ m ³ /day)	1,000	2,000	1,000	1,000	2,000	2,000
Battery limits investments (10 ⁶ US\$)	25	38	28	58	100	190
Consumption per 1,000 m ³ of pure hydrogen						
Raw materials						
Natural gas (10 ⁶ kJ)	17 ⁽²⁾		—	—	—	—
Naphtha (l)	—	—	0.22	—	—	—
Vacuum residue (l)	—	—	—	0.40	—	—
Coal (t)	—	—	—	—	—	0.73
By-products						
Sulfur (kg)	—	—	—	24	—	22
Utilities						
Fuel (10 ⁶ kJ)	—	—	6.0	—	—	—
HP steam (t)	(—) 0.9	—	(—) 0.1	—	—	0.3
MP steam (t)	0.9	—	—	—	—	—
LP steam (t)	1.2	—	—	—	—	(—) 0.3
Electricity (kWh)	30	—	45	50	—	—
Cooling water (m ³)	30	—	25	25	—	—
Process water (m ³)	1	—	1	1.5	—	2
Catalysts and chemicals (US\$)	0.9	—	0.9	0.4	—	0.9
Labor (Operators per shift)	4	—	4	8	—	20

(1) Koppers/Totzek type.

(2) Including $\approx 11 \times 10^6$ kJ as feed.

TABLE I.12b
PRODUCTION OF H₂/CO SYNTHESIS GAS WITHOUT EXTERNAL CO₂ INPUT. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 2 · 10⁶ m³/day

Raw material.....	Natural gas			Naphtha		Vacuum residue			Coal		
Process.....	Steam reforming			Steam reforming		Partial oxidation			Gasification ⁽¹⁾		
H ₂ /CO mole ratio	1/1	2/1	3/1	1/1	2/1	1/1	2/1	3/1	1/1	2/1	3/1
Battery limits investments (10 ⁶ US\$)...	120	80	40	105	70	75	80	85	120	130	135
Consumption per 1,000 m ³											
H ₂ /CO mixture											
Raw materials											
Natural gas (10 ⁶ kJ).....	20.5	13.5	10.5	—	—	—	—	—	—	—	—
Naphtha (l)	—	—	—	0.32	0.22	—	—	—	—	—	—
Vacuum residue (l).....	—	—	—	—	—	0.36	0.36	0.36	—	—	—
Coal (t).....	—	—	—	—	—	—	—	—	0.83	0.87	0.92
By-products											
Sulfur (kg)	—	—	—	—	—	13	13	13	30	30	30
Utilities											
Fuel (10 ⁶ kJ) ⁽²⁾	4.0	7.0	8.5	5.0	8.0	—	—	—	—	—	—
Steam (t)	(—) 0.4	(—) 0.3	(—) 0.6	—	—	—	0.6	0.8	—	—	—
Electricity (kWh).....	70	45	35	65	45	30	35	40	25	25	25
Cooling water (m ³).....	130	85	65	135	90	70	80	85	—	—	—
Process water (m ³).....	—	—	—	—	—	2.5	3.0	3.5	0.5	1.0	1.5
Boiler feed water (m ³)	1.5	1	0.5	1	1	0.5	0.5	0.5	—	—	—
Catalysts and chemicals (US\$)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Labor (Operators per shift).....	8	6	5	8	3	9	9	9	20	20	20

(1) Koppers/Totzek type.

(2) Natural gas.

TABLE I.12c
PRODUCTION OF SYNTHESIS GAS, ELIMINATION OF ACID GASES, ECONOMIC DATA
(France conditions, mid-1986)

Process	Chemical absorption		Physical absorption		Antipollution treatment
	Alkanolamines	Alkaline salts	Methanol		
Solvent	SNEA/DEA	Benfield K_2CO_3	Lurgi/Rectisol	Claus and tail gas treatment	—
Typical technology					
Gas source	Natural gas	Coal	Coal	Coal	Coal
Material balance					
Feedstock (10^6 m ³ /day)	5.0	5.0	5.0	—	0.15
CO ₂ content (% vol)	20	30	30	—	62
H ₂ S content (% vol)	—	0.5	1	—	35
Pressure (10^6 Pa absolute)	2.5	2.8	5.5	—	—
Acid gas (10^6 m ³ /day)	1.1	1.6	0.15	—	—
Synthesis gas (10^6 m ³ /day)	4.0	3.5	3.45	—	—
CO ₂ content (% vol)	0.05	0.015	3	—	—
H ₂ S content (% vol)	—	—	6	—	—
Miscellaneous (10^6 m ³ /day)	—	—	1.55	Sulfur	—
Battery limits investments (10^6 US\$)	20	18	50	—	9
Consumption per 1,000 m³ of feedstock					
Utilities					
HP steam (t)	0.8	0.5	0.2	—	—
LP steam (t)	—	—	—	(—)1.2	—
Electricity (kWh)	18	20	7	100	0.7
Fuel (10^6 kJ)	—	—	—	—	—
Cooling water (m ³)	—	5	5	—	—
Solvent (US\$)	0.2	0.9	6	—	—
Labor (Operators per shift)	3	3	3	—	2

1.1.3 Water decomposition techniques

Two principal methods are available for the production of hydrogen in significant quantities by the decomposition of water:

- (a) Electrolysis, requiring the generation of electricity.
- (b) Thermochemistry, which uses a combination of reactions forming a cycle, whose balance yields hydrogen separated from oxygen.

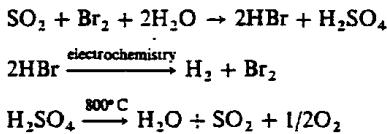
1.1.3.1 Electrolysis

This process has been known for many decades, but has been employed chiefly to produce high-purity hydrogen for the food industry. Today, the generation of electricity of nuclear and hydroelectric origin, and the existence of surplus capacity available in off-peak hours, have revived interest in this process for the massive production of hydrogen (Aswan plant in Egypt). The alternatives available include the following:

- (a) Electrolysis in a potash solution: current technology subject to improvement ($t = 120$ to 180°C , $P = 3 \cdot 10^6$ Pa absolute, high-performance diaphragm etc.).
- (b) Electrolysis which uses a solid polymer as electrolyte in a filter press cell.
- (c) Very-high-temperature (900°C) gas-phase electrolysis employing a doped zirconia electrolyte.

1.1.3.2 Thermochemistry

Thermochemistry theoretically allows the production of the energy required for the dissociation of water at an industrially acceptable temperature, by implementing a series of chemical reactions. Some of them, which are highly endothermic, are performed by heat exchange using a heat transfer fluid, helium, which is employed to cool high-temperature reactors. On the whole, they constitute a thermochemical cycle. Among the best known are those of *Westinghouse*, *General Atomic*, *Hitachi*, *Siemens* etc., and the hybrid Mark 13 cycle designed by the *EEC / Economic European Community*, which is both chemical and electrochemical, and which relies on the following sequence of reactions:



Such systems present the drawback of incurring high material and energy losses, associated with the irreversibilities encountered, particularly in heat exchanges, chemical reactions and separations.

1.1.4 Hydrogen production and uses

Table 1.13 shows the main uses of hydrogen in the United States in 1985.

TABLE 1.13
HYDROGEN SOURCES AND USES IN THE UNITED STATES IN 1985

Captive hydrogen Sources	Supply (10 ⁶ m ³ /day)	Uses (%)					Metals	Total
		Refining	Chemicals ⁽¹⁾	Hydrogenation of oils	Metals	Total		
Steam reforming ..	54.9	96.3	3.0	0.5	0.2	100.0		
Partial oxidation ..	2.7	100.0	—	—	—	100.0		
Cryogenic upgrading of off-gas	2.5	100.0	—	—	—	100.0		
Miscellaneous (Water electrolysis, ammonia dissociation..)	1.3	98.3	—	0.3	1.4	100.0		
Total	61.4⁽¹⁾	96.6	2.7	0.5	0.2	100.0		

(1) Excluding ammonia and methanol plants.

By product hydrogen Sources	Supply (10 ⁶ m ³ /day)	Uses (%)					Sales	Total
		Fuel	Hydrochloric acid	Ammonia	Miscellaneous	Sales		
Chlorine-sodium hydroxide plants	10.4	35.4	9.4	35.0	3.4	16.8	100.0	

	Supply (10 ⁶ m ³ /day)	Sources (%)					Total
		Steam reforming	Steam cracking	Refining	Cl ₂ -NaOH plants	Miscellaneous	
Merchant hydrogen	4.5	60.9	3.0	4.2	31.6	0.3	100.0

1.2 CARBON MONOXIDE

Most of the carbon monoxide (bp_{1.013} = 191.47°C, d at boiling point 0.787) consumed in the world is used in the form of gas mixtures containing hydrogen in particular. Small amounts, less than about 3 per cent volume, are used as the purified product.

1.2.1 Sources and methods for obtaining carbon monoxide

Like hydrogen, carbon monoxide is mainly produced by steam reforming and partial oxidation of hydrocarbon or organic raw materials. However, it is also present in many industrial wastes from which it can be isolated (gases from blast furnaces, oxygen refining

of cast iron, coke ovens, by-product of the ferrous alloy, phosphorus, inorganic pigment and carbon black industries, of the production of aluminum by electrolysis, acetylene manufacture etc.).

Its applications, which are usually captive, in the form of synthesis gas, are discussed in the sections concerning the manufacture of the major petrochemical intermediates which it yields:

- (a) Methanol (see Section 1.3).
- (b) Oxo alcohols (see Sections 9.3.1.2 and 9.4.2).

However, other uses, including the production of phosgene, acrylates, acetic acid, certain oxo alcohols etc., require its use in purified form.

Among the separation techniques industrially implemented in this case are absorption and cryogenic separation. Adsorption according to the PSA process described above (see Section 1.1.1.2) can also be applied, but is only economically viable for feedstock CO contents under 40 per cent, or preferably 20 per cent. This gives an effluent whose carbon monoxide concentration does not exceed 60 or 80 per cent, although the yield of the operation is very high (over 99 per cent). Cryogenic treatment is necessary for higher purities.

1.2.2 Carbon monoxide manufacture by absorption (Tenneco process)

Carbon monoxide was initially separated by means of aqueous solutions of cuprous ammonium chloride by the formation of a complex according to the following reversible reaction:



Subsequently, to minimize corrosion and metallic copper deposits on the equipment walls, chlorine ions were superseded by those obtained from weaker organic acids (formic, acetic etc.) (*ICI process : Imperial Chemical Industries*).

Tenneco Chemicals, in its Cosorb process, proposed employing a 20 to 25 per cent mol solution of copper aluminium tetrachloride (CuAlCl_4) in toluene. This technology (Fig. 1.12), which minimizes corrosion and allows operation at lower pressure, is specific to the selective separation of carbon monoxide by the exothermic formation of a complex with the solvent. However, it requires intensive prior drying of the gas feedstock on molecular sieves, according to the "Temperature Swing Adsorption" (TSA) principle (see Section 1.1.1.2) to lower the moisture content to 1 or as low as 0.1 ppm volume. It thus avoids the violent formation of hydrochloric acid gas and the excessive consumption of CuAlCl_4 through irreversible reactions. This operation may be accompanied by CO_2 removal to achieve a residual content less than 50 ppm volume.

CO is extracted by countercurrent absorption in a column operating at about $2 \cdot 10^6$ Pa absolute, with a feedstock inlet temperature of about 40°C and effluent exit around 65°C . This is accompanied by the physical dissolution of small amounts of other constituents, including hydrogen, which are salted out by cooling and expansion of the extract at $0.5 \cdot 10^6$ Pa absolute. The complex obtained is then preheated to 100 to 105°C and sent to a regeneration column. In this column, operating at $0.15 \cdot 10^6$ Pa absolute, CO is liberated

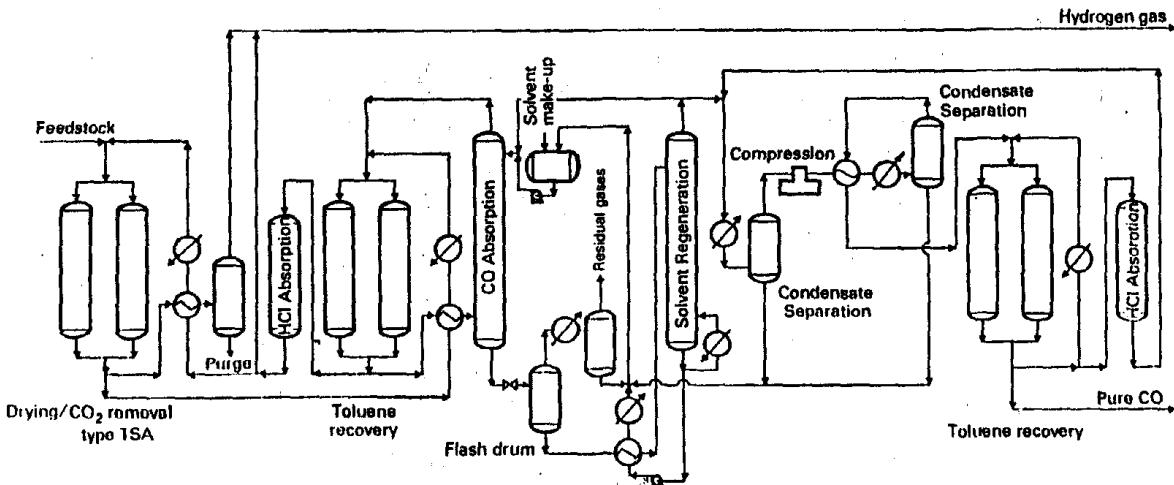


Fig. 1.1.2 Carbon monoxide manufacture. Tenneco's Cosorb process.

at the top by the effect of temperature elevation as well as stripping by reboiling of the toluene. This regenerated solvent which exits at the bottom is recycled to the absorption step.

The hydrogen-rich gas recovered at the top of the first column, together with the carbon monoxide leaving the second, carry over significant amounts of toluene. Most of this is recovered by cooling, compression and condensation, and traces are eliminated by solid adsorption. This yields carbon monoxide with a purity of over 99.5 per cent, containing less than 0.1 ppm of toluene, which can be removed by passage of the residual hydrochloric acid over ion exchange resins. This acid is a catalyst poison in certain applications, including acetic acid manufacture by the Monsanto process. In the unit itself, such treatments are provided on certain recycle streams to reduce acid corrosion. The yield of the operation is about 97 to 98 per cent volume.

1.2.3 Carbon monoxide manufacture by cryogenics

The main process licensors in this area are *Air Products*, *L'Air Liquide*, *Petrocarbon Development*, *Uhde*, and *Union Carbide*.

This operation can be conducted industrially by two principal methods:

- (a) Partial condensation of the feed components.
- (b) Scrubbing by liquefied gases, particularly methane.

1.2.3.1 Partial condensation (Fig. 1.13a)

In principle, this treatment, which applies to effluents available under pressure and previously dried, comprises the following operating phases:

- (a) Cooling of the feedstock by heat exchange with the products.
- (b) Partial condensation of certain components.
- (c) Gas/liquid separation.

These three steps are accompanied by a pressure drop. To minimize energy expenses and to improve effluent purity, they are supplemented by the following operations:

- (a) Gas expansion in a turbine with production of cold.
- (b) Partial vaporization by expansion of the liquefied products.
- (c) Separation of the components of the residual liquid phase by distillation in one or two steps, depending on the feedstock composition and the desired purity, with nitrogen and carbon monoxide obtained as distillates, and methane as bottom product.

In practice, to recover the CO contained in a feedstock produced, for instance, by steam reforming of natural gas, and which is hence virtually free of nitrogen and available at $2 \cdot 10^6$ Pa absolute, the installation has the following basic flow sheet.

The process begins by cyclic drying on molecular sieves to lower the moisture content to less than 1 ppm. This is followed by cooling at about -185°C by heat exchange with the cold effluents purified in a series of two plate exchangers and passage through the reboiler of the intermediate CO distillation column. Gas/liquid separation achieves the production

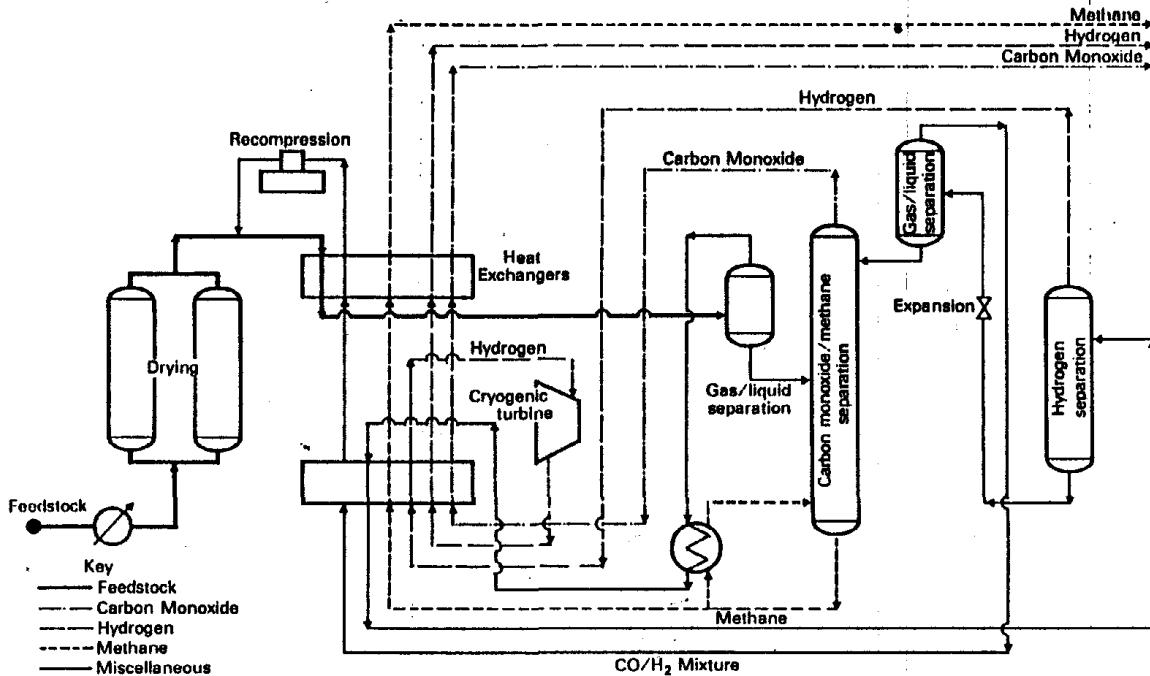


Fig. 1.13 a. Cryogenic manufacture of carbon monoxide. Partial condensation.

of hydrogen in 96 per cent volume in gaseous form, whose refrigeration capacity is exploited in heat exchanges with the feedstock and by intermediate expansion at $1 \cdot 10^6$ Pa absolute in a turbine. This operation lowers the hydrogen temperature from -110 to about -190°C . The liquid phase is also expanded at $0.25 \cdot 10^6$ Pa absolute, giving rise to partial vaporization. The gaseous fraction is exchanged with the feed, and then recompressed and recycled. The liquid fraction is refluxed to the CO distillation column which operates between -150 and -185°C . It produces carbon monoxide with a purity of 99 per cent volume at the top and methane at the bottom. The refrigeration capacity of these two effluents is recovered in plate exchangers.

1.2.3.2 Scrubbing with liquid methane (Fig. 1.13b)

This type of unit features the main steps encountered in partial condensation. The available gas mixture, previously dried on molecular sieves, is cooled to around -120°C by heat exchange in a series of plate-exchangers operating in countercurrent flow on the cold purified products, and is then introduced at the bottom of a tray column with a downflow of liquid methane. The operation takes place at a pressure of about $1.6 \cdot 10^6$ Pa absolute. It yields hydrogen with a purity better than 98.5 per cent volume, and which contains less than 10 ppm of CO. After expansion and partial vaporization, the extract feeds a distillation column operating at $0.2 \cdot 10^6$ Pa absolute, which separates the carbon monoxide at the top with a yield of at least 80 per cent at a purity over 99 per cent volume, and liquid methane at the bottom. This methane provides reflux to the scrubbing column and partly to the feed cooling unit.

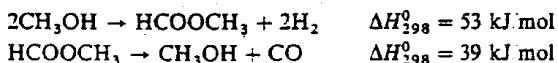
In some cases, a second intermediate liquid methane scrubbing unit is added, at $0.3 \cdot 10^6$ Pa absolute, capable of yielding 99 per cent pure CO directly at the top of the column.

A refrigeration cycle with carbon monoxide, operating between 0.2 and $1.7 \cdot 10^6$ Pa absolute, contributes the refrigeration required for the installation. It includes the expansion of a large fraction of the cycle gases in a cryogenic turbine.

For some uses of by-product hydrogen, such as ammonia manufacture in particular, it is essential to avoid the presence of excessive amounts of residual methane. This is replaced by one of the synthesis reactants, with scrubbing by liquid nitrogen (see Section 1.3.1.1).

1.2.4 Other methods for manufacturing carbon monoxide

Among the various other industrial methods, particularly chemical, for producing pure carbon monoxide, is the process recently developed by *Mitsubishi Gas Chemical*. It is based on the two-step conversion of methanol to CO by the following reaction mechanism:



The methanol is dehydrogenated in the gas phase around 190°C , at atmospheric pressure, in the presence of a copper-based catalyst on a support, promoted by other metals such as Zr, Zn, Al etc.

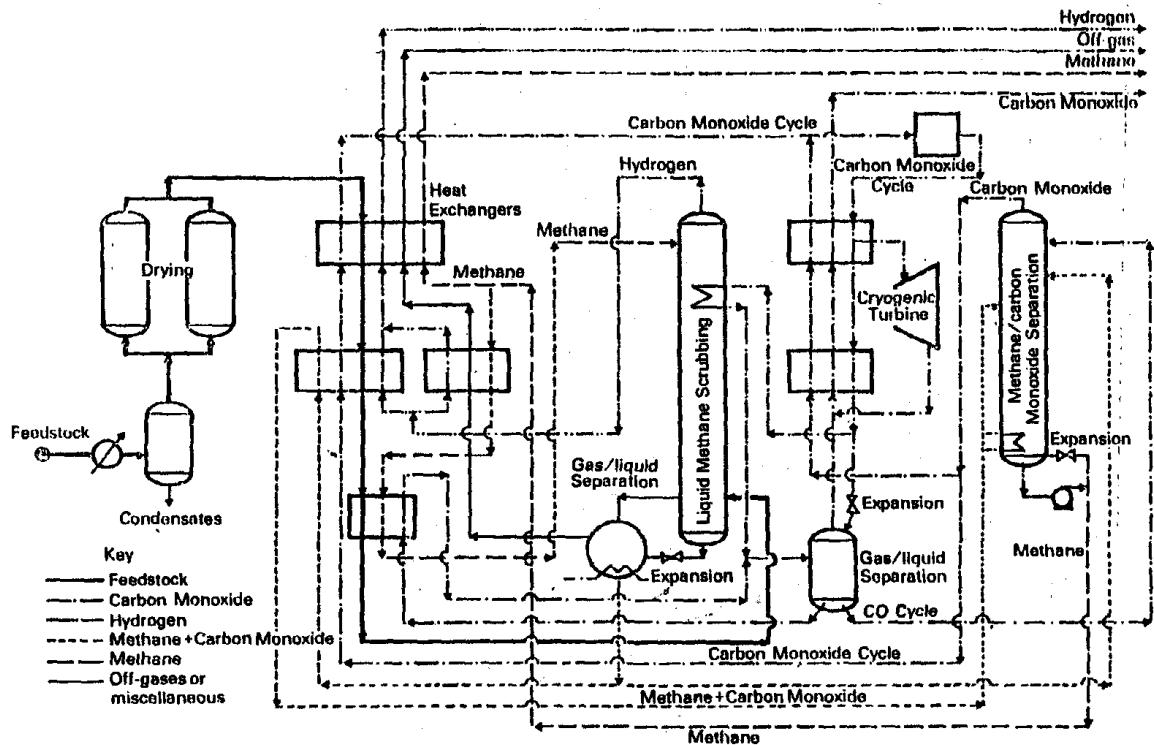


Fig. 1.13b. Cryogenic production of carbon monoxide. Scrubbing with liquid methane.

Once-through conversion is as high as 50 per cent, and selectivity is 90 mole per cent. The formate is also pyrolysed in the gas phase, in the presence of an earth alkali oxide, activated charcoal or zeolite catalyst. The total yield of the operation is about 75 mole per cent.

1.2.5 Economic data

Table 1.14 lists some economic data on the separation of carbon monoxide by absorption and cryogenics.

TABLE I.14
CARBON MONOXIDE PRODUCTION: ECONOMIC DATA
(France conditions, mid-1986)

Process	Absorption	Cryogenics
Typical technology	Cosorb/Tenneco	L'Air Liquide
Material balance (m ³ /h)		
Feedstock ⁽¹⁾	20.150	20.220
Carbon monoxide	5.000	5.000
Hydrogen gas	15.040	14.550
Fuel	100	51.0
Purity (% vol.)		
Carbon monoxide	99.7	99.0
Hydrogen	97.5 ⁽²⁾	98.5
Battery limits investments (10 ⁶ US\$)	11 ⁽²⁾	6
Consumption per 1,000 m ³ of CO		
Steam (t)	2.0	—
Electricity (kWh)	290	550
Cooling water (m ³)	65	15
Chemicals and catalysts (US\$)	5	2
Labor (Operators per shift)	2	2

(1) Feedstock composition (% vol.): H₂ = 73, CO = 24.5, CH₄ = 1.5, CO₂ = 2, N₂ = 2, H₂O = 1.

(2) Including methanation of residual CO and CO₂.

1.2.6 Uses and producers

The average commercial specifications of carbon monoxide, particularly for chemical use, are given in Table 1.15.

Table 1.16 shows the main applications of pure carbon monoxide in Western Europe, the United States and Japan, with estimated consumptions for these three geographic areas.

TABLE 1.15
AVERAGE COMMERCIAL SPECIFICATIONS OF CARBON MONOXIDE

Purity (% Wt) min.	99.5	98.5
CO ₂ (ppm)	200	2,000
O ₂ (ppm)	20	20
N ₂ (ppm)	80	80
Dew-point (°C)	-60	-35

TABLE 1.16
USES OF PURE CARBON MONOXIDE IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Acetic acid	40	30	55
Phosgene ⁽¹⁾	60	70	45
Total	100	100	100
Consumption ⁽²⁾ (10 ³ t/year)	400	710	130

(1) Toluenediisocyanate, polymethylenepolyphenylisocyanate, polycarbonate resins.

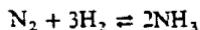
(2) Estimated from acetic acid and phosgene production statistics.

1.3 AMMONIA SYNTHESIS

Ammonia (mp = -77°C, bp_{1.013} = -33.3°C, d₄⁻²⁰ = 0.6650)⁽⁴⁾ recovered during the water scrubbing of raw coke oven gases accounts for only a very small fraction in comparison with ammonia manufactured from its elements.

1.3.1 Preparation of synthesis gas

It is necessary to prepare the nitrogen hydrogen mixture corresponding to the stoichiometry of the reaction:



This can be achieved after a series of operations employing partial oxidation or the gasification of heavy hydrocarbon fractions or coal or the steam reforming of methane or naphtha.

(4) Specific gravity, 4/39.2.

1.3.1.1 Schemes comprising partial oxidation with oxygen

The sequence of operations concerned in this case is as follows (Fig. 1.14a):

- Air distillation.
- Partial oxidation of the hydrocarbon by oxygen.
- Removal of carbon and recovery of heat.
- Possible removal of H_2S and conversion to sulfur.
- Catalytic conversion of CO by steam (shift conversion).
- CO_2 removal.
- CO removal by liquid nitrogen which introduces the nitrogen required to form the mixture $\text{N}_2 + 3\text{H}_2$.

On the whole, these treatments are not different from those used to produce hydrogen. However, since an excessive amount of inert gases (methane, argon, helium) cannot be tolerated in the synthesis gas, the operating conditions of partial oxidation are set so that the methane content is low (see Fig. 1.5). Moreover, scrubbing with liquid nitrogen must be carried out at a temperature at which the vapor pressure of nitrogen is such that the scrubbed gas removes the necessary amount of gaseous nitrogen, so that:

$$\frac{\text{N}_2}{\text{CO} + \text{H}_2} = \frac{1}{3}$$

This operation (Fig. 1.15), which is specific to the use of hydrogen produced for ammonia synthesis, is similar in principle to the one used to separate carbon monoxide by scrubbing with liquid methane (see Section 1.2.3.2). Its value is therefore twofold:

- To avoid the presence of residual hydrocarbons, which act as diluents, in the hydrogen obtained, by replacing them by nitrogen, which is a reactant. The effluent produced thus contains less than 1 ppm volume of CO and CH_4 . On the other hand, the nitrogen content is at least 2 to 8 per cent volume, which normally precludes any other application.
- To adjust the composition of ammonia synthesis gas according to the needs of the reaction.

Among the adaptations made to the liquid methane scrubbing scheme is the replacement of the carbon monoxide refrigeration cycle by a similar system operating with nitrogen.

1.3.1.2 Schemes based on hydrocarbon steam reforming

If a conversion of this type is carried out, the series of operating sequences is as follows (diagram b in Fig. 1.14):

- Steam treatment (primary reforming).
- Conversion of residual methane by air, which contributes the nitrogen required (secondary reforming or post-combustion).
- Catalytic conversion of CO by steam (shift conversion).
- CO_2 removal.
- CO removal by treatment with cuprous derivatives (Cosorb process for example) or with methanol; methanation can also be resorted to if one can tolerate the

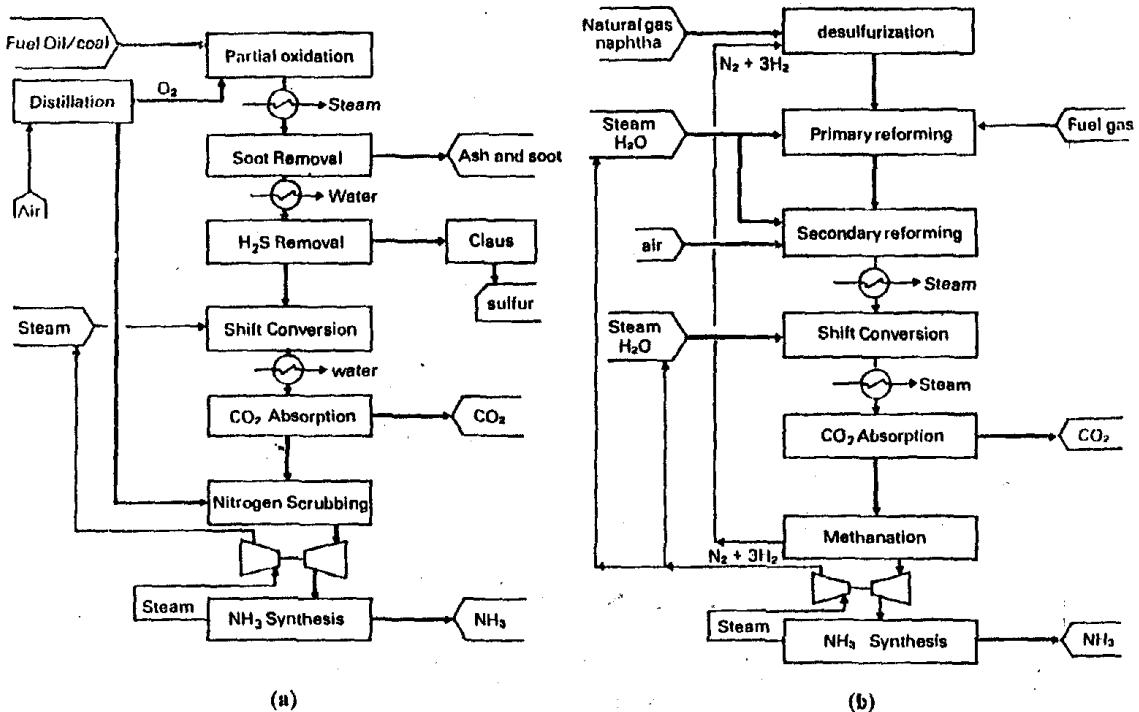


Fig. 1.14. Main ammonia manufacture base schemes.

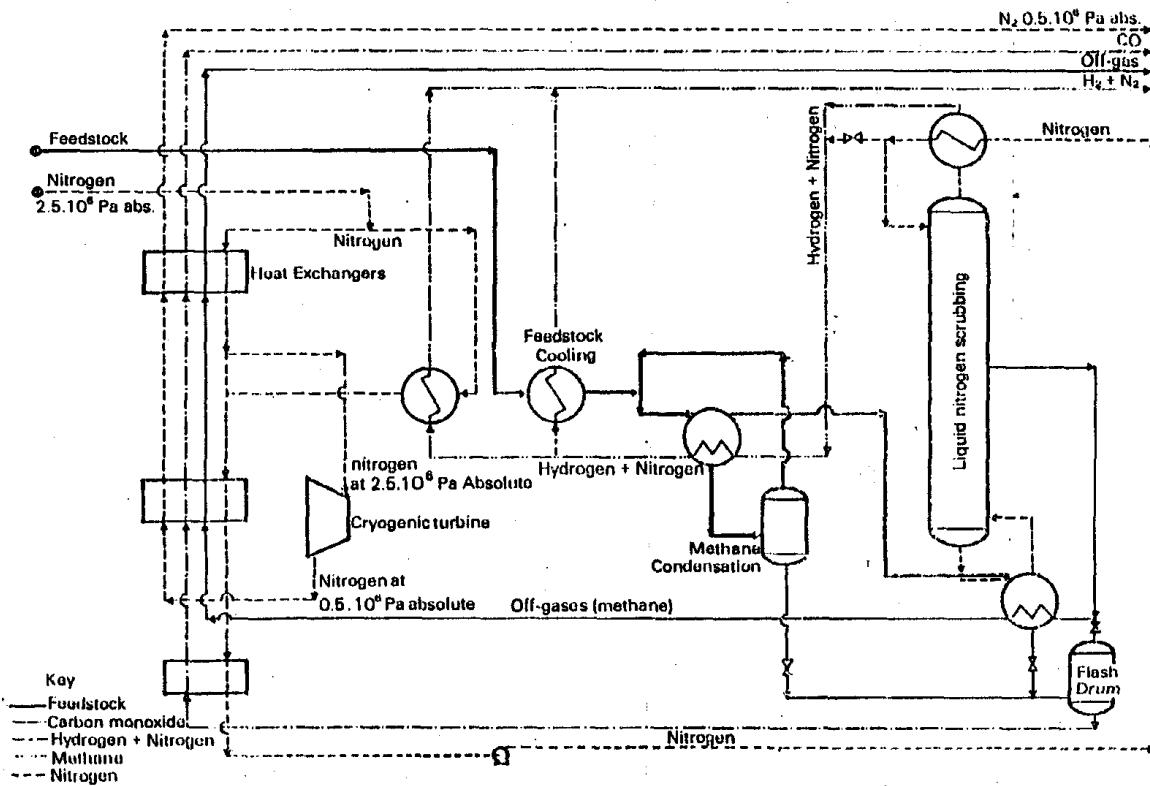


Fig. 1.15. Ammonia manufacture. Removal of carbon monoxide by liquid nitrogen scrubbing.

TABLE I.17
POST-COMBUSTION WITH AIR (SECONDARY REFORMING)

Primary reforming feedstock	Natural gas		Naphtha
Post-combustion	Feedstock ⁽¹⁾	Product	Product
Composition (% vol)			
H ₂	69.30	55.30	56.10
CO	9.70	13.00	10.20
CO ₂	10.40	7.50	11.20
CH ₄	10.60	0.35 ⁽²⁾	0.37 ⁽²⁾
N ₂	—	23.60	21.90
Ar	—	0.25	0.23
Total	100.00	100.00	100.00
Air/dry gas	0.41	—	0.40
H ₂ O/dry gas	0.77	0.57	0.56
Radiator exit temperature (°C)	—	1,000	1,000
Pressure (10 ⁶ Pa absolute)	—	3.1	1.5

(1) See the third column of Table I.8.

(2) The methane content can be reduced to 0.1 % vol.

TABLE I.18
CATALYTIC CONVERSION OF CO

Compositions and conditions	First reactor	Second reactor	Single reactor
Feedstock (% vol)			
CH ₄	0.37	0.35	0.37
CO ₂	11.20	18.22	11.20
CO	10.20	1.40	10.20
H ₂	56.10	59.60	56.10
N ₂	21.90	20.23	21.90
Ar	0.28	0.20	0.23
Pressure (10 ⁶ Pa absolute)	1.4	1.4	1.4
Steam/dry gas	1.25	1.25	1.25
Inlet temperature (°C)	370	260	200
Product (% vol)			
CH ₄	0.35	0.34	0.34
CO ₂	18.22	19.00	19.00
CO	1.40	0.20	0.20
H ₂	59.60	60.10	60.10
N ₂	20.23	20.16	20.16
Ar	0.20	0.20	0.20
Steam/dry gas	1.05	1.20	1.10
Outlet temperature (°C)	415	275	260

amount of CH_4 corresponding to that of carbon monoxide in the gas intended for ammonia synthesis.

In this scheme, the first steam reforming is regulated so that some methane subsists in the gas produced so that the next operation, conducted in the presence of air, provides the volume of nitrogen required. If the latter conversion, called secondary reforming or post-combustion, were a simple selective conversion of methane yielding carbon monoxide, carbon dioxide and steam, each residual hydrocarbon molecule would contribute seven to eight molecules of nitrogen. At the outlet of the primary reforming stage, the gas composition should satisfy the following equation:

$$(\text{H}_2 + \text{CO})/\text{CH}_4 = 21 \text{ to } 24 \text{ by volume}$$

Since 10 per cent carbon dioxide is formed at the operating temperatures of the reforming reactors, it is easy to calculate that the effluent must contain about 3.5 to 4.2 per cent residual methane. According to Table 1.8, this value can only be reached at high temperature, low pressure and high steam ratio.

It therefore appears preferable to convert the methane by air, so as to introduce the nitrogen required. This operation is performed at a comparable temperature, in order to maintain the required thermal levels of the successive operating sequences and to avoid excessively disturbing the stream compositions. This is done in the presence of nickel-based catalysts similar to those employed in the primary reforming reactor, to guarantee the conversion of low hydrocarbon contents in a dilute medium. Post-combustion is thus carried out adiabatically, between 850 and 1000°C, at a pressure that is also close to that of the initial steam reforming.

Table 1.17 gives some typical results of post-combustion treatment by air of effluents produced by primary reforming, either of natural gas or of naphtha.

In addition to avoiding an excessively severe initial steam reforming, post-combustion offers the advantage of improving the total heat recovery at high thermal level.

Catalytic conversion of the carbon monoxide contained in the gaseous mixture obtained after secondary reforming is carried out in the same way as for the production of hydrogen, namely in two reactors or only one. Table 1.18 gives a number of characteristic results. The VHSV varies from 1500 to 3000 h^{-1} .

1.3.2 Thermodynamic aspects of ammonia synthesis

The reaction:



is exothermic and endentropic.

$$\Delta H_T^0 = -77,294 - 54.24T + 0.01919T^2 \quad (\text{in joules})$$

Thus

$$\Delta H^0 = -107.8 \text{ kJ/mol at } 500^\circ\text{C}$$

Starting with an approximate expression of the value of the equilibrium constant (K_p) as:

$$\lg K_p = \frac{2940}{T} - 6.178$$

it can be shown that the production of ammonia is favored by high pressure and low temperature. Figure 1.16 shows this result graphically by giving the equilibrium composition of the stoichiometric mixture $N_2 + 3H_2$.

These thermodynamic considerations imply that, in practice :

- Once-through conversion of the feed gas is limited: recycling of the unconverted fractions results in the use of a "synthesis loop" operating at high pressure.
- Obtaining the high pressures associated with partial conversion of the reactants incurs large mechanical energy expenditures.
- The use of low temperatures, which partly offsets these drawbacks, tends to reduce the reaction rate.

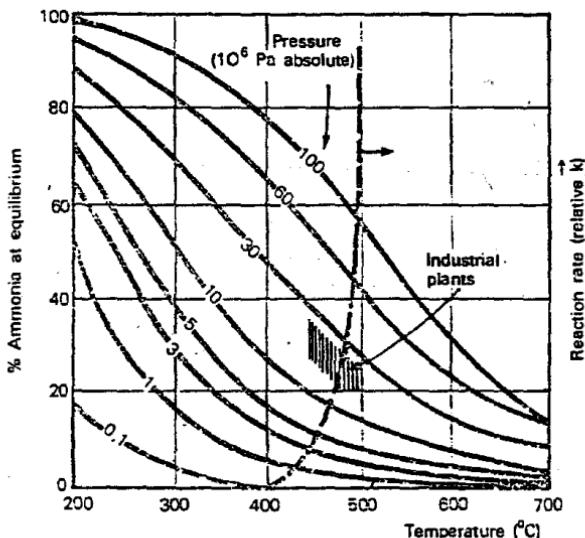


Fig. 1.16. Equilibrium of ammonia synthesis.

1.3.3 Kinetic aspects of ammonia synthesis

To accelerate the approach to equilibrium, the oxide catalysts employed are based on Group 7 metals, exclusively iron in practice (Fe_2O_3). A number of promoters help to improve performance, including Al_2O_3 which increases the active surface area of the particles, and K_2O , SiO_2 , MgO , CaO etc., which improve stability, and increase activity and resistance to poisoning. Systems currently under development make use of ruthenium

derivatives, to replace or to be used together with those of iron, modified by rubidium, titanium and cerium compounds.

The catalyst may be supplied to the users:

- In its initial oxide form, which must then be reduced in the unit itself by the mixture $N_2 + 3H_2$: this means a conditioning interval lasting from 4 to 10 days.
- In a prereduced, non-pyrophoric form, which is immediately operational but more expensive.

Standard catalyst systems are only active above 400°C (Fig. 1.16). They are especially stable provided the following requirements are observed:

- The temperature in the bed must not exceed 550°C.
- The make-up gas must be free of sulfur, arsenic and phosphorus compounds, as well as chlorine and, in general, halogenated derivatives which constitute permanent poisons.
- Its content of oxygen compounds, which represent temporary poisons, must satisfy certain limitations, such as $O_2, CO_2 < 1 \text{ ppm}$; $CO, H_2O, CO + CO_2 < 2 \text{ ppm}$. The requisite purity level is reached by repeating the liquid nitrogen scrubbing or methanation treatment, as required. Moisture is then removed by drying or by cryogenics.

Methane and argon are not catalyst poisons, but since they are inert in the reaction, they are liable to build up in the synthesis loop if they are not removed by a continuous purge. This may be implicit and natural by simple dissolution and entrainment in the ammonia produced, if the contents in the make-up gas are low, less than 0.01 per cent, for example, in schemes including cryogenic nitrogen scrubbing. It is mandatory for high concentrations, which are over 1 per cent if methanation is performed, and, in this case, the recycle gas may contain more than 10 to 15 per cent of methane and argon. Depending on the operating conditions, catalyst life may be as long as ten years.

The basic equation most widely accepted to express the kinetics of ammonia synthesis is that of Temkin and Pyzhev (1940). It expresses the reaction rate as a function of the partial pressures of the reactants and products:

$$\frac{dP_{NH_3}}{dt} = k_1 \frac{P_{N_2} \cdot P_{H_2}^{1.5}}{P_{NH_3}} - k_2 \frac{P_{NH_3}}{P_{H_2}^{1.5}}$$

where k_1 and k_2 are the rate constants of the synthesis and decomposition reactions.

Accurate calculations must consider the activity of the different components of the mixture and the presence of the catalyst. One of the many derivative equations which account for the influence of these factors is that of Dyson and Simon (1968), which uses the following expression:

$$V_{NH_3} = k_2 \left[k_a^2 f_{N_2} \left(\frac{f_{H_2}^3}{f_{NH_3}^2} \right)^a - \left(\frac{f_{NH_3}^2}{f_{H_2}^3} \right)^{1-a} \right]^{(5)}$$

⁽⁵⁾ The Temkin and Pyzhev equation is reproduced if $a = 0.5$.

where $k_2 = k_{20} \exp\left(-\frac{E_2}{RT}\right)$ and

V_{NH_3} = reaction rate of NH_3 production (moles kg of $\text{NH}_3/\text{h} \cdot \text{m}^3$ of catalyst),

k_2 = rate constant of the decomposition reaction (moles $\text{kg} \cdot \text{h} \cdot \text{m}^3$),

k_{20} = constant,

E_2 = energy of activation,

R = ideal gas constant,

T = absolute temperature,

f_{N_2} } fugacities of reactants and products,

f_{H_2}

f_{NH_3}

k_a = equilibrium constant,

a = constant depending on the type of catalyst (≈ 0.5 for iron oxides).

To provide a general idea, for the Montecatini catalyst, $a = 0.55$, $E = 163,473 \text{ kJ/mol}$,
 $\lg k_{20} = 14.7102$, and for the Haldor Topsøe catalyst $a = 0.692$, $E = 179,529 \text{ kJ/mol}$,
 $\lg k_{20} = 15.2059$.

For very small catalyst particles, this equation must itself be corrected by an efficiency factor to account for diffusion in industrial catalyst systems, in which the particle diameter reaches 6 to 12 mm.

In its simplified form (Temkin and Pyzhev), the expression of the conversion rate can be represented by the network of curves in Fig. 1.17. An examination of this graph shows that, to obtain a maximum reaction rate, irrespective of the conversion, the reactor must be designed to achieve the temperature gradient which, at any point, serves to reach these optimal values.

As a rule, the kinetic analysis shows that the maximum reaction rate is obtained if an initial H_2/N_2 ratio of 2.5/1 prevails in the reactor, whereas the stoichiometry is 3/1 (Fig. 1.18). The VHSV normally ranges from 10,000 to 50,000 h^{-1} .

1.3.4 Processes

Concerning the synthesis itself, until around 1965 units operated at pressures above 30 to $35 \cdot 10^6 \text{ Pa}$ absolute. Most of the processes subsequently adopted low-pressure operation, at about 20 to $25 \cdot 10^6 \text{ Pa}$ absolute and even 15 to $20 \cdot 10^6 \text{ Pa}$ absolute for very pure feeds produced by a scheme including liquid nitrogen scrubbing, for example. To enhance the energy optimization, certain *ICI*, *SNAM Progetti* (*Società Nazionale Metanodotti*) and *Pullman-Kellogg* projects recommend operation at even lower pressure, less than $5 \cdot 10^6 \text{ Pa}$ absolute. However, this means using much larger initial catalyst loads and much higher unconverted gas recirculation rates. The temperatures range around 480 to 500°C.

A standard flow sheet for an ammonia synthesis operation currently comprises the following main elements (Fig. 1.19):

- (a) A multi-stage centrifugal compressor driven by a steam turbine, which pressurizes the fresh feed as well as the recycle gases.

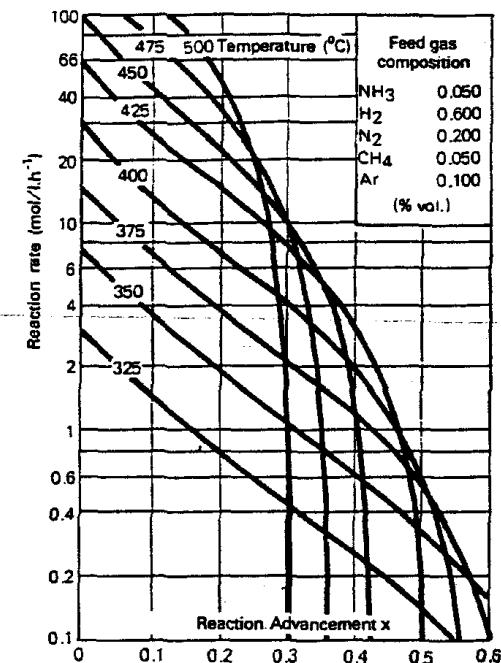


Fig. 1.17. Reaction rate of ammonia synthesis.

The percentage of NH₃ is related to the degree of advancement x by the equation :

$$\% \text{NH}_3 = 100 \left(\frac{2x + 0.25}{5 - 2x} \right)$$

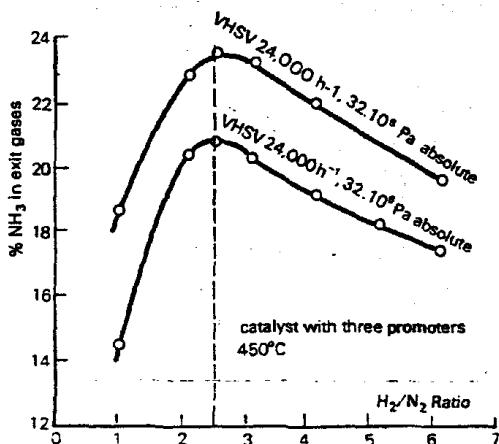


Fig. 1.18. Determination of maximum reaction rate of ammonia synthesis (From Nielsen).

- (b) A multi-layer reactor, normally vertical, with axial stream flow, designed to achieve internal circulation of the gaseous effluents, intended to preheat the feed and, above all, to remove the heat generated by the reaction.
- (c) A train of heat exchangers and a high-pressure separator designed to obtain liquid ammonia and to recirculate unconverted gases to the compressor, making up the synthesis loop. In certain recent installations, a quench boiler is installed at the reactor exit, with double concentric tubes or fume tubes, for the production of HP steam used to drive the turbines.
- (d) An NH_3 refrigeration cycle by Joule Thomson compression/expansion comprising three temperature stages (13.5°C , -7.5°C and -33.5°C) to liquefy the ammonia produced to around -23.5°C .

Synthesis loops are normally of two types, depending on whether the NH_3 is recovered before or after compression. The first flow sheet (Fig. 1.19) uses less energy, but both loops scrub the recirculation gases with liquid ammonia, allowing partial dissolution of the impurities and extending catalyst life.

The innovative feature of these processes obviously resides in the type of catalyst employed, and also, at the technological level, in the reactor design.

Two types of equipment are normally available, tubular and multiple-bed reactors. Three generations can be distinguished chronologically:

- The first concerns vertical reactors with production capacities less than 600 t/day, operating at high pressure (> 30 to $35 \cdot 10^6$ Pa absolute), and axial flow, and which are:
 - (a) Of the heat exchanger type, with shell and tubes of catalysts cooled externally : *Ammonia Casale* and *TVA* (*Tennessee Valley Authority*).
 - (b) Or of the multiple-bed type with intermediate cooling :
 - . By injection of quenching gas : *BASF*.
 - . By water tubes and steam production : *Montecatini* and *OSW* (*Österreichische Stickstoff Werke*).
- The second, currently in operation, allows for unit production capacities of 1500t/day, in vertical reactors with multiple catalyst beds (normally two) usually operating with axial flow, at a pressure of 20 to $25 \cdot 10^6$ Pa absolute. Cooling systems are of two types :
 - (a) By injection of quenching gas : *Kellogg* (diagram a in Fig. 1.20), *Topsoe* (radial flow), *Ammonia Casale* and *ICI*.
 - (b) By water tubes and steam production : *Uihde*, *Montedison* and *C. F. Braun* (two shells with one intermediate external heat exchanger).
- The latest on the drawing-boards concerns the following reactors adapted to high unit production capacities :
 - (a) *Kellogg* : horizontal system, axial flow, catalyst bed, quenching by gas injection and low pressure drop.
 - (b) *Topsoe* (series 200) : vertical, radial flow, catalyst bed, built-in gas/gas exchanger (diagram b in Fig. 1.20).
 - (c) *Ammonia Casale* : vertical, axial and radial flow, catalyst bed, adapted to loops operating at low pressure ($< 5 \cdot 10^6$ Pa absolute) and with high catalyst volumes.

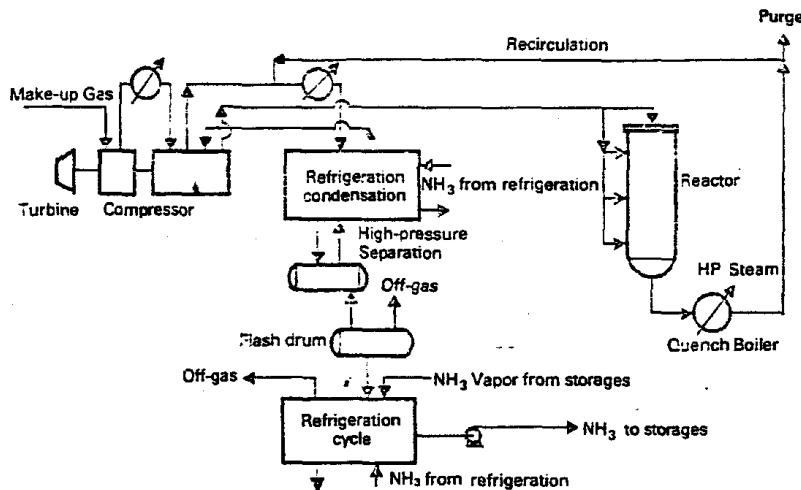


Fig. 1.19. Base scheme of ammonia synthesis loop.

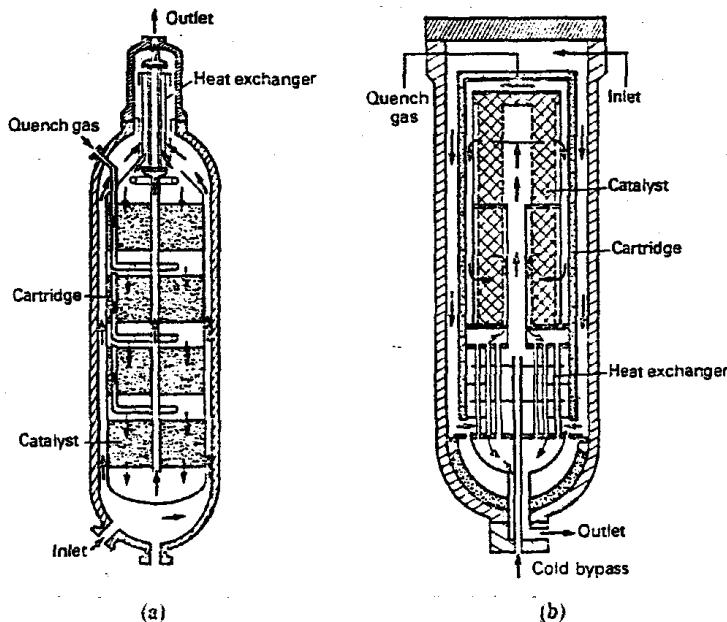


Fig. 1.20. Examples of ammonia synthesis reactors.

- Kellogg reactor (axial).
- Standard Topsoe reactor (radial).

To provide an illustration, a conventional reactor has the following characteristics:

Unit production capacity	1.200 t/day
Operating pressure	$35 \cdot 10^6$ Pa absolute
Weight	386 t
Catalyst volume	36 m ³
Shell length	22 m
Shell diameter	2 m

Figures 1.21 and 1.22 give flow sheets for two types of installation:

- (a) The first is built around the partial oxidation of hydrocarbons.
- (b) The second is based on hydrocarbon steam reforming.

The latest improvements in ammonia production by steam reforming of natural gas include the following:

- (a) ICI/AMV process, characterized by the introduction of excess air in the secondary reforming step, which cuts total energy consumption substantially.
- (b) The Fertimont (a Montedison subsidiary) process.
- (c) Byas technology, proposed by *Humphreys and Glasgow* for the revamping of existing reforming units, with the direct introduction of part of the feed in the secondary reforming step.
- (d) KTI Parc technique, which is ideal for low capacity installations.

1.3.5 Economic data

Due to the rapid increase, especially since 1960, of demand for ammonia for fertilizers, for a number of technological improvements in the construction of large centrifugal compressors which have become increasingly reliable, and for the use of active catalysts at low pressure (20 to $25 \cdot 10^6$ Pa absolute), installations with significantly higher nominal capacity have been designed. At the present time, 1500 to 1800 t/day of ammonia is normal, as compared with less than 200 t/day in 1955. The advantage offered by the scale effect can be appreciated by comparing the economic data in Table 1.19 concerning production capacities of 330 and 1500 t/day.

An overall review of the world activity of existing units shows that they operate on the average with a high stream factor, which is around 310 days/year, and which tends to improve with increasing size. The main cause of incidents is still the synthesis compressor, but also the primary reforming step.

In units employing natural gas feedstock the expenditure was formerly about $37 \cdot 10^6$ kJ/t of ammonia produced (980 m^3 of natural gas approximately). A number of optimizations helped to lower this consumption to $31 \cdot 10^6$ kJ and even $27 \cdot 10^6$ kJ⁽⁶⁾ (ICI/AMV process), while allowing for lower capital investment. Table 1.20, which gives the average energy consumption of a unit producing 1000 t/day of ammonia, as a function of the raw material employed, shows that, from this standpoint, natural gas remains the most economically interesting hydrocarbon feedstock.

(6) The theoretical minimum required is about $25 \cdot 10^6$ kJ.

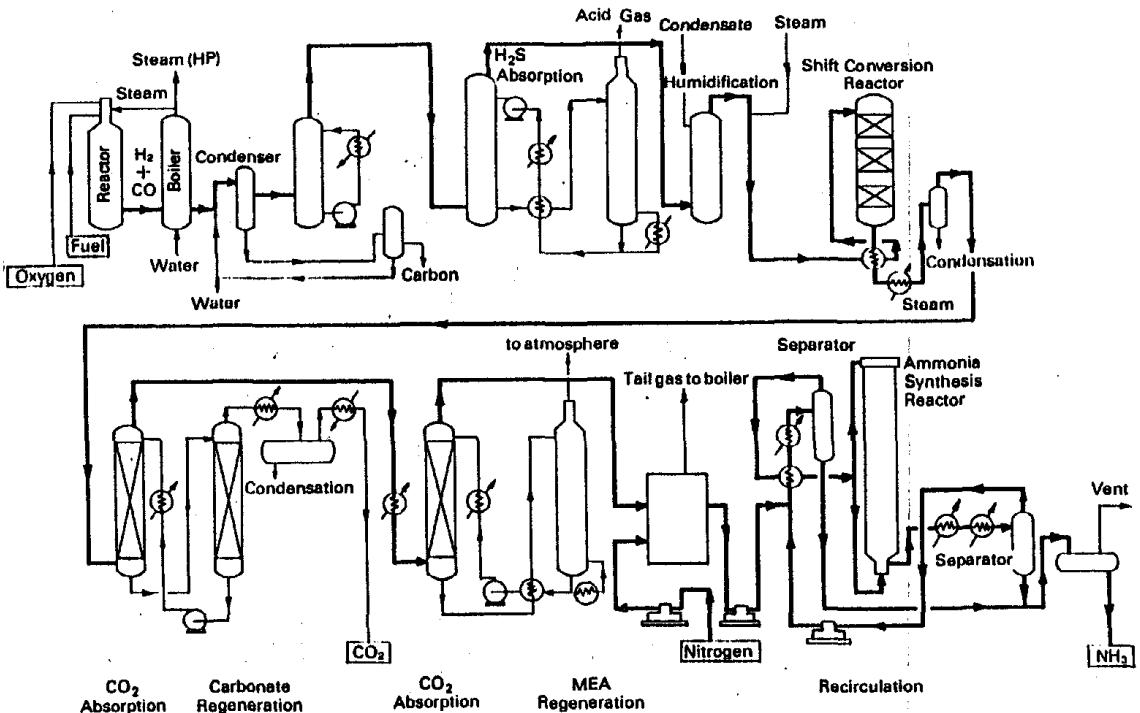


Fig. 1.21. Ammonia synthesis by partial oxidation of hydrocarbons.

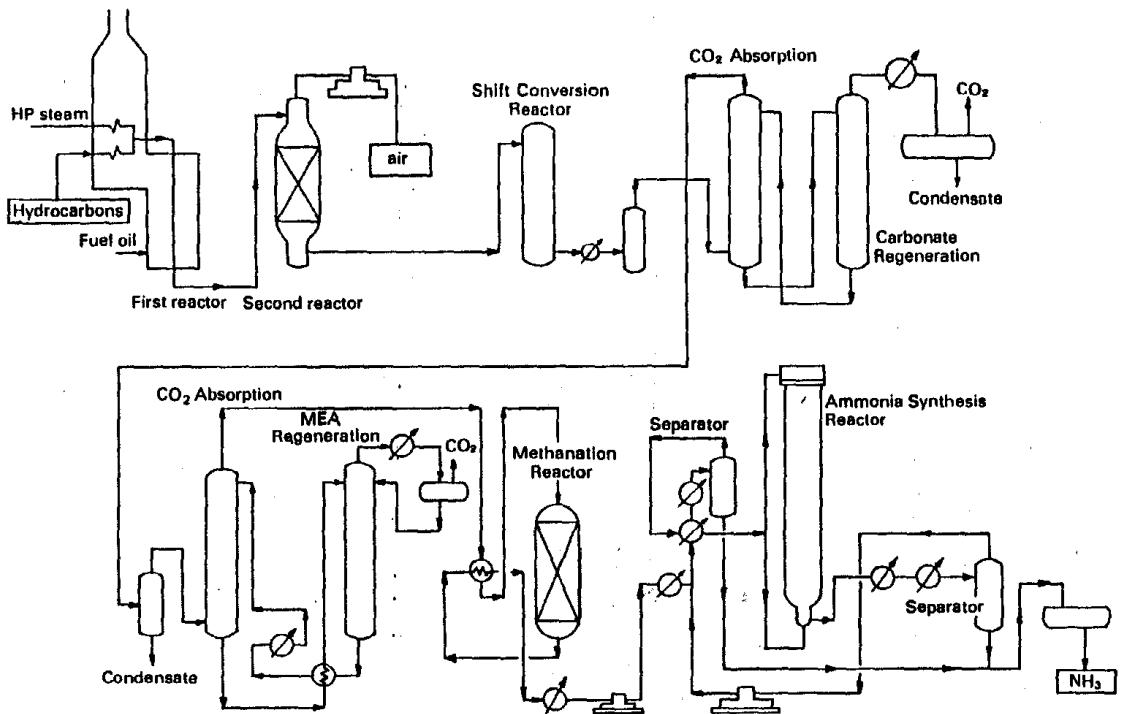


Fig. 1.22. Ammonia synthesis by steam reforming of hydrocarbons.

TABLE 1.19
AMMONIA PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Raw material	Natural gas	Naphtha	Heavy fuel oil	Coal
Process	Reforming	Reforming	Partial oxidation with air	Gasification in oxygen
Capacity (t/day)	330/1,000/1,500	1,000	1,000	2,500
Theoretical stream factor (days/year)	340	340	330	320
Battery limits investments (10^6 US\$)	45,95/135 ⁽¹⁾	110	120	340
Consumption per ton of ammonia				
Raw materials				
Natural gas (10^6 kJ) ⁽²⁾	33 ⁽³⁾ to 27 ⁽⁴⁾	—	—	—
Naphtha (t)	—	0.55	—	—
Fuel oil (t)	—	—	0.85 ⁽⁵⁾ to 1.05	—
Coal (t)	—	—	—	2.0 to 2.2
Oxygen (t)	—	—	—	0.9
Utilities				
Fuel (10^6 kJ)	—	14	—	—
Electricity (kWh)	18	50	50	35
Cooling water (m ³)	240	270	340	4
Boiler feedwater (m ³)	1	1.2	1.5	0.5
Catalysts and chemicals (US\$)	1.2	1.4	1.6	1.6
Labor (Operators per shift)	5	5	8	25

(%)

(1) Preparation of synthesis gas	61
Refrigeration cycle	11
Ammonia synthesis and recovery ..	28
Total	100

(2) Including $23 \cdot 10^6$ kJ as feed.

(3) Conventional processes : C.F. Braun, Fluor, Humphreys and Glasgow (Lead and MDF processes), Kellogg, Lummus, etc.

(4) Low-pressure processes : Kellogg, ICI, Montedison (LEA process), SNAM Progetti, etc.

(5) Improved processes : Kellogg, etc.

TABLE 1.20
ENERGY REQUIREMENTS FOR AMMONIA PRODUCTION
ACCORDING TO RAW MATERIAL (10^6 kJ)

Process and raw material	Consumption per ton of NH ₃
Conversion of natural gas with steam	33
Conversion of naphtha with steam	42
Partial oxidation of fuel oil	44
Coal gasification (at $2.5 \cdot 10^6$ Pa absolute)	55
Coal gasification (at atmospheric pressure)	70
Electrolysis of water	130

TABLE 1.21
AVERAGE COMMERCIAL SPECIFICATIONS OF ANHYDROUS AMMONIA

Uses	Chemicals and fertilizers	Refrigeration	Metallurgy
Ammonia (% Wt) min.	99.5	99.98	99.99
H ₂ O (% Wt) max.	10.5	0.015	0.003
Liquid organic compounds (ppm)	5	3	2
Uncondensable gases (ml/g) max.	—	0.2	10
Dew-point (°C)	—	—	-61.5

TABLE 1.22
AMMONIA PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
Fertilizers	84	85	57	88
Fibers and plastics		8		
Explosives	16	3	43	12
Animal feeds		2		
Miscellaneous		2		
Total	100	100	100	100
Sources (% product)				
Natural gas	80	95	23	68
Naphtha	9	—	34	10
Coal and coke	2	2	14	6
Miscellaneous ⁽²⁾	9	3	29	16
Total	100	100	100	100
Production (10 ⁶ t year)	16.2	14.7	2.0	106
Capacity (10 ⁶ t year) ⁽³⁾	17.4	17.2	3.4	128
Consumption (10 ⁶ t year)	18.5	17.1	2.0	106

(1) Expressed in tons of ammonia.

(2) Refinery gases, petroleum residues, electrolysis hydrogen.

(3) In 1986 the worldwide production capacity of ammonia was 119.0 · 10⁶ t year with the following distribution:

United States	15.5	Western Europe	15.2	Middle East	3.4
Canada	3.2	Eastern Europe	30.4 ^(a)	Japan	2.3
Latin America	8.0	Africa	6.3	Asia and Far East ^(b)	25.7

(a) Including USSR 27.6.

(b) Including China 8.6.

1.3.6 Uses and producers

Table 1.21 provides an idea of the average commercial specifications of anhydrous ammonia depending on uses for the production of fertilizers, refrigeration and metallurgy.

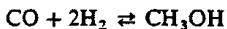
Table 1.22 shows the uses of ammonia in 1984 in Western Europe, the United States, Japan and the world, as well as production, capacities and consumption for these geographic areas. Capacities are also given for 1986.

1.4 METHANOL SYNTHESIS

Methanol or methyl alcohol ($\text{mp} = -97.8^\circ\text{C}$, $\text{bp}_{1.013} = 64.6^\circ\text{C}$, $d_4^{20} = 0.792$ ⁽⁷⁾) produced by the distillation of wood accounts for only a few per cent of total production. This also applies to its production by the direct oxidation of hydrocarbons. Most methanol is synthesized from mixtures of H_2 , CO and CO_2 .

1.4.1 Preparation of synthesis gas

Methanol production is chiefly based on the implementation of the following reaction :



To a lesser degree, it also relies on the conversion of carbon dioxide:



Hence, according to the proportion of CO and CO_2 , the gaseous mixture required for conversion must have a hydrogen to carbon molar ratio between 2 and 3⁽⁸⁾. Such a gas can be obtained, as mentioned above, by partial oxidation, gasification, or steam reforming.

1.4.1.1 Schemes involving partial oxidation with oxygen

To convert methane⁽⁹⁾ (see Fig. 1.5), it is theoretically possible to adjust the oxygen content to obtain an effluent in which the H_2/CO ratio is close to 2. In practice, it is necessary to consider the losses resulting from the formation of methane during the synthesis of methanol, and aim for an H_2/CO ratio of around 2.25, which is ideal for this conversion.

(7) Specific gravity, 68.0/39.2.

(8) The overall stoichiometry is such that $\text{H}_2/(\text{CO} + 1.5\text{CO}_2) = 2$.

(9) Contrary to the final objective in the production of hydrogen or ammonia, the intermediate formation of CO_2 does not need to be avoided in the manufacture of methanol. Hence, in this case, the partial oxidation of methane can offer an economically interesting solution.

This value can be obtained by diverting part of the gas stream to a steam converter that removes excess CO and supplies an equivalent amount of hydrogen (shift conversion). Using a standard absorption process, it is then necessary to remove the CO₂ up to the maximum concentration acceptable by the catalyst employed to conduct the methanol synthesis.

The basic scheme is hence very similar to those used to produce hydrogen and ammonia. The same applies to the conversion of heavy products, for which partial oxidation and gasification are generally more suitable. The presence of sulfur compounds in the raw materials used requires the consideration of two main variants, depending on the possibilities of the catalyst for CO shift conversion (diagrams a and b in Fig. 1.23).

- (a) Scheme a: this catalyst cannot tolerate sulfur derivatives. The feedstock must therefore first be desulfurized to a residual sulfur content of 0.05 to 0.1 ppm. The gas then partly passes through the CO conversion unit, and is then remixed with the untreated fraction and partly decarbonated.
- (b) Scheme b: the catalyst is resistant to sulfur compounds. Partial CO conversion is followed by simultaneous desulfurization and decarbonation.

In both schemes, the installation of a sulfur barrier (such as zinc oxide) is recommended to protect the synthesis catalyst, which does not tolerate sulfur compounds.

With the processes currently used to obtain methanol, which operate at low pressure (6 to 9 . 10⁶ Pa absolute), it is possible to eliminate the auxiliary compressor, which was formerly indispensable to introduce the synthesis gas in the requisite operating conditions.

Among the other technological variants are two effluent cooling possibilities at the exit of partial oxidation or gasification, namely the generation of high-pressure steam or direct water quench. The latter is uninteresting for the production of methanol, since intensive conversion is not the ultimate objective.

Since desulfurization must be total whereas decarbonation is only partial, it is interesting to employ a solvent capable of removing not only H₂S but also COS, performing this selectively in relation to CO₂. The ideal processes in these conditions are those employing physical solvents (Selexol, Rectisol, etc.).

1.4.1.2 Schemes based on hydrocarbon steam reforming

These are considerably simplified in comparison with those for the production of high-purity hydrogen or synthesis gas for ammonia. This is because CO conversion, CO₂ removal and methanation are eliminated. However, an auxiliary compressor is necessary in this case.

As shown in Fig. 1.24, the unit is reduced to two major sections:

- (a) Feedstock pretreatment designed to remove all traces of sulfur compounds or other impurities detrimental to the synthesis catalyst, such as chlorine.
- (b) The steam reforming furnace with its auxiliary flue-gas heat recovery facilities.

This simplification is associated with the actual reforming operation which, as shown by Table 1.23, leads, for methane, to a hydrogen/carbon ratio normally lying between 3 and 4, depending on the CO and CO₂ content of the effluent, whereas the desired value should lie between 2 and 3.

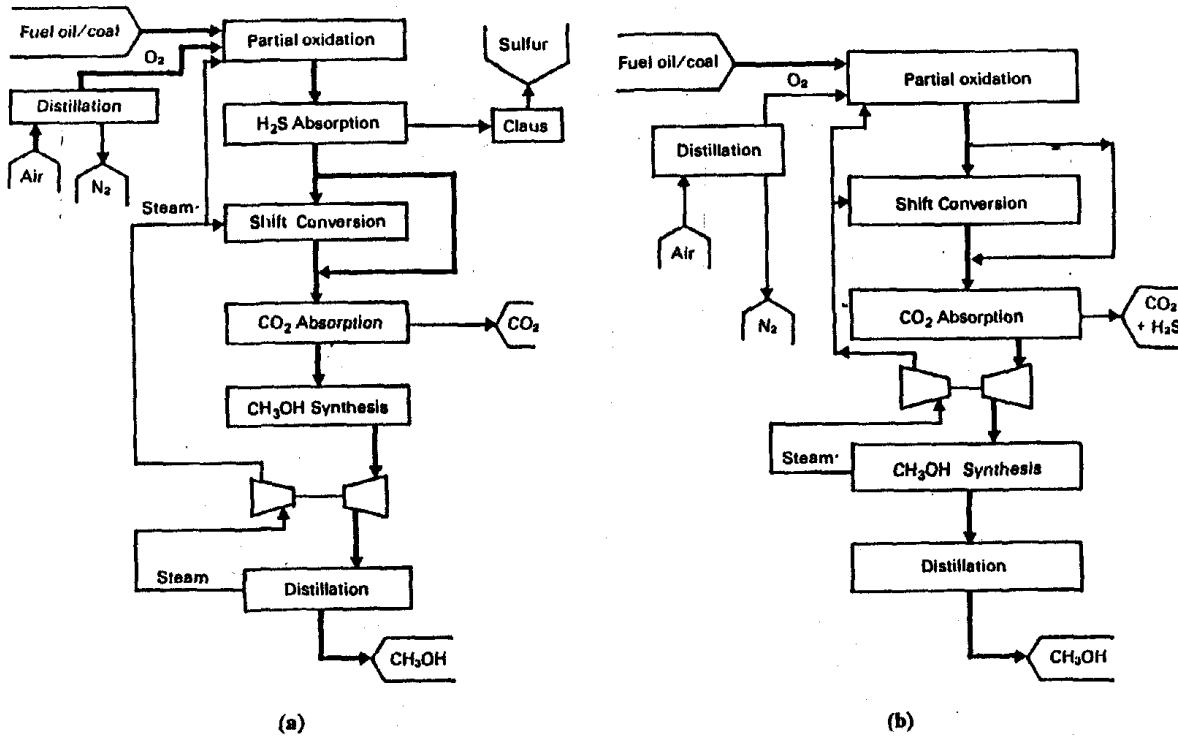


Fig. 1.23. Base schemes for methanol manufacture using partial oxidation.

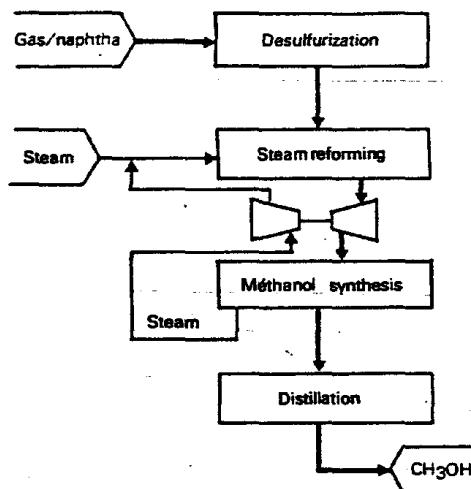


Fig. 1.24. Base scheme for methanol manufacture using steam reforming.

TABLE 1.23
 $\text{H}_2\text{O}/\text{CH}_4$ RATIO VARIATIONS IN STEAM REFORMING

T (°C)	650	700	800	850	990
1. $\text{H}_2\text{O}/\text{CH}_4 = 1$ H ₂ /CO	4.66	4.00	3.07	3.00	3.00
2. $\text{H}_2\text{O}/\text{CH}_4 = 1.5$ H ₂ /CO	5.75	4.63	3.96	3.70	3.70
3. $\text{H}_2\text{O}/\text{CH}_4 = 2$ H ₂ /CO	6.90	5.00	4.70	4.54	4.48
4. $\text{H}_2\text{O}/\text{CH}_4 = 3.5$ H ₂ /CO	-	-	-	-	10.25

The gas obtained from methane is hence either too rich in hydrogen, or too poor in carbon. This can be remedied as follows:

- (a) By purging, which results in a loss of energy connected in particular with the separation and compression of excess hydrogen.
- (b) Or by the addition of CO₂, taken for example from the CO₂ removal unit associated with ammonia production, or recovered from the flue gases of the reforming furnace. This addition can be made upstream or downstream of the steam reforming unit. The former alternative is more interesting in principle, because part of the CO₂ is then converted to CO, and, in the case of a temporary

shortage of make-up carbon dioxide, the composition of the reformed gas varies only slightly.

Unconverted methane present in the reforming effluent behaves in the successive operations like an inert diluent. To prevent its build-up in the recycle, which constitutes the methanol "synthesis loop", a purge is necessary.

The carbon deficit observed in methane steam reforming does not occur if naphtha feedstock is converted. In autothermal processes using fuel oil as a feedstock, sufficient quantities of excess carbon dioxide are available within the installation itself. This gas is recycled from a scrubbing unit.

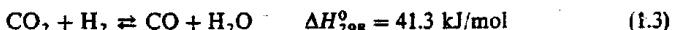
1.4.2 Thermodynamic aspects of methanol synthesis

The two main reactions used for methanol synthesis:



are exothermic and endothermic.

The second may be considered as the resultant of conversion (1.1) and of the reverse reaction of CO steam conversion



so that reaction (1.1) is the basic step, for which:

$$\Delta H_{T(0)}^0 = -74,653 - 63.98 T + 32.61 T^2 + 8.53 \cdot 10^{-6} T^3 - 7.77 \cdot 10^{-9} T^4 \quad (10)$$

As shown in Fig. 1.25, to calculate the production of methanol at thermodynamic equilibrium, in accordance with temperature and pressure conditions, use can be made of the expressions of the equilibrium constant K_p as a function of these parameters, i.e. :

- Equations such as:

$$\ln K_p \text{ (Eq. 1.1)} = \frac{8,980}{T} - 7.697 \ln T + 22.697 + 3.922 \cdot 10^{-3} T + 0.514 \cdot 10^{-6} T^2 \quad (11)$$

and

$$\ln K_p \text{ (Eq. 1.3)} = \frac{4,764}{T} - 1.945 \ln T + 5.102 + 5.630 \cdot 10^{-3} T - 2.170 \cdot 10^{-6} T^2 \quad (11).$$

- The actual definition of this constant:

$$K_p \text{ (Eq. 1.1)} = \left(\frac{N_{\text{CH}_3\text{OH}} \cdot N_T^2}{N_{\text{CO}} \cdot N_{\text{H}_2}^2 \cdot P^2} \right) \left(\frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}} \cdot \gamma_{\text{H}_2}^2} \right)$$

(10) From P. Boucot (IFP).

(11) From P. Boucot (IFP).

and

$$K_p(\text{Eq. 1.3}) = \frac{(N_{\text{CO}} \cdot N_{\text{H}_2\text{O}})}{(N_{\text{CO}_2} \cdot N_{\text{H}_2})} \left(\frac{\gamma_{\text{CO}} \cdot \gamma_{\text{H}_2\text{O}}}{\gamma_{\text{CO}_2} \cdot \gamma_{\text{H}_2}} \right)$$

where

N_i = moles kg of product i in the mixture,

N_T = total number of moles kg,

γ_i = activity or fugacity coefficient of product i .

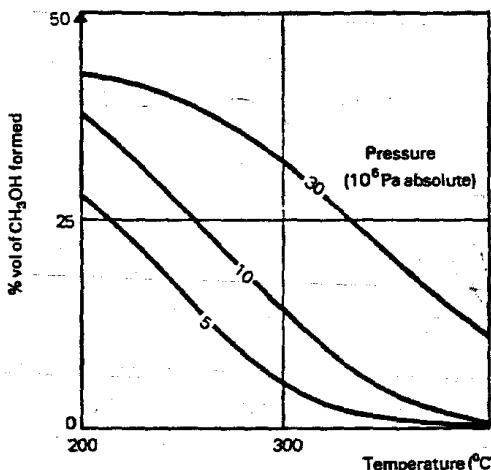


Fig. 1.25. Equilibrium of methanol synthesis from a reformed gas produced by the steam reforming of methane.

1.4.3 Kinetic aspects of methanol synthesis

Practically speaking, in order to achieve the simultaneous conversion of CO and CO₂ to methanol, one can also introduce the concept of carbon efficiency, defined as follows:

$$\text{carbon efficiency} = \frac{\text{number of moles of ethanol produced}}{\text{number of moles of } (\text{CO} + \text{CO}_2) \text{ in the synthesis gas}} \times 100 \text{ (per cent)}$$

Experimental correlations are then made, such as those in Figs. 1.26 and 1.27, which furnish the following for effluents produced by steam reforming:

- For a methane feedstock, the pseudo-equilibrium temperature at which a given carbon efficiency can be obtained at a given pressure.
- The influence of feedstock (methane or naphtha) on the pressure to be applied to obtain the same efficiency.

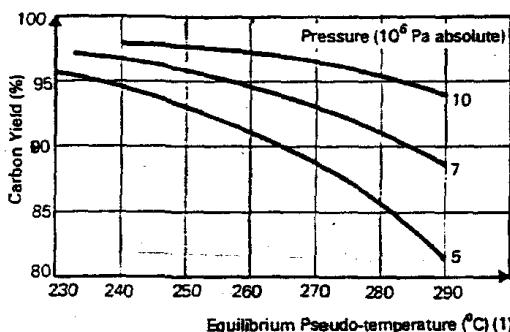


Fig. 1.26. Influence of temperature and pressure on carbon yield (case of a reformed gas produced by steam treatment).

(1) Pseudo-temperature = Reaction temperature - Approach to equilibrium.

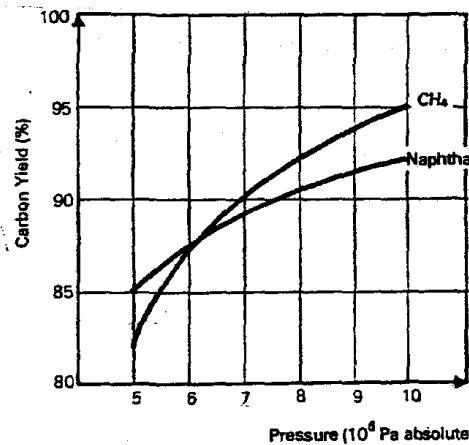
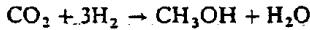


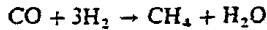
Fig. 1.27. Influence of type of feedstock, treated by steam reforming, on carbon yield.

The gains in selectivity are directly related to the actual thermal level. The most important side reactions are:

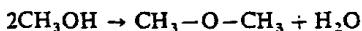
(a) Reaction of residual carbon dioxide with hydrogen:



(b) Methanation:



(c) Formation of methyl ether:



The first two conversions are limited by reducing the CO_2 content in the synthesis gas employed, and also, and above all, by limiting the reaction temperature to 400°C . Below this temperature, the methanation rate remains low, or even negligible, on the catalysts employed.

The kinetic equation which expresses the results of CO conversion to methanol is due to Natta, and is written :

$$\frac{P_{\text{CO}} \cdot P_{\text{H}_2}^2 - \frac{P_{\text{CH}_3\text{OH}}}{K_p}}{(A + B \cdot P_{\text{CO}} + C \cdot P_{\text{H}_2} + D \cdot P_{\text{CH}_3\text{OH}})^3}$$

where A, B, C and D are constants which depend on the catalyst used. The calculation of the pressures appearing in this expression must take account of the activities.

An analysis of this equation shows that, as in the case of ammonia synthesis, the maximum conversion rate at any point of the reactor can only be achieved by establishing a temperature gradient. This must be supplemented by the analysis of the kinetics relative to the reverse reaction of CO shift conversion. The models that can be constructed on the basis of published experimental results⁽¹²⁾ show that, with catalysts based on copper oxide, at $5 \cdot 10^6$ Pa absolute, the approach to equilibrium capable of being reached is about 12°C for CO conversion and 7°C for CO/CO_2 conversion.

These calculations show that the production of methanol is favored by :

- (a) Elevation of pressure.
- (b) Reduction of temperature.
- (c) Increase of the CO/CO_2 ratio in the synthesis gas.
- (d) Increase of the hydrogen content of the reformed feed, at least for pressures above $6 \cdot 10^6$ Pa absolute.

Lowering the temperature results in slower reaction rates, and consequently a poor approach to thermodynamic equilibrium. Activators must be used to overcome these drawbacks.

Two main types of catalyst are available industrially :

- (a) Zinc/chromium systems which, until the late 1960s, accounted for virtually all methanol production. Consisting of homogeneous mixtures of chromium and zinc oxides, they were subsequently superseded by copper-based catalysts. This was due to their low relative activity, which required operation between 300 and 400°C . At this temperature, a pressure of about 30 to $35 \cdot 10^6$ Pa absolute is necessary to attain satisfactory conversion rates, and this incurs a high cost in terms of energy and economics.
- (b) Copper-based systems, familiar for many years for their performance but originally highly sensitive to certain poisons, especially sulfur and halogenated compounds.

(12) From P. Boucot (IFP).

The improvement in catalyst resistance and the production of impurity-free synthesis gases led to their industrialization. Hence it is now possible to achieve comparable or better performance than that allowed by zinc/chromium systems, to the extent that the great selectivity of copper-based catalysts reduces the quantity of by-products, by operating between 240 and 270°C, at only $5 \text{ to } 10 \cdot 10^6 \text{ Pa}$ absolute, with VHSV ranging from 10,000 to 15,000 h^{-1} STP (Standard Temperature Pressure) and catalyst lives of over three years. This decisive improvement was achieved on the initiative of ICI.

1.4.4 Processes

The existence of two generations of catalysts on the industrial scale accordingly contributed to the development of two main types of process:

- The earliest operate at high pressure, between 30 and $35 \cdot 10^6 \text{ Pa}$ absolute, at temperatures from 350 to 400°C, in reactors which are:
 - (a) Isothermal (i.e. with catalyst tubes, externally cooled by gas circulation or, more generally, coolant fluid).
 - (b) Or adiabatic (i.e. with multistage catalyst beds, with intermediate cooling by injection of a quenching fluid).

These technologies have been industrialized by *Chemico (Chemical Construction), Commercial Solvents, Foster Wheeler-Casale, Girdler, ICI, Inventa-Vulcan, Lummus, Montecatini, Badger, BASF, Haldor-Topsøe, Hoechst-Uhde, Humphrey and Glasgow, Hydrocarbon Research, Kellogg, Kuhlmann, Pritchard, Power Gas, SIR (Societa Italiana Resine), Stone and Webster, Sumitomo etc.*

- The latest operate at low pressure, preferably between 5 and $10 \cdot 10^6 \text{ Pa}$ absolute, at temperatures from 240 to 270°C, in vertical reactors of design varying with the company. The main current industrial technologies are those of the following licensors:

- (a) *ICI*: commercialized since 1970, this process is the most widespread and accounts for more than half of all methanol production capacity existing in 1986 worldwide, and for 70 per cent of projects under way. Using a single catalyst bed, cooled by injection of a quenching gas by means of lozenge axial flow distributors, this type of adiabatic reactor can be scaled up directly to unit production capacities of 3000 t/day (diagram a in Fig. 1.28).
- (b) *Lurgi*: the isothermal reactor features catalysts tube side and boiling water shell side, so that high pressure steam is obtained (diagram b in Fig. 1.28).
- (c) *Ammonia-Casale*: the reactor features multiple catalyst beds, with intermediate cooling by gas/gas heat exchange and axial as well as radial flow, with low pressure drops. It can be scaled up directly to unit production capacities of 5000 t/day.
- (d) *Topsøe*: the reactor features radial flow across three concentric catalyst beds in separate vessels. Heat exchange is external.
- (e) *Mitsubishi* etc.

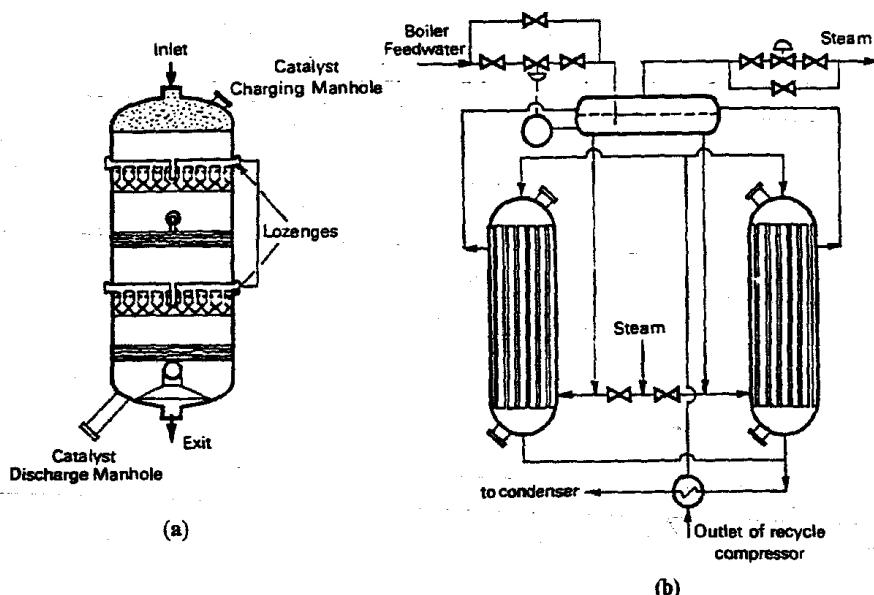


Fig. 1.28. Methanol manufacture. Typical reactors.

- ICI reactor.
- Lurgi reactor.

As a rule, this process offers the following conversion yields:

	Conversion (per cent)	
	Once-through	Total
CO	45 to 60	90 to 97
CO ₂	20 to 40	80 to 92

Figure 1.29 shows the basic flow sheet of the methanol synthesis and purification section obtained according to ICI technology. Whether produced by steam reforming or partial oxidation, the product gas first passes through a double-body make-up compressor and is then mixed with the recycle gas. The mixture is then picked up by a circulator consisting of a single-body centrifugal compressor, driven by a back-pressure steam turbine. At the exit, the pressurized gas is preheated by heat exchange with the reactor effluent, and then divided into two streams:

- The first (about 40 per cent) is sent to the reactor after undergoing supplementary preheating, also by countercurrent flow with the products formed.
- The second (60 per cent) is used as a quenching fluid, injected at different levels of the reactor, to achieve effective temperature control.

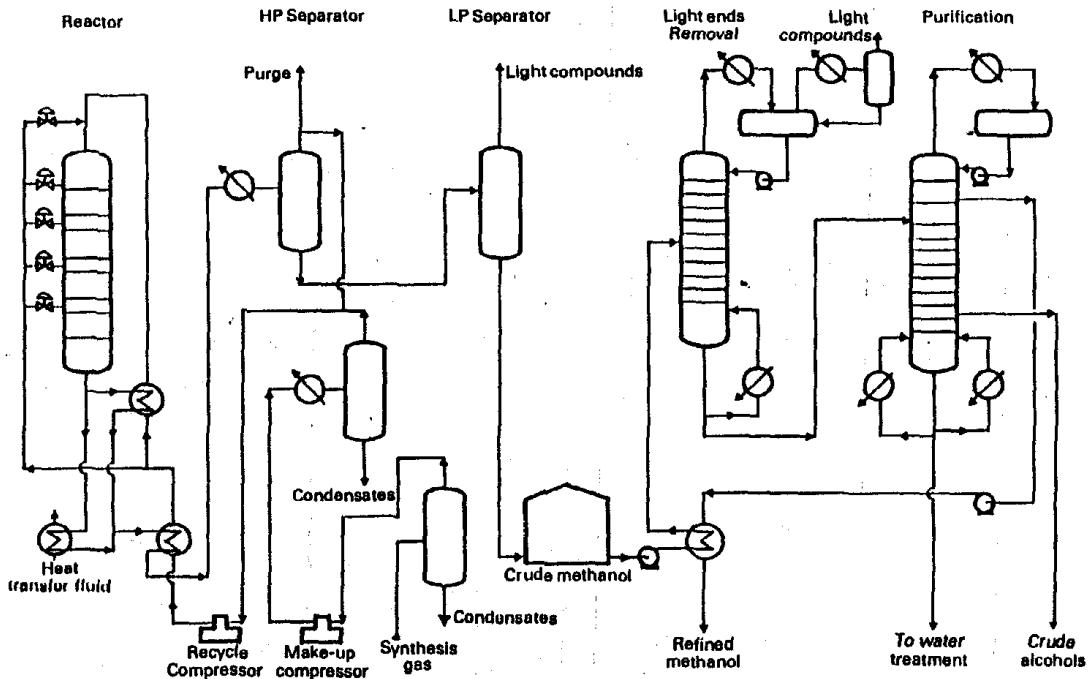


Fig. 1.29. Methanol manufacture. ICI process.

At the exit of the reaction zone, the gas stream obtained is first cooled by heating the feed and water required by the high-pressure steam generators, and then by passage through an air-cooled exchanger in which the methanol and water are condensed. Gas/liquid separation is then carried out in a vertical drum, operating under pressure. The gas fraction is essentially recycled: a purge helps to keep the inert gas content in the reaction loop at a suitable level. The crude methanol is degassed by flash and then distilled. It contains 17 to 23 per cent weight of water, 0.4 per cent of impurities (dimethyl ether, methyl formate, ethanol, propanol, butanols etc.), and must therefore be purified in a series of two columns, to meet commercial specifications of methanol for chemical uses (10 ppm ethanol for Grade AA). The first is a light-ends column that eliminates the light components (gas, ethers, ketones etc.), while the second performs the following separations:

- (a) At the top, purified methanol, drawn off below the pasteurization section.
- (b) The heavier alcohols as a sidestream.
- (c) Water at the bottom.

Remarks. Due to problems of phase separation in the presence of water and the formation of *vapor locks* that are detrimental to motor operation, the use of methanol as a fuel requires the addition of higher molecular weight oxygen compounds (higher alcohols than ethanol in particular). For such an application, it is important to maintain certain impurities in the methanol product, or even to favor their formation. Thus, the purification flow sheet can be simplified by combining light ends separation and rectification in a single operation, or by increasing the content of the higher homologues of methanol by conducting the conversion in the same reactor (*Lurgi, Vulcan* etc.) or in different units, for better control of the changes in the reaction medium (*IFP, SNAM Progetti* etc.).

Recent developments are aimed to manufacture methanol in a liquid or mixed phase. This applies to the technologies designed by *Aker, Chemical Systems, IFP* etc.

1.4.5 Economic data

Table 1.24 summarizes the economic data available on methanol production from various feedstocks and by various processes.

1.4.6 Uses and producers

Table 1.25 gives the average commercial specifications of chemical grade methanol.

Table 1.26 lists the applications of methanol in Western Europe, the United States, Japan and the world in 1984, as well as the production, capacities and consumption for these geographic areas. Capacities are also given for 1986.

TABLE I.24
METHANOL PRODUCTION: ECONOMIC DATA
(France conditions, mid-1986)

Raw material	Natural gas			Naphtha	Vacuum residues	Coal
	ICl		Lurgi	-	Texaco	Koppers/Totzek
Typical technology	No	No	Yes	No	No	No
Make-up CO ₂						
Production capacity (t/day)	1,000	1,800	1,800	1,800	500	1,800
Battery limits investments (10 ⁶ US\$)	75	130 ⁽¹⁾	120	135	45	220
Consumption per ton of methanol						
Raw materials						
Natural gas (10 ⁶ kJ)	32 ⁽³⁾ to 33.5 ⁽⁴⁾		32.0	33.5	-	-
Naphtha (t)	-	-	-	-	0.55	-
Residues (t)	-	-	-	-	-	0.90
Coal (t)	-	-	-	-	-	2.05
Oxygen (t)	-	-	-	-	-	0.85
Carbon dioxide (t)	-	-	0.5	-	-	-
By-products						
Sulfur (kg)	-	-	-	-	30	30
Utilities						
Steam (t)	-	0.12	(-) 0.5	0.8	-	4.5
Fuel (10 ⁶ kJ)	-	-	-	15	-	17
Electricity (kWh)	65	55	60	35	55	270
Cooling water (m ³)	90	190	155	245	2	340
Process water (m ³)	2	1	3	1	1	6
Catalysts and chemicals (US\$)	2.1	2.1	2.1	2.6	1.4	2.6
Labor (Operators per shift)	7	7	7	7	15	20

(%)

(1) Steam reforming	43	(2) Coal storage and preparation	3
Compression	12	Gasification	35
Methanol synthesis	36	Conversion with steam	5
Purification	9	Acid gas removal	13
Total	100	Methanol synthesis and purification	13
(3) Improved process.		Air distillation	29
(4) Including about 30.5 . 10 ⁶ kJ as feedstock.		Antipollution treatment	2
		Total	100

TABLE 1.25
AVERAGE COMMERCIAL SPECIFICATIONS OF METHANOL FOR CHEMICALS

Grade	A	AA
Methanol (% Wt) min.	99.85	99.85
d_{20}^{20} ⁽¹⁾	792.8	792.8
Acetone and aldehydes (ppm) max.	30	30
Acetone (ppm) max.	—	20
Ethanol (ppm) max.	—	10
Acids (as acetic acid) (ppm) max.	30	30
H_2O (ppm) max.	1,500	1,000
Distillation range at 1.013 . 10^6 Pa absolute	1°C must include 64.4°C	1°C must include 64.6°C
Color (Pt/Co scale) max.	5	5
Non-volatile residue (g/100 ml)	0.001	0.001
Permanganate test at 17 to 18°C min.	30	30

(1) Specific gravity, 68.0/68.0.

TABLE 1.26
METHANOL PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
Acetic acid	4	12	9	6
Chloromethanes	4	8	4	4
Dimethylterephthalate	4	1	1	5
Formaldehyde	48	34	45	37
Methyl methacrylate	2	3	7	2
Methyl tertio butyl ether	5	7	—	4
Gasoline blending	9	8	—	5
Solvent	14	7	13	12
Miscellaneous ⁽¹⁾	10	20	21	25
Total	100	100	100	100
Sources (% product)				
Natural gas	75	56	100	79
Offgases, refinery gases	—	20	—	7
Residues, fuel	22	13	—	10
Coal	—	4	—	1
Naphtha and other	3	7	—	3
Total	100	100	100	100
Production (10^6 t/year)	2.0	3.4	0.26	13.1
Capacity (10^6 t/year) ⁽²⁾	2.8	4.6	0.40	16.9
Consumption (10^6 t/year)	3.5	3.8	1.23	12.8

(1) Methylhalides, methylene chloride, methylamines, agricultural products, synthetic resins, polyvinylalcohols.

(2) In 1986 the worldwide production capacity of methanol reached $20.8 \cdot 10^6$ t/year with the following distribution:

United States	4.0	Western Europe	2.5	Middle East	1.7
Canada	1.8	Eastern Europe	5.6	Japan	0.3
Latin America	0.8	Africa	0.8	Asia and Far East	3.3

1.5 FORMALDEHYDE

Formaldehyde ($\text{mp} = -118^\circ\text{C}$, $\text{bp}_{1.013} = -19^\circ\text{C}$, $d_4^{-20(13)} = 0.8153$) is normally a gas. It is chiefly marketed in the form of aqueous solutions of formalin containing 37 to 60 per cent weight of the pure product. These solutions tend to polymerize, even more easily in high concentrations. Hence if they are not used immediately, they must be stabilized by the addition of methanol (7 to 15 per cent weight). A small amount of formaldehyde is sold in the form of solid polymers (paraldehyde, trioxane).

Formaldehyde can be manufactured by two categories of processes:

- Oxidation of paraffinic hydrocarbons.
- Oxidation of methanol, to which can be added that of a by-product of its manufacture, dimethyl ether.

1.5.1 Direct oxidation of hydrocarbons

A small part of the formaldehyde produced industrially is manufactured by direct hydrocarbon oxidation, of which it is only a by-product (Celanese Co., see Section 8.1.3).

No specific processes currently exist for the manufacture of formaldehyde on the commercial scale from natural gas. Some investigations have led to a pilot project (West German processes: Gute Hoffnungshütte and Hibernia).

1.5.2 Methanol oxidation

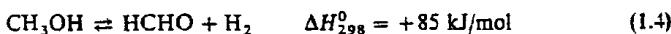
In principle, this operation consists in passing a mixture of air and methanol vapor over a catalyst bed at about atmospheric pressure, and absorbing the product in water. Two main methods are available, which essentially differ in the type of catalyst employed, and which lead either to dehydrogenation combined with partial oxidation, or to oxidation. Many variants have been developed around these two basic situations.

1.5.2.1 Reaction characteristics

A. Reactions involved

The main reactions are the followings:

- For partial oxidation combined with dehydrogenation:



(13) Specific gravity, 4.0:39.2.

The presence of air causes the combustion of a fraction of the hydrogen:



This means that the following oxidation reaction partially occurs:



The equilibrium values of transformation (1.4) are 50 per cent at 400°C, 90 per cent at 500°C, and 99 per cent at 700°C. It is therefore necessary to operate at about 600°C to obtain high once-through conversions.

- For oxidation only:



This highly exothermic reaction is complete. It can be carried out at the optimal temperature to guarantee high selectivity and high conversion.

- During these two main conversions, several side reactions of complete combustion of methanol and formaldehyde take place and reduce the overall yield of the operation.

B. Feedstock composition

Since the air/methanol mixture is flammable in a methanol concentration range between 6 to 25 and 9 to 37 per cent volume according to temperature and pressure, operations can be carried out in two ways:

- Above the upper limit, in other words with excess of methanol or deficiency of air. This is practised by partial oxidation processes.
- Below the lower limit, in other words with an excess of air or oxygen. This is the case of oxidation processes for which the feedstock contains 8 to 9 per cent volume of methanol.

Operation with excess alcohol implies its subsequent separation and recycling. This factor is only valid if methanol once-through conversion remains limited. In fact, the latest industrial variants achieve high conversion levels by employing catalyst systems capable of withstanding higher service temperatures. In these conditions, the upper flammability limit can be exceeded by making use of supposedly inert substances, consisting of steam or gases such as nitrogen. The injection of water has the advantage of improving catalyst life and performance, by absorbing part of the heat of reaction, but is costly in terms of energy during vaporization. The optimum is actually characterized by a methanol-to-water ratio of 1.5 by weight. Inert gas injection achieves the same result but is less effective. However, it can be performed at lower cost by recirculating a fraction of the residual light gaseous products produced by combustion in particular. An economic compromise can be found between these two alternatives, as proposed by BASF, for example, which carries them out simultaneously in its new process. This gaseous effluent recirculation is employed more systematically in the current techniques of oxidation alone, to raise the methanol content of the reaction medium and hence to reduce the size of the streams treated.

C. Catalysts

a. Partial oxidation

The silver-based catalyst is in the form of a metal gauze or crystals, which may be deposited on a support. It can also be used in these two forms simultaneously. Other metals, such as copper and platinum, employed originally by Hofmann in 1868, also catalyze the conversion, but are not employed industrially.

Dehydrogenation accounts for about 45 per cent of the production of formaldehyde and oxidation for 55 per cent. Oxygen, which burns the hydrogen as it is formed, maintains the activity of the catalyst and pushes the reaction equilibrium in the favorable direction. Thus operations can take place at lower temperature, with hydrogen combustion supplying the heat required to maintain temperature.

These catalyst systems, which operate with a deficiency of air and which were initially developed by BASF, Du Pont de Nemours, Selden, etc., have given rise to three generations of processes :

- (a) The first, using silver wires or gauzes, with excess methanol at a temperature of 400 to 550°C, for which once-through conversion ranges from 60 to 80 per cent maximum.
- (b) The second, which guarantees once-through conversion of 75 to 85 per cent in the presence of silver gauzes or crystals, at a temperature of 600 to 650°C.
- (c) The most recent, operating between 680 and 720°C on a thin multi-layer bed of silver crystals, with once-through conversions of over 95 per cent, which avoid the separation of unconverted methanol and its recycling. Selectivity is as high as 90 molar per cent, and this, combined with absence of distillation during which formaldehyde oxidation can continue, helps to obtain a formic acid content of about 100 ppm in the final product, which is sharply lower than the commercial specifications (300 ppm). Catalyst life is about four months.

The total molar yield of the processes employing silver ranges between 85 and 91 per cent.

b. Oxidation alone

The catalysts used in this case are based on iron molybdenum oxide, with or without dopes. The dopes proposed are essentially aimed at increasing the activity and/or selectivity, improving resistance to crushing or attrition and hence increasing the catalyst life, allowing more efficient removal of the heat of reaction by avoiding hot spots, and possibly developing a fluidized bed system. The main additions include compounds of vanadium, chromium, cobalt, nickel, manganese etc.

These catalyst systems normally operate between 300 and 400°C depending on the promoter employed, with large excess of air which, in the recent technologies (as shown above), is reduced by the recirculation of residual gases. They guarantee virtually complete conversion of the methanol in a single pass, about 95 to 99 per cent, with a total formaldehyde molar yield of 90 to 95 per cent. Although no distillation is necessary, by using some of them, the earliest, formic acid is formed at the rate of 1000 to 1200 ppm in the final product, which must therefore be treated by passage on ion exchange resins. Modern catalysts, which display higher activity, help to reduce this content to 10 ppm.

In this case, residence time is about 0.1 to 0.3 s. Catalyst life is as long as one year or longer with these systems, which also exhibit better mechanical strength.

1.5.2.2 Industrial processes

A. Base schemes

These are more or less identical in both types of process, and comprise the following:

- (a) The production of the air/methanol mixture, usually with additions of water and possibly residual gases from the subsequent absorption stage. This is obtained by vaporizing the methanol by flash or heat exchange with the reactor effluent, followed by the addition of air and previously compressed recycle gas, or possibly by the passage of this mixture through alcohol at a suitable temperature.
- (b) The reaction system; vapors of the preheated feeds are sent to the reactors containing the catalyst. In the case of oxidation/dehydrogenation, the reactor operates adiabatically and the operation is regulated so that the overall reaction is substantially athermic. This eliminates the need for any heat exchange system in the reactor. Above 600°C, however, formaldehyde is subject to thermal decomposition into hydrogen and carbon monoxide. As soon as it is formed, it must therefore be quenched in a boiler, which produces low-pressure steam. In the case of oxidation, the catalyst is placed in a tube bundle around which flows a heat transfer fluid designed to keep the temperature of the operation constant and used to produce low-pressure steam.
- (c) Absorption of formaldehyde and subsequent purification; the reactor effluent flows in countercurrent streams in water scrubbers which play a dual role: to cool the gases and to rid them of unconverted formaldehyde and methanol. As required, the unconverted methanol is separated by distillation and recycled, together with a formaldehyde solution whose concentration can be adjusted to the customer's standards.

B. The different processes

a. Processes using silver catalysts

Partial oxidation techniques were the first to be industrialized. After having been outclassed for some time by iron molybdate processes, they have marked substantial improvements in recent years. The main processes include the following:

- (a) Bayer, Chemical Construction, Ciba, Du Pont, IG Farben (Interessengemeinschaft der Farben Industrie), Fischer (industrialized by Hoechst-Uhde), modified Fischer (marketed by Borden), Gulf, Lambiotte, Léonard (developed by Monsanto), Meissner, Mitsubishi Koatsu etc.
- (b) The CdF (*Charbonnages de France*) Chimie process (formerly *Usines Chimiques de Mazingarbe*), which employs a catalyst consisting of silver-coated carborundum. Absorption takes place at 200°C in a three-stage column with overhead water injection. Heat is removed by appropriate liquid recycling. The aqueous solution of crude formaldehyde is fractionated under vacuum in a 60-plate column. Formaldehyde containing 45 per cent weight is obtained with a maximum of 1 per cent methanol and less than 500 mg/l of formic acid.

- (c) The BASF process (Fig. 1.30) of which two versions exist:

The earliest employs supported silver crystals. It leads to a heat balance equalized between the vaporizer and the exchanger/reactor stage. It avoids methanol distillation and recycling, and achieves sufficient once-through conversion to leave the residual alcohol in the formaldehyde solution. The total yield is 87.5 molar per cent based on the methanol introduced, and 91 per cent in relation to the methanol converted⁽¹⁴⁾. The formaldehyde concentration of the final product ranges from 40 to 44 per cent weight.

The latest version recirculates the residual gases over a multi-layer silver crystal catalyst at a higher temperature (680 to 720°C), allowing once-through conversion of over 98 per cent and a yield close to 90 molar per cent. The absorption step is designed to obtain formalin solutions containing 50 to 55 per cent weight that can be used directly to manufacture urea/formaldehyde glues.

- (d) The ICI process: the catalyst system, consisting of silver crystals, forms a shallow layer 1 cm thick and 1.7 m in diameter inside the reactor for production of 45,000 t/year of formaldehyde containing 37 per cent weight. This reactor is also mounted directly on the system that recovers heat from the reactor effluent. Catalyst life is 8 to 18 months, and it can be regenerated on site. Unconverted methanol is recycled.
- (e) The Degussa process: excess methanol is used instead of make-up water in the feed to facilitate heat transfers. The temperature is about 515 to 550°C in a reactor containing a bed of silver crystals held by silver metal gauze. Heat is recovered from the reactor effluent immediately afterwards. A distillation stage guarantees recycling of the excess methanol and the desired formaldehyde purity. The yield is 91 molar per cent and catalyst life is from 6 to 8 months.

b. Processes employing iron/molybdenum catalysts

The main processes are as follows:

- (a) The Formox processes by *Reichhold* and *Perstorp*, as well as the Perstorp Formaldehyde process (Fig. 1.31). Like the other techniques employing this type of catalyst, they operate with a multi-tube reactor with coolant flow on the shell side, where medium-pressure steam is produced. They comprise the recirculation of a fraction of residual gases, and absorption designed to obtain a solution containing 60 per cent weight of formaldehyde and less than 1 per cent methanol. The yield is higher than 91 molar per cent, for a once-through conversion greater than 98 per cent. In catalysis by iron and molybdenum oxides, this technology is currently the most widespread.
- (b) The Fischer-Adler, Hiag-Lurgi, IFP-CdF Chimie, Lummus, Montedison, Nikka-Topsoe, Protex, SIR-Euteco, Soviet Union, Western processes etc.: from the technological standpoint, they display only minor differences between each other and with the Perstorp techniques, and are mainly distinguished in relation to the catalyst (composition, use, preparation and performance, including resistance and life).

(14) The difference is due to methanol left in solution in the formaldehyde.

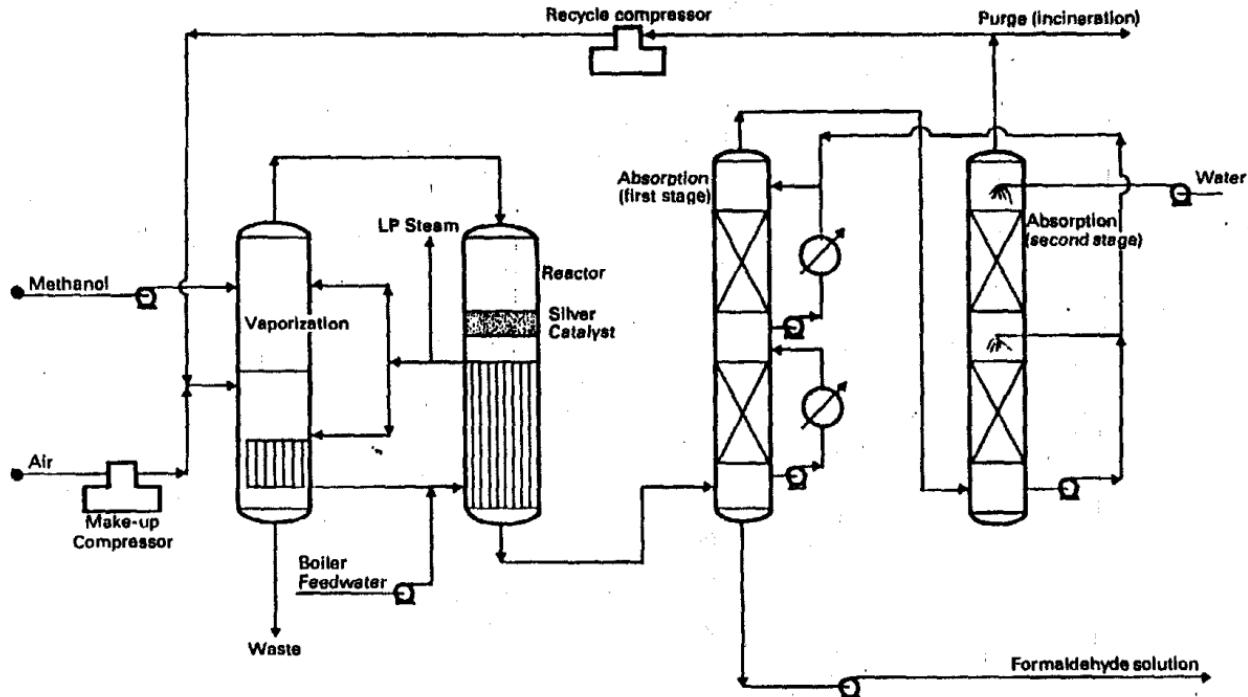


Fig. 1.30. Formaldehyde manufacture by silver catalysis. BASF process with off-gas recycle.

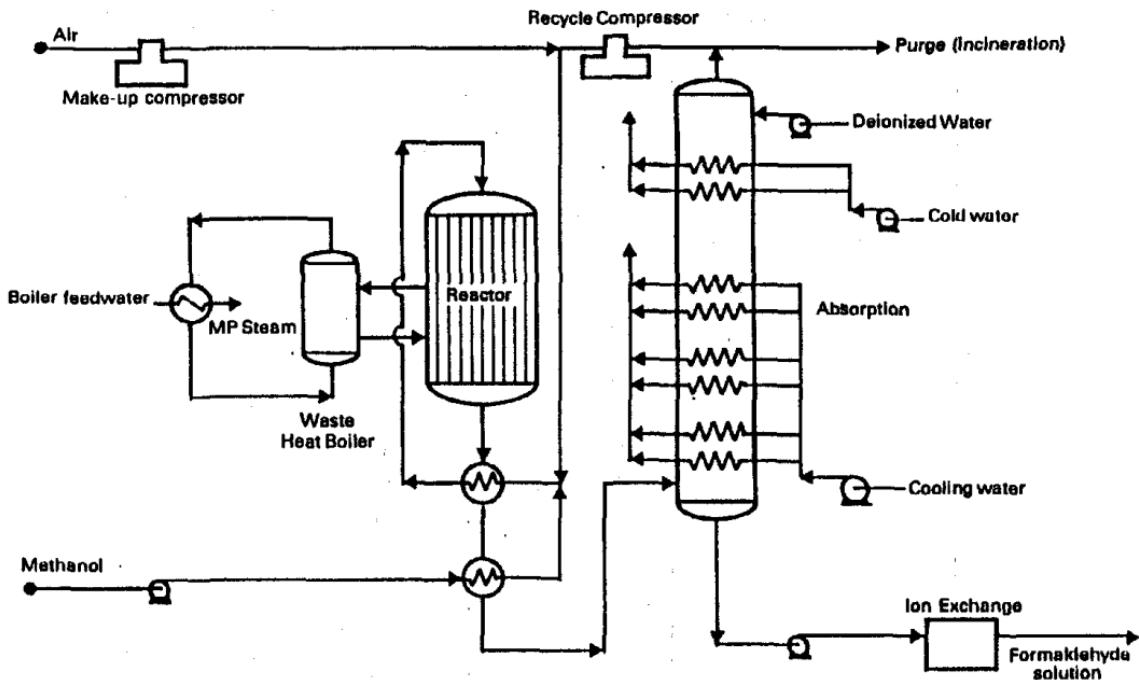
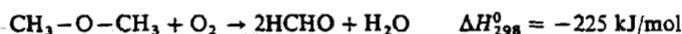


Fig. 1.31. Formaldehyde manufacture by iron molybdate catalysis. Reichhold-Perstorp processes.

c. Remarks

- Recent techniques attempt to develop a catalyst system that can be used in a fluidized bed, allowing better dispersion of heat within the catalyst and more effective control of selectivity.
- The oxidation of dimethyl ether, a process developed by the Japanese company *Akita Petrochemicals*, is similar to the foregoing techniques. It is based on the oxidation of dimethyl ether, which is a by-product of methanol synthesis in the high-pressure processes:



The catalyst is a mixture of metallic oxides deposited in a fixed bed in a multi-tube reactor and operating in the vapor phase. The heat of reaction is removed by the circulation of molten salts. Conversion takes place at 450 to 500°C, at $0.1 \cdot 10^6 \text{ Pa}$ absolute, with VHSV ranging from 1000 to 4000 h^{-1} . Once-through conversion ranges from 90 to 100 per cent and yield from 70 to 80 molar per cent. One unit is in operation in Japan.

1.5.3 Economic data

Table 1.27 summarizes the average economic data concerning formaldehyde manufacturing processes using silver and iron molybdenum catalysts. They refer to the latest technologies and a capacity of 67,500 t/year of 37 per cent weight formalin.

TABLE 1.27

FORMALDEHYDE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

PRODUCTION CAPACITY 67,500 t/year OF AQUEOUS FORMALDEHYDE (37% Wt)
(25,000 t/year of 100% FORMALDEHYDE)

Catalyst	Silver	Iron molybdenum oxide
Typical technology	BASF	Perstorp
Battery limits investments ($10^6 \text{ US\$}$)	5.3	7.9
Consumption per ton of aqueous formaldehyde (37% Wt)		
Raw materials		
Methanol (t)	0.437	0.425
Utilities		
LP steam (t)	(-) 0.3	(-) 0.6
Fuel (10^6 kJ)	(-) 1.4	-
Electricity (kWh)	40	80
Cooling water (m^3)	40	20
Process water (m^3)	0.5	1.0
Boiler feedwater (m^3)	0.3	0.6
Catalyst and chemicals (US\$)	1.4	2.5
Labor (Operators per shift)	2	2

1.5.4 Uses and producers

Table 1.28 provides an indication of the average commercial specifications of industrial formalin solutions.

Table 1.29 lists the main uses of formaldehyde in Western Europe, the United States and Japan in 1984, as well as the production, capacities and consumption in these three geographic areas. Capacities are also given for 1986.

TABLE 1.28
AVERAGE COMMERCIAL SPECIFICATIONS OF FORMALIN SOLUTIONS

Solution	Inhibited	Non-inhibited				
Formaldehyde (% Wt)	37	44	37	44	50	56
Methanol (% Wt) max.....	5.8	6.7	1.8	2.0	2.0	2.0
Color (Apha) max.....	5	5	5	5	5	5
Turbidity (Hellige) max.....	5	5	5	5	5	5
Acidity (% Wt)	0.03	0.03	0.03	0.04	0.05	0.04
Iron (ppm) max.....	.1	0.5	1	1	1	0.75
Non-volatile residue (ppm) max.....	40	40	40	40	40	40

TABLE 1.29
FORMALDEHYDE⁽¹⁾ PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
1,4-butanediol	5	11	—
Hexamethylene tetramine.....	3	5	5
Methylene diisocyanate ⁽²⁾	2	4	2
Paraformaldehyde	—	—	7
Pentaerythritol	8	7	8
Polyacetal resins	6	8	19
Thermosetting resins	61	58	46
Melamine/formaldehyde resins	6	4	6
Phenol/formaldehyde resins	9	22	9
Urea/formaldehyde resins	46	32	31
Miscellaneous	15	7	13
Total	100	100	100
Production (10 ⁶ t/year)	3.95	2.65	1.15
Capacity (10 ⁶ t/year) ⁽³⁾	5.95	3.95	1.60
Consumption (10 ⁶ t/year)	3.95	2.65	1.15

(1) Based on 37% Wt of aqueous formaldehyde solutions.

(2) Methylene bis-4, 4' phenylisocyanate.

(3) In 1986 the worldwide production capacity of formaldehyde was about $14 \cdot 10^6$ t/year, with $6.0 \cdot 10^6$ t/year in Western Europe, $3.95 \cdot 10^6$ t/year in the United States and $1.65 \cdot 10^6$ t/year in Japan.

1.6 UREA

Urea ($\text{mp} = 132.7^\circ\text{C}$, $d_4^{20} = 1.335$ ⁽¹⁵⁾) occurs in normal conditions in the form of a solid that decomposes before reaching its boiling point, and which is industrially synthesized by the reaction of ammonia with carbon dioxide. It is a vitally important intermediate for the manufacture of fertilizers.

1.6.1 Process characteristics

1.6.1.1 Reactions

Urea is manufactured from ammonium carbamate by dehydration according to the following main reactions:



where g = gas; l = liquid.

The first conversion is exothermic and endentropic. The second is endothermic and exentropic. Both are balanced and, in the operating conditions, it is impossible to achieve:

- (a) Total conversion of the reactants (NH_3 and CO_2).
- (b) Complete disappearance of the intermediate product, ammonium carbamate.

This situation, which is due to the thermodynamic properties of the reactants and products, is further aggravated by the fact that the carbamate-to-urea conversion reaction is much slower than carbamate formation. This makes it necessary to operate in two steps:

- (a) In the first, the effluent obtained consists of urea (40 to 60 per cent weight), ammonium carbamate, and unconverted ammonia and carbon dioxide.
- (b) In the second, ammonium carbamate is removed by decomposing it by the reverse of the formation reaction, thus regenerating the initial reactants.

It should also be added that the ammonium carbamate solution produced by the first step is an extremely corrosive mixture, whose handling must be minimized.

The main side reaction leads to the formation of biuret, especially during the recovery and purification of urea, when the crude effluent is raised to an excessively high temperature:



Biuret is a poison to flora if its content is too high. Its concentration must be kept below 0.9 per cent weight. In practice, urea contains less than 0.3 per cent weight.

(15) Specific gravity, 68.0/39.2.

1.6.1.2 Operating conditions

A. Synthesis reaction

Urea is synthesized from ammonia and carbon dioxide at temperatures ranging from 170 to 210°C, at pressures between 12 and $30 \cdot 10^6$ Pa absolute. The present tendency is to use a pressure of about $15 \cdot 10^6$ Pa absolute.

The reaction temperature must be such that:

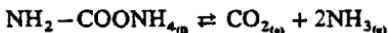
- (a) The ammonium carbamate is liquid ($> 183^\circ\text{C}$).
- (b) Conversion at equilibrium is a maximum: calculations show that this temperature rises directly with the NH_3/CO_2 ratio, and the range of 180 to 190°C is generally selected.

The processes usually differ by the composition of the reactor feed gas. Some processes employ a large excess of ammonia with NH_3/CO_2 ratio ranging from 4 to 6. This achieves high conversion of carbon dioxide (75 to 80 per cent). Others use only a small excess or even operate with reactants in stoichiometric proportions. This leads to lower conversion (40 to 50 per cent) and requires recycling of the unconverted gases.

In view of the inhibiting effect of oxygen in the corrosive action of the reaction medium, small amounts of air are added to the carbon dioxide feed. This addition is claimed to allow the easier removal of certain impurities. However, if the CO_2 employed is obtained from an ammonia plant, it must first be rid of the hydrogen it contains by catalytic oxidation, to avoid subsequent explosion hazards.

B. Ammonium carbamate decomposition reaction

This is the point where the processes display the widest differences. Two methods are theoretically available to carry out the decomposition reaction:



a. Lowering the temperature and pressure

Lowering the temperature and pressure shifts the equilibrium towards the initial reactants. The gaseous mixture is then recompressed, causing its recombination, and the carbamate solution is recycled.

If ammonia is present in excess, it separates from the carbamate solution and is recycled in gaseous form. To minimize the total costs of recompression of the gaseous compounds, decomposition is carried out in two stages, and the gases produced are recycled after each. As a rule, the first operates at $2 \cdot 10^6$ Pa absolute, and the second at 0.1 to $0.2 \cdot 10^6$ Pa absolute, at temperatures in the range of 160 to 200°C.

b. Shift of the dissociation equilibrium

Based on the law of mass action and Dalton's law, it can be shown that the dissociation pressure (P) of liquid carbamate into its gaseous components is governed by the equation:

$$P = \frac{0.53}{\sqrt[3]{x_{\text{NH}_3}^2 \cdot x_{\text{CO}_2}}} P_1$$

where P_1 is the dissociation pressure for the stoichiometric mixture $\text{NH}_3, \text{CO}_2 = 2$. This is a function of the temperature. x_{NH_3} and x_{CO_2} are the molar fractions in the gas phase.

Clearly, if the proportion of one of the components in the gas phase is increased, $x_{\text{NH}_3} \rightarrow 1$, or $x_{\text{CO}_2} \rightarrow 1$, the dissociation pressure tends towards infinity. Hence it appears possible to achieve the decomposition of the carbamate by ammonia or carbon dioxide stripping.

This expedient offers the advantage of achieving the decomposition of the carbamate at a pressure equal to that of the synthesis, and accordingly reducing the costs of recompression of the carbon dioxide/ammonia mixture.

C. Biuret formation reaction

Biuret mainly appears during urea concentration and prilling treatments. Its rate of formation⁽¹⁶⁾ during evaporation varies directly with the temperature and reaction rate, and inversely with the pressure.

1.6.2 Industrial manufacture

1.6.2.1 Main schemes

Two main types of process can be distinguished:

- (a) Conventional techniques.
- (b) Technologies featuring the decomposition of ammonium carbamate by gas stripping.

A. Conventional processes

The different industrial processes of this type differ as follows.

a. Once-through processes

These are the earliest, operating at $24 \cdot 10^6$ Pa absolute, and around 180 to 190°C, in which the carbamate is decomposed at about 160°C by simple flashing in two stages (1.7 and $0.2 \cdot 10^6$ Pa absolute). The ammonia and carbon dioxide recovered are sent to other units (nitric acid, ammonium sulfate, ammonium nitrate etc.).

This type of installation, which was industrialized by *Chemico* (I), *CPI* (*Chemical Processes of Ohio Inc.*)-*Vulcan*, *Inventa*, *Stamicarbon*, *Weatherly* etc., was abandoned with the increase in unit manufacturing capacities, and the consequent need to find markets for the by-products.

b. Processes with partial recycle of liquid ammonia

The effluent from the synthesis reactor is flashed and sent to a column, in which the excess ammonia is separated, condensed and recycled as a liquid to the reactor. The

(16) The following semi-empirical formula has been proposed:

$$B (\text{g } 100 \text{ g urea/min}) = 0.55W^{0.4} \cdot P^{0.35} (\text{mmHg}) \cdot 10^{12.35 - 6.058 T^\circ\text{K}}$$

↓
gH₂O evaporated per 100 g urea/min

carbamate is then decomposed by two-stage expansion. This technique was developed in particular by *Chemico*, *CPI-Allied*, *Inventa*, *Montecatini* etc.

c. Total-recycle processes

Ammonium carbamate is decomposed by flash in several stages (two to four). Ammonia and carbon dioxide in excess or liberated can then be recycled to the reactor which operates at about 20 to $21 \cdot 10^6$ Pa absolute, and around 200°C, by two possible variants:

- (a) In gaseous form, which presents the drawback of generating high recompression costs, although a significant improvement was provided by the introduction of centrifugal compressors. Processes of this type are those of CPI-Allied, Chemico (II) (Thermo Urea Process) etc.
- (b) In liquid form (ammonia and ammonium carbamate), by associating with each expansion stage (normally two) an absorber operating at the same pressure. This operation, in the presence of water, guarantees the recombination of the reactants after their condensation, yielding an aqueous solution of carbamate at the bottom, as well as the evaporation, at the top of the column, due to the exothermicity of the reaction, of excess ammonia which is then recondensed. These liquid recycles eliminate the need for compressors, but give rise to substantial corrosion. Among the earliest liquid recycle processes are those of Chemico (I), Inventa, Lonza-Lummus, Montecatini-Fauser, Pechiney-Grace, SNAM (I), Stamicarbon (I) etc. Among the latest optimized versions are the techniques developed by *Mitsui Toatsu* (Advanced for Cost and Energy Saving : ACES process), *Montedison* (Iso-baric Double Recycle : IDR process), *Urea Technologies Inc.* (Heat Recycle Urea Process : HRUP) etc.

d. Integrated processes

This version, developed in particular by *SNAM*, *Mitsui Toatsu*, *Ammonia-Casale* etc., integrates the ammonia and urea manufacturing units. It offers the following advantages:

- (a) Elimination of the compression costs of CO₂, which is produced directly by the preparation of ammonia synthesis gas.
- (b) Direct use of ammonia.
- (c) Simplification of the CO₂ absorption stage in the ammonia manufacturing unit, because the absorbent regeneration section disappears, since the carbon dioxide is directly recovered by means of an aqueous solution of carbamate and ammonia.

B. Processes with carbamate decomposition by gas stripping

These are total-recycle processes operating with an unconverted product recirculation loop at nearly constant pressure, ranging between 15 and $20 \cdot 10^6$ absolute.

As in the conventional techniques, urea is produced at about 180 to 200°C. On the other hand, the residual carbamate is decomposed at the synthesis pressure, by reducing its partial pressure by means of gas stripping. The recombination of the reactants thus liberated occurs after their condensation, by passage in an absorber or a scrubber, which also serves to recondense the fractions vaporized during the reaction, and to achieve recycling entirely in liquid form. To minimize corrosion problems, the different effluents are normally caused to flow by gravity, or by vaporization, or even by means of ejectors.

Industrial processes operating under this principle are distinguished by the type of stripping gas selected:

- (a) Stamicarbon II: carbon dioxide.
- (b) SNAM II: ammonia.
- (c) Montedison: ammonia and carbon dioxide in succession, acting in a two-step decomposition.

1.6.2.2 Technical characteristics of total-recycle processes

A. Base scheme (Fig. 1.32)

The reactants, purified to remove carbon monoxide and moisture, are compressed separately and then introduced into the reactor, where the carbamate is rapidly formed. The reactor normally operates adiabatically, and the temperature must be stringently controlled due to severe corrosion by ammonium carbamate solutions above 200°C.

The reactor effluent, consisting of urea, ammonium carbamate and unconverted reactants, is subjected, by altering the operating conditions, to a decomposition that converts part of the ammonium carbamate to carbon dioxide and ammonia. The resulting gaseous product is compressed and condensed. This leads to renewed formation of carbamate which is recycled to the reactor in aqueous solution, while the excess ammonia is mixed with fresh ammonia. The entire operation is repeated to decompose all the carbamate. The final solution obtained contains 72 to 76 per cent weight of urea, and the final purity desired can be obtained by a finishing treatment.

If the biuret content has to be in the range of 0.7 to 0.9 per cent (standard fertilizer), several evaporation operations are first conducted under vacuum with limited residence time, followed by centrifuging, and terminating in spraying of the product in a prilling tower. Lower biuret contents (0.2 to 0.3 per cent) require fractionated crystallization followed by granulation.

Conventional prilling techniques make use of towers in which melted urea is introduced at the top as a spray. These natural and forced-draft prilling towers also act as coolers. Hence, to obtain large-sized prills (4 to 6 mm), required for certain fertilizer uses, they may be up to 50 to 80 m in height. They also require auxiliary antipollution facilities to remove the fines from the gases discharged to the atmosphere. Several optimized systems, with fluidized beds, for example, have been developed to reduce the size of these towers (*Stamicarbon, SNAM, Mitsui Koatsu, Montedison etc.*). The trend today is to replace them by rotary units (drums, tanks, trays etc.) which are more compact, less pollutant, but of limited unit capacity (500 t/day), and to generalize the use of fluidized beds. This is reflected by the granulation techniques developed by *MTC/TEC (Mitsui Koatsu/Toyo Engineering Co.), NSM (Nederlandse Stikstof Maatschappij NV), Norsk Hydro etc.*

B. Stamicarbon processes (*Nederlandse Staats Mijnen: DSM*)

The Stamicarbon I process is a conventional total-recycle technique. Its special feature consists in introducing small amounts of oxygen into the reaction medium to minimize corrosion.

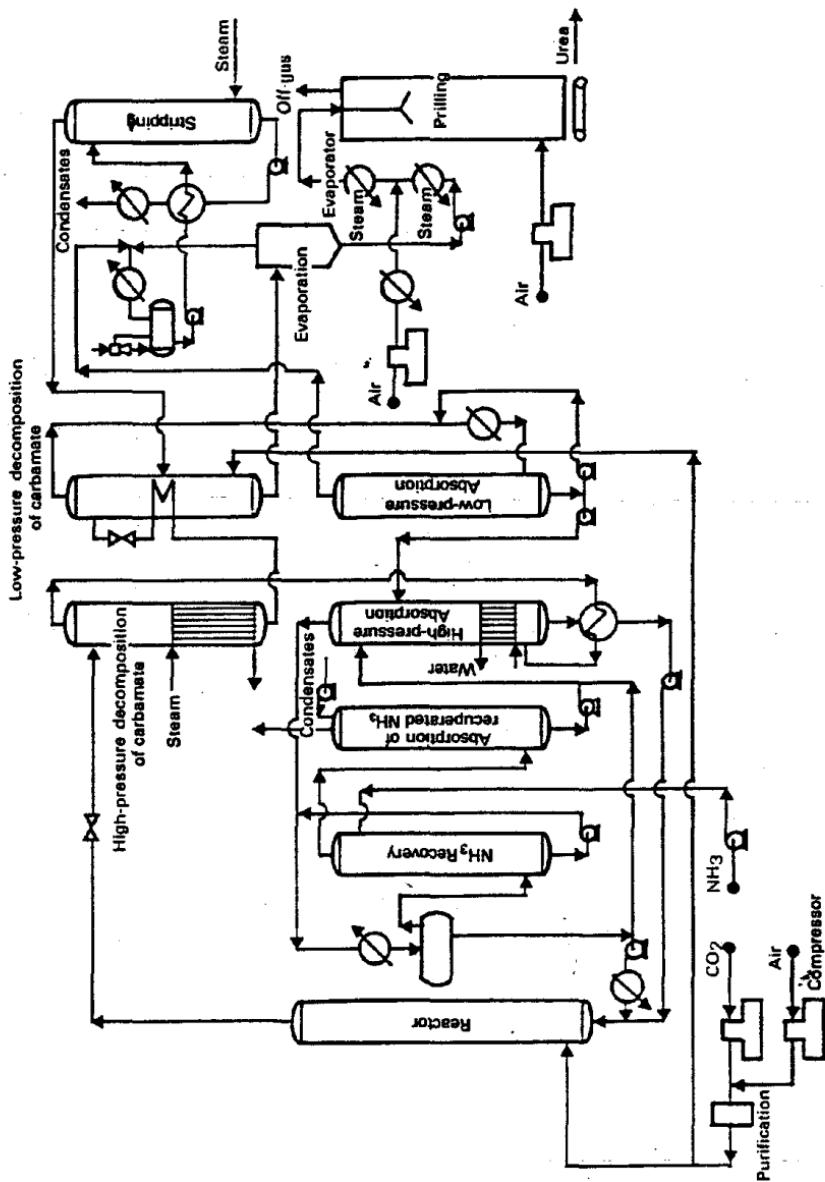


Fig. 1.32. Urea manufacture. Conventional Mitsui Tontsu process.

This was followed by the Stamicarbon II process, based on the decomposition of ammonium carbamate by carbon dioxide stripping (Fig. 1.33). The urea synthesis loop features four main steps in this case:

- (a) Condensation of CO_2 and ammonia to form the carbamate. This operation takes place in a conventional heat exchanger, between 150 and 170°C, at about $14.5 \cdot 10^6$ Pa absolute. It uses the liquid feed ammonia as well as the secondary recycling of an aqueous phase, consisting of carbamate and residual reactants, which are introduced together by means of an ejector to minimize corrosion problems at elevated temperature. The condensation also takes place on the primary recycling of unconverted reactants which, together with make-up CO_2 , is taken from the carbamate decomposition stage by gas stripping. The reaction is exothermic and produces low-pressure steam.
- (b) Conversion of the carbamate to urea, in a vertical reactor operating between 170 and 185°C, at $14.5 \cdot 10^6$ Pa absolute, with an N/C ratio of 2.8 to 2.9 (theoretical value 2.4), residence time of 45 to 60 min, and once-through conversion of about 60 per cent.
- (c) Decomposition of unconverted carbamate by entrainment using feed CO_2 . This also takes place at $14.5 \cdot 10^6$ Pa absolute, around 185°C, in a falling film heat exchanger, heated on the shell side by high-pressure steam. The make-up carbon dioxide is first rid of the hydrogen it contains by oxidation on a platinum catalyst. This operation helps to separate 85 per cent of the unconverted CO_2 and ammonia.
- (d) Recycling of unconverted reactants, either directly in gaseous form, or indirectly in liquid form, after treatment of the aqueous urea solution from the stripping stage. After flash at 0.2 to $0.3 \cdot 10^6$ Pa absolute, this operation includes distillation during which the gaseous fractions, after cooling and partial condensation, recombine partly to form the carbamate. The residual gases are scrubbed to minimize reactant losses.

Apart from the concentration of urea in a series of evaporators, the rest of the flow sheet comprises passage through a prilling tower, as well as antipollution and recovery treatment on the different gas and liquid streams.

C. SNAM Progetti processes

The techniques developed by *SNAM Progetti* have witnessed developments similar to those of *Stamicarbon*. The SNAM I process is comparable to the conventional total-recycle versions. The SNAM II technology, which has led to several variants, uses high-pressure ammonia stripping of the ammonium carbamate decomposition products (Fig. 1.34). Initially, this operation took place directly with make-up ammonia. But, given its high solubility in the aqueous solution of urea, it was subsequently decided to presaturate the medium and generate the gaseous ammonia required for stripping *in situ* by heating.

The synthesis loop also comprises four main stages, three under high pressure and the fourth under reduced pressure:

- (a) Carbamate formation by condensation, in a unit of the reboiler type, of gases produced by the stripping stage, to which a cold recycle stream is added, consisting

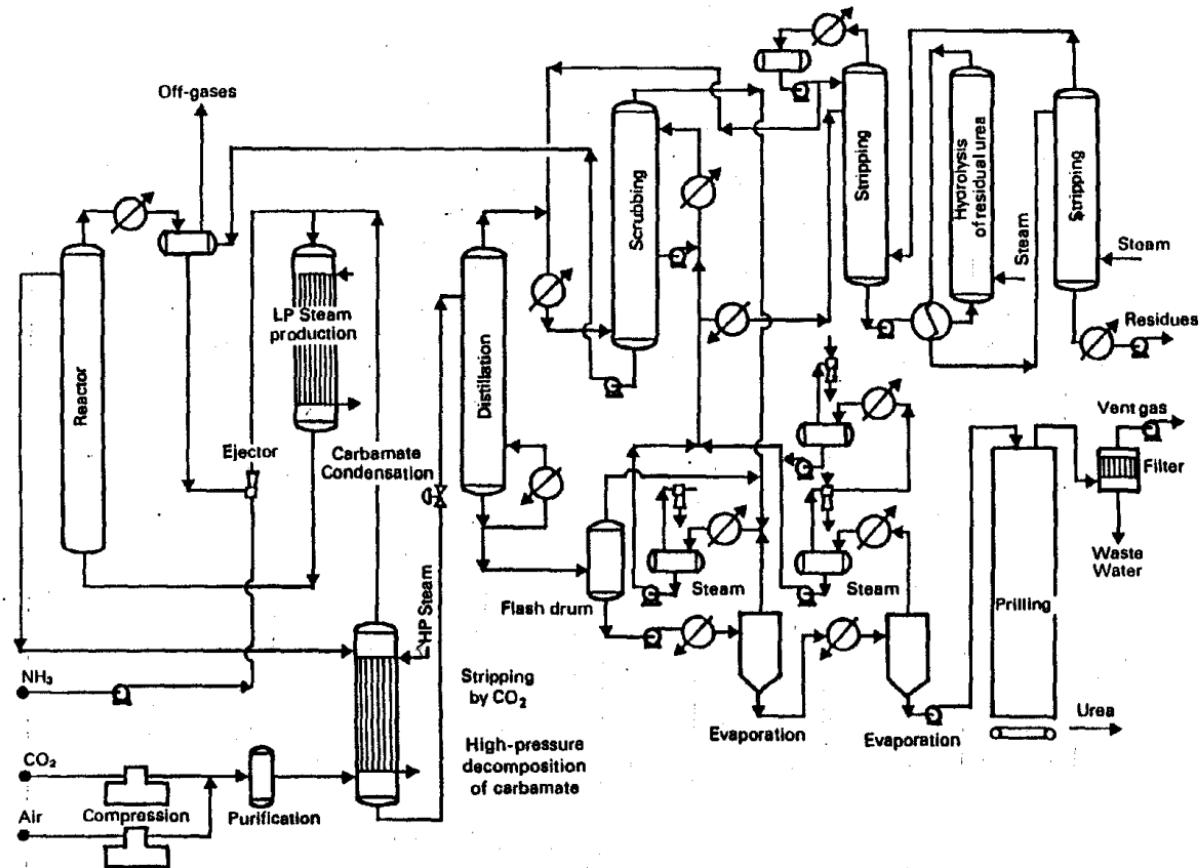


Fig. 1.33. Urea manufacture. Stamicarbon process.

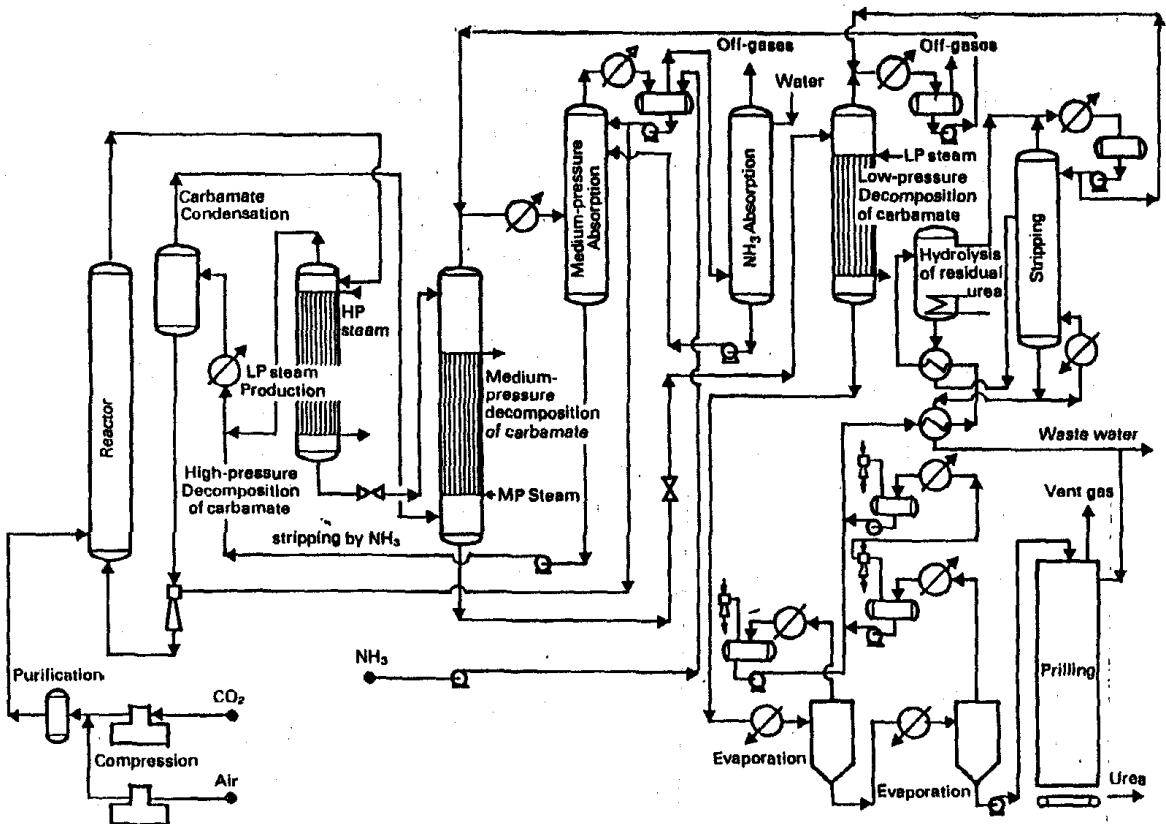


Fig. 1.34. Urea manufacture. SNAM/Progetti process.

partly of reactants and partly of carbamate in aqueous solution, and produced by subsequent recovery treatments. This conversion, which takes place around 180 to 190°C at $14.5 \cdot 10^6$ Pa absolute, allows the recovery of low-pressure steam.

- (b) Urea production in a vertical reactor, operating at $15 \cdot 10^6$ Pa absolute, at about 190 to 200°C, with an N/C ratio of about 3.6 to 3.8, residence time of around 45 min, and once-through conversion of carbamate from 65 to 70 per cent. This operation combines the rapid exothermic formation of carbamate at the reactor bottom, from feed CO₂ and excess ammonia present in the reaction medium, with the much slower endothermic decomposition of carbamate to urea. The excess ammonia, which inhibits the production of biuret, helps to operate at a higher temperature and hence to increase the dehydration yield. The passage of the aqueous solution from the condenser to the reactor takes place by gravity and by means of an ejector. The make-up CO₂ is purified by prior catalytic oxidation in order to reduce equipment corrosion.
- (c) Decomposition of unconverted carbamate, which takes place in three steps, the first at high pressure ($14.5 \cdot 10^6$ Pa absolute), around 200 to 210°C, by stripping by gaseous ammonia, generated *in situ* from the excess present in liquid form. A falling film heat exchanger is used for the purpose, heated on the shell side by high-pressure steam.
- (d) Recycling of unconverted reactants, whether recombined or not, at low temperature (< 100 or even 50°C) on completion of the other two carbamate decomposition stages, at 1.8 and $0.5 \cdot 10^6$ Pa absolute respectively. This removal takes place both by gas stripping and reduced pressure, followed by absorption, particularly of the ammonia, and condensation during which the recombination takes place.

The aqueous solution of urea thus purified then undergoes concentration and prilling treatment similar to those already described.

D. Other total-recycle processes

The processes of the following licensors are worth mentioning among the remaining total-recycle processes for urea synthesis:

- *Mitsui Toatsu Chemicals*, which developed a whole series of variants around a standard basic scheme including:
 - (a) "Recycle C, Improved Process": $\cong 200^\circ\text{C}$, $25 \cdot 10^6$ Pa absolute, decomposition of the carbamate by lowering the pressure in two steps (1.8 and $0.3 \cdot 10^6$ Pa absolute).
 - (b) "D Process"; similar to the C process, but with an additional high-pressure-separation.
 - (c) The "Advanced Process for Cost and Energy Saving" (ACES), licensed through *Toyo Engineering Corporation (TEC)*: 185°C , $17.5 \cdot 10^6$ Pa absolute, N/C ratio $\cong 4$, with decomposition of the carbamate by CO₂ stripping at high pressure and then reduced pressure (2 and $0.3 \cdot 10^6$ Pa absolute), and prilling.
- *Chemico (Chemical Construction Corporation)*, which commercialized a number of versions of a liquid flow process (variant I) and proposed the "Thermo Urea Process"

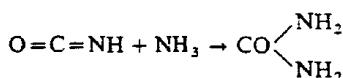
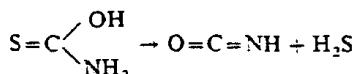
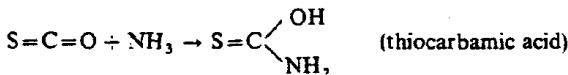
(variant II) which recycles the product in the gas phase by means of centrifugal compressors.

- *CPI-Allied (Vulcan Cincinnati)*, which uses monoethanolamine to absorb selectively the CO₂ contained in the gaseous effluent produced by the decomposition of the carbamate and thus only recycles the ammonia.
- *Montedison*, which originally participated in the *Montecatini-Fauser* joint venture to market a number of total-recycle variants, and now presents its IDR (Isobaric Double Recycle process) technique. This process operates at 20 . 10⁶ Pa absolute, around 190 to 200°C, with an N/C ratio of 4 to 5 in the reactor. Unconverted carbamate is decomposed in two successive gas stripping steps, one with ammonia, and the second with CO₂, in the pressure conditions of urea synthesis, i.e. 20 . 10⁶ Pa absolute.
- *Ammonia-Casale*, which proposes a technology that remodels the processes with carbamate decomposition by gas stripping : the SRR (Split Reaction Recycle) process. This involves adding to the synthesis loop in place a side reaction section operating at 20 to 22 . 10⁶ Pa absolute, with an N/C ratio of 4 to 5, making it possible to reach the high conversion level achieved by techniques without gas stripping (70 to 75 per cent).
- *Urea Technologies Inc. (Mavrovic)*, which offers the Heat Recycle Urea Process, (HRUP), whose main feature is the hot recirculation of the aqueous carbamate solution, which enhances the energy balance. This is a conventional technique, operating at 20 to 22 . 10⁶ Pa absolute, 190 to 200°C, N/C ratio ≈ 4, and once-through CO₂ conversion ≈ 71 to 72 per cent.

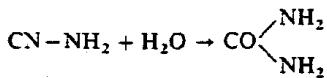
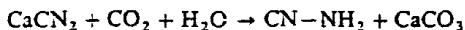
1.6.3. Other methods for synthesizing urea

These methods attempt to avoid the use of ammonium carbamate, and investigations have focused on two main processes :

- (a) The Lion Oil process (*Monsanto*), which carries out the following reactions at 120°C and 2 . 10⁶ Pa absolute :



(b) The calcium cyanamid process:



1.6.4 Economic data

Table 1.30 lists some of the available economic data on the principal urea manufacturing processes.

TABLE 1.30
UREA PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
CAPACITY 500,000 t/year

Typical process	Stamicarbon II	SNAM II		Mitsui Toatsu	MTC/TEC
Biuret content (%).....	0.8	0.2-0.25	0.75	0.8	0.8
Finishing method	Evap.	Crys.	Evap.	Evap.	Prilling
Battery limits investments (10 ⁶ US\$) ..	42	46	47	51	46
Consumption per ton of urea					
Raw materials					
Ammonia (t)	0.57	0.57	0.57	0.57	0.57
Carbon dioxide (t)	0.75	0.75	0.75	0.75	0.75
Utilities					
LP steam (t)	0.8	0.9	0.9	1.0	0.9
LP steam (t) (credit)	(-) 0.2	(-) 0.4	(-) 0.2	(-) 0.4	-
Electricity (kWh) ⁽¹⁾	15-115	40-135	20-120	45-135	40-150
Cooling water (m ³)	65	60	75	70	90
Labor (Operators per shift)	4.5	4.5	4.5	4.5	5

(1) With or without auxiliary compressors electrically driven.

1.6.5 Uses and producers

Table 1.31 offers some information about the average commercial specifications for urea in two of its main uses.

Table 1.32 lists the main uses of urea in Western Europe, the United States and Japan in 1984, as well as the production, capacities and consumption in these three geographic areas. Capacities are also given for 1986.

TABLE 1.31
AVERAGE COMMERCIAL SPECIFICATIONS OF UREA

Grade	Fertilizer	Technical (Low biuret content)
Nitrogen (% Wt)	46.3	46.3
Water (% Wt) max.	0.3	0.3
Biuret (% Wt) min.	0.9	0.4
Free ammonia (ppm) max.	150	100
Iron (ppm) max.	2	1
Ash (ppm) max.	—	20
Hydrocarbons (ppm) max.	—	20
Color (Apha) max.	—	15
Turbidity (Apha) max.	—	20
pH min.	—	6.6

TABLE 1.32
UREA PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Fertilizers	85	80	31
Industrial uses ⁽¹⁾	10	10	} 69
Miscellaneous ⁽²⁾	5	10	
Total	100	100	100
Production (10 ⁶ t/year)	5.2	7.15	1.15
Capacity (10 ⁶ t/year) ⁽³⁾	7.4	7.60	1.75
Consumption (10 ⁶ t/year)	4.3	7.65	0.85

(1) Melamine, urea-formaldehyde resin, adhesives and plastics.

(2) Animal feeds.

(3) In 1986 the worldwide production capacity of urea was 87.8 · 10⁶ t/year with the following distribution:

United States	7.3	Western Europe	7.7	Middle East	4.2
Canada	2.4	Eastern Europe	20.4 ^(a)	Japan	2.2
Latin America	5.7	Africa	3.1	Asia and Far East	34.8 ^(b)

(a) Including USSR 12.5. (b) Including China 11.0.

Chapter 2

SOURCES OF OLEFINIC AND AROMATIC HYDROCARBONS

2.1 STEAM CRACKING

The vast growth of petrochemicals, connected with the expansion of the industries producing plastics, synthetic fibers, synthetic rubbers, detergents and many other organic chemicals, steadily requires greater amounts of hydrocarbon raw materials each year.

Natural gas and the petroleum fractions obtained after the primary fractionation of crude oil by distillation consist chiefly of saturated, paraffinic and naphthenic hydrocarbons, whose chemical reactivity is mediocre, precluding the development of diversified families of chemical compounds of varying complexity. This can only be achieved by using unsaturated aliphatic or aromatic hydrocarbons which, due to their many reactive potentialities, offer outstanding flexibility for organic synthesis. In this respect, acetylene, which was for many years the most widely used basic hydrocarbon in aliphatic chemistry, has gradually been superseded by ethylene, propylene and butadiene according to the synthesis considered, owing to its high production cost. Despite the fourfold increase in the price of crude oil which occurred in 1973 and its subsequent steady increase, ethylene still retained its economic advantage over acetylene from natural gas or from coal. Of course, for the time being, the lower price of crude oil makes using ethylene more attractive.

At the outset, ethylene was produced industrially by the liquefaction and fractionation of coke oven gases, by the dehydration of ethyl alcohol, and even by the partial hydrogenation of acetylene. This situation subsisted in many countries until the end of the Second World War. Simultaneously, however, inasmuch as ethylene demand continued to grow, producers turned increasingly to the pyrolysis of petroleum fractions (light gases, petrochemical naphtha, gas oil). At the industrial level, this technique was first developed in the United States. As early as 1920, *Union Carbide and Carbon Co.* built a pilot plant operating on ethane and propane, and this company went on to create the first chemical complex utilizing products derived from the pyrolysis of gas oil. This type of facility only made significant headway in Western Europe, beginning with the United Kingdom, and in Japan, after the end of the Second World War. In 1942, *British Celanese* built the first European steam cracking unit at Spordon operating on gas oil, with a

production capacity of 6000 t/year of ethylene. In 1946, *Shell Chemical* built the first petrochemical complex at Stanlow, using refinery gases as the pyrolysis feedstock. During the 1940-1950 period, the minimum capacity of ethylene production plants grew progressively from 10,000 to 50,000 t/year. Giant installations subsequently appeared, routinely producing 300,000 t/year of ethylene from petrochemical naphtha.

Steam cracking primarily produces ethylene, but also propylene, and, as secondary products, depending on the feedstock employed, a C₄ cut rich in butadiene and a C₅-cut with a high content of aromatics, particularly benzene. This inventory ignores the light and heavy products which, within the field of steam cracking, provide a substantial energy source allowing a certain degree of energy self-sufficiency.

The variety of products obtained by steam cracking makes this a key process around which to build the complex of user installations.

At the process level, steam cracking consists of the pyrolysis of saturated hydrocarbons from natural gas or petroleum fractions, in the presence of steam. Before going into the technological study of these units, it is first important to examine the physicochemical properties of the reactions involved (dehydrogenation, pyrolysis, dehydrocyclization and dealkylation).

2.1.1 Physicochemistry of the pyrolysis of saturated hydrocarbons

2.1.1.1 Thermodynamic considerations

The desired unsaturated hydrocarbons only appear to be stable in relation to the saturated structures from which they are derived at relatively elevated temperatures. This fact is illustrated by Fig. 2.1, which shows the variation of the free enthalpy of formation $\Delta G_{f,rxn}^0$ as a function of temperature, related to a carbon atom, of a number of characteristic hydrocarbon compounds. In this graph, and at a given temperature, a substance is unstable in relation to all the compounds or elements (C + H₂), whose representative point remains below its own, since formation from these compounds or elements requires an input energy: the substance is stable in the opposite case. Accordingly, hydrocarbons are unstable at all temperatures in relation to their elements, except for methane, which is stable at the low and medium temperatures.

Acetylene only becomes stable in relation to the simplest paraffins at temperatures substantially above 1000°C. The situation is more favorable for unsaturated hydrocarbons with lower energy content, such as ethylene, which is stable in relation to ethane above 750°C, and benzene, which is favored in relation to normal hexane above 350 to 400°C.

Given the extreme simplicity of the chemical structure of a saturated hydrocarbon, thermal activation can only cause the scission of a C—C or C—H bond. In the former case, the random scission of a C—C bond of the carbon chain — the cracking reaction — produces a paraffin and an olefin:



$$\Delta G_f^0 = 75,200 - 142T \quad \text{in J/mol}$$

The scission of a C—H bond gives rise to the formation of an olefin by dehydrogenation,

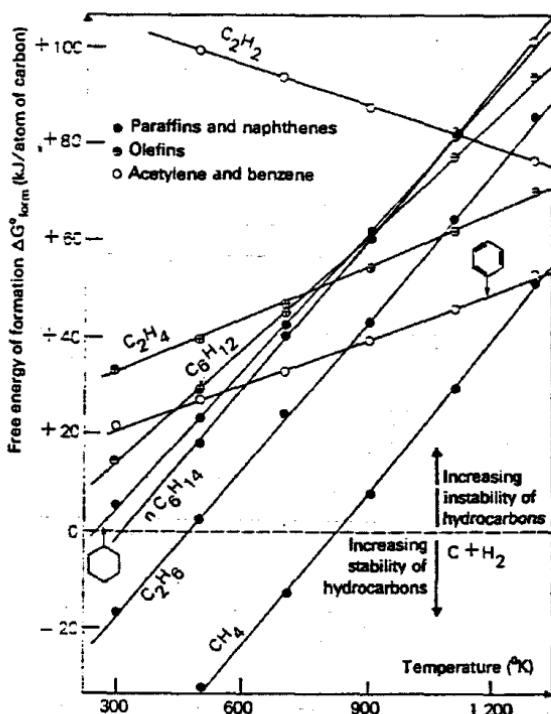


Fig. 2.1. Thermodynamic stability of hydrocarbons.

with the same number of carbon atoms as the initial saturated hydrocarbon, as well as hydrogen:



$$\Delta G_f^{\circ} = 125.400 - 142T \quad \text{in J/mol (for } p > 4\text{)}$$

These conversions are highly endothermic and take place with an increase in the number of molecules, which are therefore favored in terms of thermodynamics at high temperature and low pressure.

The comparison of the energies of the C–C and C–H bonds (345 kJ/mol and 413 kJ/mol respectively) also confirms that the primary act of the pyrolysis of saturated hydrocarbons resides in the scission of a C–C bond, because this process requires much less energy than that required to split a C–H bond.

2.1.1.2 Kinetic characteristics

The basic reaction governing the cracking of heavy fractions consists in the cracking of a saturated aliphatic hydrocarbon into a paraffin and an olefin (Fig. 2.2, reaction I).

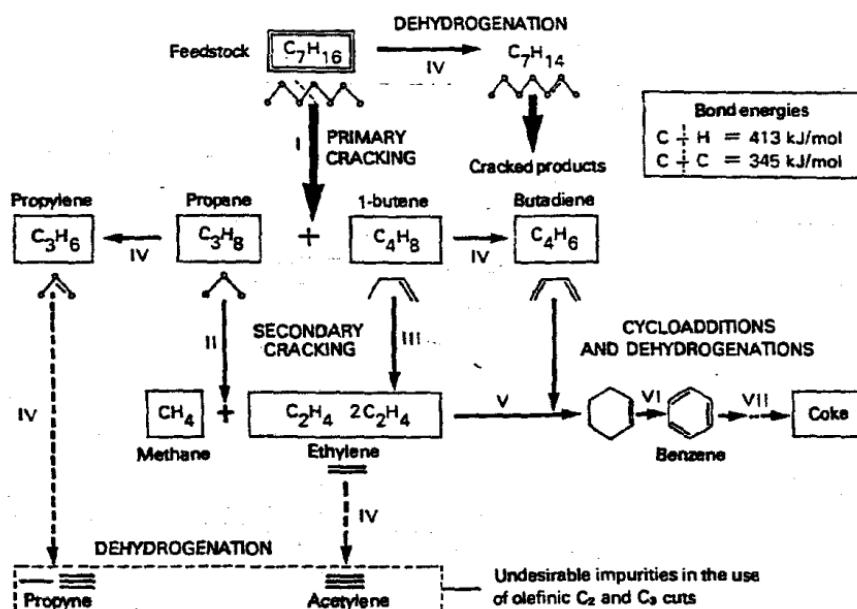


Fig. 2.2. Main reactions involved in hydrocarbon pyrolysis (From D. Decroocq, IFP).

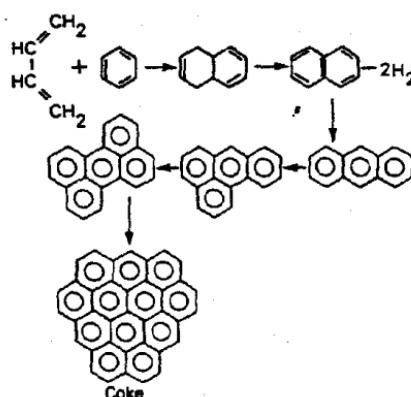


Fig. 2.3. Side products of pyrolysis. Formation of aromatic hydrocarbons and coke.

This is called primary cracking. By secondary cracking reactions (reactions II and III), the entities thus formed give rise, at various points of their hydrocarbon chain, to a number of light products, rich in olefins, whose composition and yield depend on the operating conditions selected.

Reactions achieving the more thorough dehydrogenation of olefins directly produced by cracking provide highly unsaturated compounds, such as acetylene derivatives (reaction IV), which are undesirable impurities in the use of C_2 and C_3 olefinic streams, or diolefins derivatives (reaction IV), which display pronounced chemical reactivity. In fact, the latter react in the reverse direction to cracking, and give rise to heavy products by the Diels and Alder reaction or cycloaddition (reaction V).

The compounds thus formed, if subjected to subsequent intense dehydrogenation (reaction VI), are capable of producing a number of aromatic hydrocarbons and particularly benzene. These constitute the natural precursors of condensed polycyclic substances which, according to their pasty or solid state, are designated by the general names of tars and coke (reaction VII and Fig. 2.3). This product can in no way be compared with graphite: this is because, although it is rich in carbon, its hydrogen content is still substantial and variable, depending on the feedstock and the operating conditions.

Whereas the cracking reaction rate becomes significant above 700°C, dehydrogenations only take place substantially above 800 to 850°C. Moreover, the processes of the formation of polycyclic hydrocarbons and coke only occur rapidly at temperatures above 900 to 1000°C. The adoption of long residence times or the elevation of the reaction temperatures hence favor the reaction yielding heavy aromatic derivatives at the expense of the production of light olefins by cracking.

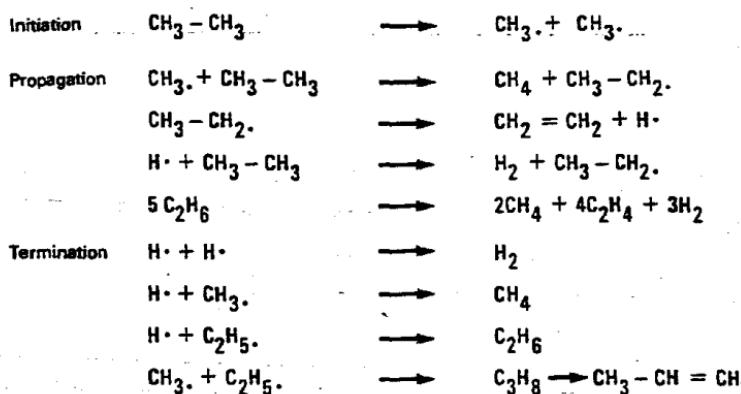
As for the polymerization of unsaturated aliphatic compounds (olefins, diolefins and acetylene derivatives), due to their high intrinsic reactivity, their polymerization is extremely rapid, even at low temperatures. However, since these reactions represent the reverse of cracking, they are not favored from the thermodynamic standpoint in the operating conditions of pyrolysis.

As a rule, with respect to the actual steps in cracking, the reactivity of the hydrocarbons increases with the number of carbon atoms, in each family. For a given number of carbon atoms, paraffins also exhibit higher reactivity than alkylaromatics, but lower than that of olefins.

The fact that the pyrolysis reaction proceeds by a free radical and a chain mechanism were pointed out by F.O. Rice. Initiation takes place by the homolytic scission of a C-C bond with the production of free radicals. These give rise to the reaction chain by extracting a hydrogen atom from the hydrocarbon and by forming a new free radical.

Considering the simple case of ethane, the ethyl radicals are obtained by attacking ethane by methyl radicals. The ethyl radicals are stabilized by supplying ethylene and a hydrogen radical (atomic hydrogen), which in turn attacks an ethane molecule to form an ethyl radical, and the reaction continues in this manner (Fig. 2.4). Through this mechanism, a single methyl radical can initiate the conversion of large quantities of ethane to ethylene and hydrogen. In fact, the radicals disappear in a number of so-called termination reactions which culminate in the stoppage of the chain. Whenever a new chain is initiated, a methane molecule is formed. Hence the pyrolysis of ethane produces hydrogen, methane and ethylene as primary products.

1) Case of ethane



2) General case

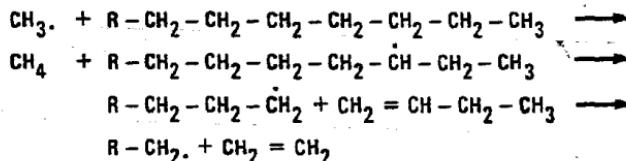
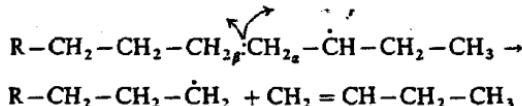


Fig. 2.4. Thermal cracking. Reaction mechanisms.

In the more general case, for example that of the pyrolysis of a long-chain paraffin, the radical formed by the scission of a C-C bond attacks one of the carbon atoms of the hydrocarbon and creates a new radical. This radical is stabilized by the scission of the bond located at the β position of the radical, constituting the β scission:



This type of scission of the molecule complies with the general principle of the least change in structure.

The new radical can either transfer its single electron to a new hydrocarbon molecule, and be converted itself to a paraffin, or undergo another scission at β . Hence the successive alkyl radicals decompose into olefin molecules until the remaining radical becomes either a hydrogen atom, or a methyl or ethyl radical, which serves as an initiator, so that the cycle is repeated.

In fact, the stripping of a hydrogen by alkyl radicals is not random: it depends on the degree of substitution of the carbon atom. The C-H bond is split more easily on

a tertiary carbon than on a secondary carbon, since the primary hydrogen is the most difficult to remove.

Due to this production of free radicals, pyrolysis reactions exhibit pronounced sensitivity to the geometry of the reactor, and the walls tend to favor the recombination of atoms and intermediate light radicals.

The thermodynamic and kinetic characteristics of pyrolysis examined above therefore impose a number of requirements concerning industrial operating conditions:

- (a) Considerable input of heat at a very high level.
- (b) Limitation of the hydrocarbon partial pressure in the reactor.
- (c) Very short residence times, to minimize the development of slower condensation processes.
- (d) Effective quench of the reactor effluents to fix the composition and prevent any subsequent change.

A variety of techniques is able to meet these requirements. They differ basically in the manner in which the heat is added. This transfer can hence be provided by means of solids or gases.

In the case of a solid heat carrier, the preheated feedstock is placed in contact with a refractory mass raised to a high temperature. Cracking lowers the temperature and generates coke deposits that must be removed. The state of the solid and the initial operating conditions are restored by combustion. These operations can take place in the same reactor cyclically on a fixed refractory (Wulff process) or in distinct units in which the solid exists in the form of moving or fluidized particle beds. In this case the hydrocarbon feedstock is injected in the combustion gases.

In industrial practice, however, the most widespread technique consists in passing a mixture of hydrocarbons and steam through tubes placed in a furnace. The hydrocarbons, which are raised to high temperature, are pyrolysed and the resulting products are separated after a rapid quench. Coke deposits are periodically removed by controlled combustion. This is the technology of steam cracking, which is the main focus of this chapter.

2.1.2 Operating variables of steam cracking

In a reactor that is the site of a thermal reaction in the gas phase, the main operating variables are the temperature, which sets the level of activation of the system, the residence time left to the reaction mixture to evolve in the conditions selected, and the pressure and reactant content of the feedstock, which are reflected in this case by the partial pressure of the hydrocarbons.

2.1.2.1 Reaction temperature

The feedstock cannot be raised to the reaction temperature instantaneously in a furnace tube. The temperature varies along the tube according to a certain profile. Figure 2.5 offers an illustration for three outlet temperatures (805, 815 and 825°C). The figures on the x-axis do not directly represent the length of the tube but the number of coils (ver-

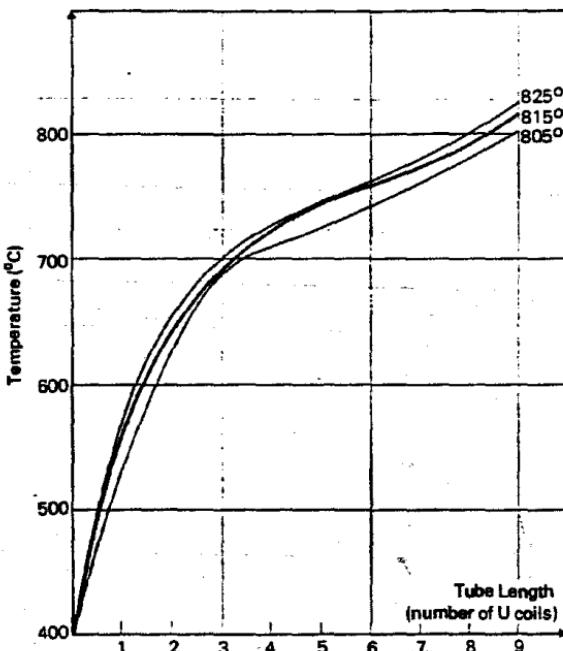


Fig. 2.5. Temperature profile in a naphtha pyrolysis tube.

tical tube sections between two top fixing points). The change in the slope occurring around 700°C marks the beginning of the cracking reactions, and the first part of the pyrolysis tube merely raises the hydrocarbon feedstock to the minimum temperature required by the kinetic characteristics of the conversion. In such a reactor, which features a steep thermal gradient, the temperature profile alone represents a reality that varies with each type of furnace and in accordance with the operating conditions adopted. At the industrial level, however, the effluent exit temperature is generally considered a significant indicator of the operation of a furnace.

These temperatures range from 700 to 900°C according to the type of feedstock treated. For ethane, they lie between 800 and 850°C in practice, whereas for heavy saturated hydrocarbons, such as those present in a gas oil, the operation is conducted at a thermal level 100°C lower due to their greater intrinsic reactivity.

As a rule, the temperature of the metallic wall of the tube is much higher than that of the gas stream passing through it. Hence, for a furnace exit temperature of 885°C, the "skin temperature" varies between 995 and 1040°C at different locations of the tube.

2.1.2.2 Residence time

Due to the existence of a high thermal gradient along a pyrolysis furnace tube, it is difficult to pinpoint the concept of residence time. A frequent solution is to define an

equivalent time, which is merely the residence time required, in an isothermal reactor operating at the furnace exit temperature, to achieve the conversion of the feedstock identical to that observed in a variable temperature furnace tube. In the case of an isothermal reactor, feedstock conversion is related to residence time by the equation:

$$\ln \frac{1}{1 - X_f} = k_1 \theta$$

where

X_f = molar conversion calculated from the molar flow rates of the reactant at the reactor inlet N_R^0 and outlet N_R^f :

$$X_f = \frac{N_R^0 - N_R^f}{N_R^0}$$

k_1 = first order rate constant for the reactor operating temperature,

θ = residence time given by the ratio of the reactor volume v to the feedstock volume flow rate in the reaction conditions D_R^0 :

$$\theta = \frac{v}{D_R^0}$$

In the presence of a temperature gradient, the rate constant k_1 varies between the inlet and outlet of the reactor according to Arrhenius' law:

$$k_1 = A \exp\left(-\frac{E}{RT}\right)$$

In these conditions:

$$\ln \frac{1}{1 - X_f} = \int_0^\theta k_1 dt = \int_0^\theta A \exp\left(-\frac{E}{RT}\right) dt$$

t is the residence time between the reactor inlet and the cross-section where the temperature of the reaction mixture reaches the temperature T . The definition of the thermal gradient in the form of an equation $T = f(t)$ serves to integrate the second member of this equation.

For an isothermal reactor operating at the final temperature T_f at the pyrolysis tube exit, the equivalent residence time θ_{equiv} , which serves to achieve an identical conversion of the feed, is given by the equation:

$$\ln \frac{1}{1 - X_f} = k_{1f} \cdot \theta_{equiv}$$

where $k_{1f} = A \exp\left(-\frac{E}{RT_f}\right)$ is the rate constant corresponding to the furnace outlet temperature.

Consequently:

$$\ln \frac{1}{1 - X_f} = \int_0^\theta k_1 dt = k_{1f} \cdot \theta_{equiv}$$

The equivalent residence time $\theta_{\text{equiv.}}$ is therefore expressed by:

$$\theta_{\text{equiv.}} = \frac{\ln \frac{1}{1 - X_f}}{k_{1f}} = \frac{\int_0^{\theta} k_1 \, dt}{k_{1f}}$$

Residence time is longer for heavy than for light feedstocks. Thus, in the steam cracking of ethane, propane and, to a lesser degree, butane, the differences in product yields for residence times ranging from 0.2 to 1.2 s are slight. For liquid feedstocks, on the other hand, residence times range from 0.2 to 0.3 s. Theoretically, even shorter residence times should improve the ethylene and propylene selectivity, but a number of technical and economic factors (strength of materials, furnace cost etc.) ensure that the lower limit is 0.2 s in practice.

However in the 1980's, the latest furnace designs offered times ranging from 0.2-0.08 s. Millisecond technology, developed by Kellogg Co and industrialized by Idemitsu Petrochemical Company at their Chiba factory in 1985 is operating at the lowest end of that range.

2.1.2.3 Hydrocarbon partial pressure and the role of steam

From the thermodynamic standpoint, pyrolysis reactions producing light olefins (cracking and dehydrogenation) are more advanced at low pressure, a range in which the condensation reactions are highly disadvantaged. This is why, owing to the pressure drops inherent in the circulation of the reaction mixture, furnace tubes operate at exit pressures close to atmospheric pressure.

Moreover, the condensation side-reaction rate is much more heavily influenced by the hydrocarbon content of the reaction mixture than the rate of the primary reactions, which are substantially of the first order with respect to the reactants. A decrease in the partial pressure of the hydrocarbons, by dilution with steam, for example, reduces the overall reaction rate, but also helps to enhance the selectivity of pyrolysis substantially in favor of the light olefins desired. Apart from this specifically kinetic role, steam exerts a number of other beneficial effects:

- (a) Heat input during the introduction of steam into the feedstock.
- (b) Decrease in the quantity of heat to be furnished per linear meter of tube in the reaction section.
- (c) Contribution to the partial removal of coke deposits in furnace tubes by reaction with steam: $C + H_2O \rightleftharpoons CO + H_2$.

Given the very high temperature (1000°C) required, this conversion nevertheless plays only a minor role in the cleaning of pyrolysis tubes.

The use of steam also involves a number of drawbacks which impose a limit value to its content in the feedstock. Since the steam must be heated to the reaction temperature, its presence increases the reaction volume required and hence the furnace investment. And its separation from the hydrocarbon effluents requires very large condensation areas and results in high utility consumption.

The amount of steam employed, which is normally expressed as the weight of steam per weight of feedstock, depends on the molecular weight of the hydrocarbons treated.

This ratio is 0.25 to 0.40 for ethane, but may be as high as 0.5 to 1 t/t of feed for petroleum cuts which display a much more pronounced tendency to produce heavy by-products.

For a given raw material, the composition of the reaction effluents is obviously related to the variables of temperature, residence time, pressure, and steam dilution rate. At the industrial level, the individual optimization of these parameters normally leads to contradictory requirements: hence the solution adopted is generally the result of a compromise in the choice of furnace design on the one hand, and operating conditions on the other. However, an attempt is made to express the overall influence of these factors on the performance of the reaction section by means of a representative value that can indicate the degree of severity of the treatment.

In this respect, industrial units are said to operate at low, medium, high and very high severity.

2.1.2.4 Analysis of the severity concept

The definition of severity varies with the different manufacturers, and may differ according to the type of hydrocarbon treated. In the case of the steam cracking of ethane and propane, for instance, it is convenient to express the severity of the operating conditions in terms of feed conversion X_f . In the treatment of liquid petroleum fractions with very complex compositions, the degree of feed gasification is generally employed, measured by the weight yield of light products containing three carbon atoms or less (C_3 - cut).

Process licensors have tried to supplant this overall assessment by a finer analysis of the severity of operation of a pyrolysis furnace operating on a complex feed. Among the values thus determined are the MCP (Molecular Collision Parameter) for the treatment of naphthas, based on considerations stemming from the kinetic theory of gases and developed by Wall and Witt of the *Selas Corporation*, and especially the KSF (Kinetic Severity Function) proposed by Zdonik *et al.* of *Stone and Webster Engineering*.

The KSF severity index is defined as a logarithmic function of the conversion X_f of a reference hydrocarbon present in the feed. Zdonik selected *n*-pentane, a compound that is always present in naphthas, and which offers the advantage that it cannot be formed in the pyrolysis of the other components by a side reaction.

The simple determination of *n*-pentane at the furnace inlet and exit gives the conversion value X_f . The KSF is determined from this:

$$KSF = \ln \frac{1}{1 - X_f}$$

as well as the equivalent residence time:

$$\ln \frac{1}{1 - X_f} = KSF = k_{1f} \theta_{\text{equiv.}} \quad \text{or} \quad \theta_{\text{equiv.}} = \frac{KSF}{k_{1f}}$$

The severity index allows an approximate evaluation of the conversion by thermal cracking of the other hydrocarbons in the feed by means of equations such as:

$$\ln \frac{1}{1 - X'_f} = k'_{1f} \theta_{\text{equiv.}}$$

where X'_f represents the conversion of the compound concerned and $k'_{1,f}$ its conversion rate constant. However, this calculation implies that the different hydrocarbons react independently, whereas this actually constitutes a very rough approximation for a set of reactions yielding free radicals.

In the case of gas oils, the severity of the treatment can always be defined by the ethylene or C_3 -yield. However, due to their complex composition, which varies widely according to the source of the crude oils from which they were produced, and due to their pronounced tendency to favor the formation of coke, it is very difficult to establish correlations designed to predict the relative production of the other different hydrocarbons, and consequently to define, as for the naphthas, a value or an index that is sufficiently general and representative.

It must be pointed out that the severity of steam cracking affects not only the conversion of the feed and the overall yield of C_3 -products, but also the distribution of the different compounds obtained. As illustrated by Fig. 2.6 for the pyrolysis of naphthas, the results are as follows:

- (a) At low and medium severities, the primary cracking and dehydrogenation reactions predominate. They cause a sharp increase in the yields of methane, ethylene,

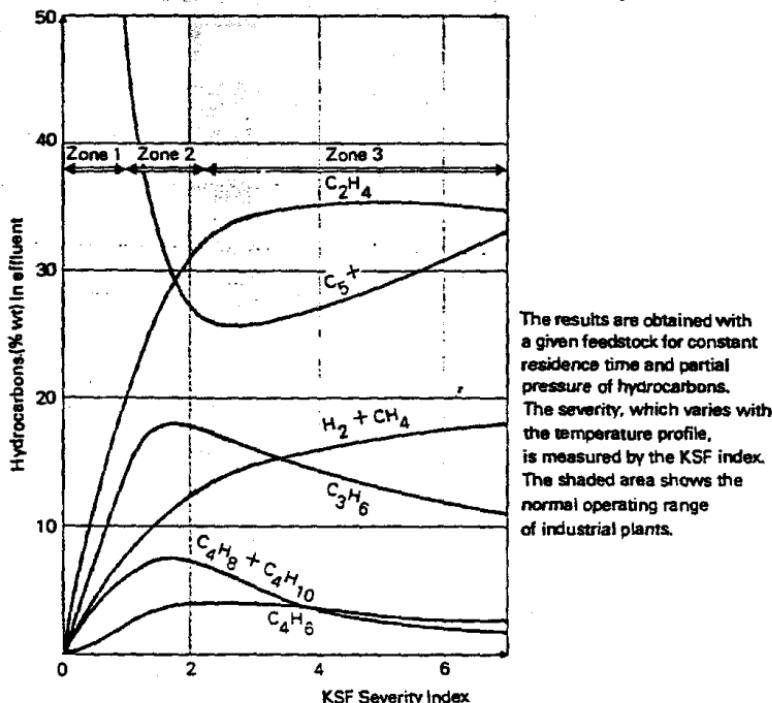


Fig. 2.6. Naphtha pyrolysis. Typical variation in effluent composition as a function of operation severity.

propylene and hydrocarbons with four carbon atoms (C_4 cut). Simultaneously, a significant reduction is observed in hydrocarbons with five or more carbon atoms (C_5+ cut) reflecting a more thorough conversion of the feedstock components into light products.

- (b) At very high severities, the methane and ethylene yields level off, while those of propylene and C_4 cut reach a peak and then decline. Consequently, the ratio of ethylene and propylene yields increases with the severity, which hence favors the formation of ethylene. The relative production of the C_5+ cut passes through a minimum, and, at the very high severities, tends to increase. This reverse development of the yields of C_3 - C_4 cuts and pyrolysis gasoline denotes the action of condensation side reactions, which cause the partial conversion of unsaturated light products to heavier aromatic compounds.

2.1.3 Influence of the type of feedstock on unit performance

The feedstocks used for pyrolysis vary widely and range from light saturated hydrocarbons such as ethane, propane, and even ethane/propane blends, to heavier petroleum cuts such as petrochemical naphtha and light and heavy gas oils. In this respect, the situation is clearly in favor of light hydrocarbons in the United States, a country that is rich in natural gases containing methane as well as ethane and propane, and which still mainly uses the latter two to manufacture ethylene. In Europe and Japan, by contrast, petroleum cuts traditionally supply the steam cracker feedstocks (Table 2.1).

Table 2.2 lists the pyrolysis product yields for different feedstocks treated at very high severity with recycle of the ethane produced or unconverted at the inlet of the reaction section. Indeed, ethane is an ideal raw material for the formation of the lower olefins. It may be observed that the relative production of ethylene decreases as the feedstock becomes heavier. Also worth noting is that the ratio of the ethylene and propylene yields (C_2/C_3 ratio) decreases steadily from ethane to the gas oils, whereas the percentage of pyrolysis gasoline (C_5 -200°C cut) increases simultaneously. As to the butadiene yield, this varies slightly with the type of feedstock in the treatment of liquid petroleum fractions.

2.1.3.1 Steam cracking of ethane, propane and butane

As shown by Table 2.2, ethane produces high ethylene yields. However, selectivity decreases as conversion proceeds. In practice, operations are conducted at about 60 per cent once-through conversion, leading to a molar yield of about 80 per cent after recycling of the unconverted fraction.

In the case of propane, the two chief products are ethylene and propylene. In practice, operations are conducted to 70 to 90 per cent conversion depending on the desired ethylene to propylene ratio. At 90 per cent once-through conversion, a final ethylene yield of about 45 molar per cent is obtained after ethane recycling, and the propylene yield varies from 26 per cent for 75 per cent once-through conversion to 16 molar per cent for 90 per cent conversion.

At the present time, butane is also used to supplement liquid steam cracker feeds. Considered independently at very high severity (95 per cent conversion), it allows a final ethylene yield of 35 molar per cent after ethane recycling.

2.1.3.2 Steam cracking of naphtha

The term naphtha is used to denote a petroleum cut whose lightest components have five carbon atoms, and whose end boiling point may be as high as about 200°C. According to their distillation temperatures, a distinction is drawn between short naphthas, whose

TABLE 2.1
BREAKDOWN OF STEAM CRACKER FEEDSTOCKS IN 1986 (% Wt)

Feedstock	Western Europe	United States	Japan	World
Ethane	8.0	57.5	—	30.5
LPG	11.0	19.0	7.5	11.0
Naphtha	69.0	9.5	92.5	49.0
Gas oils	12.0	14.0	—	8.5
Miscellaneous ⁽¹⁾	—	—	—	1.0
Total	100.0	100.0	100.0	100.0

(1) Ethanol (Brazil, India) and coal-derived gases (Poland, South Africa).

TABLE 2.2
INFLUENCE OF FEEDSTOCK ON STEAM CRACKER YIELDS (% Wt)

Products	Feedstock					
	Ethane	Propane	Butane	Medium-range Naphtha	Atmospheric gas oil	Vacuum gas oil
Hydrogen 95% vol.	8.8	2.3	1.6	1.5	0.9	0.8
Methane	6.3	27.5	22.0	17.2	11.2	8.8
Ethylene	77.8	42.0	40.0	33.6	26.0	20.5
Propylene.....	2.8	16.8	17.3	15.6	16.1	14.0
Butadiene	1.9	3.0	3.5	4.5	4.5	5.3
Other C ₄	0.7	1.3	6.8	4.2	4.8	6.3
C ₅ -200 gasoline	1.7	6.6	7.1	18.7	18.4	19.3
Benzene	0.9	2.5	3.0	6.7	6.0	3.7
Toluene	0.1	0.5	0.8	3.4	2.9	2.9
C ₈ aromatics	—	—	0.4	1.8	2.2	1.9
Non-aromatics	0.7	3.6	2.9	6.8	7.3	10.8
Fuel oil	—	0.5	1.7	4.7	18.1	25.0

The values given are obtained at very high severity after recycling to the furnaces of ethane and/or propane that is unconverted or formed in pyrolysis.

end boiling point ranges from 100 to 140°C, and long naphthas whose end boiling point lies around 200 to 220°C.

Table 2.3 gives the main physicochemical properties of a number of "naphtha" cuts derived from Kirkuk and Hassi-Messaoud crudes. The steam cracking of these naphthas yields a wide variety of products, ranging from hydrogen to highly aromatic heavy liquid fractions.

Table 2.4 gives a typical distribution of the compounds obtained at different severities, with and without ethane recycle. This operation, which is justified by the fact that this

TABLE 2.3
PHYSICO-CHEMICAL PROPERTIES OF VARIOUS NAPHTHAS

Crude	Specific gravity 15/4	TBP cut (°C)	% vol.	$d_1^{15(1)}$	Composition (% vol.)		
					P	N	A
Kirkuk	0.844	C ₅ -132	17.47	0.696	77.1	20.5	2.4
		C ₅ -173	26.49	0.722	69.8	22.4	7.8
		132-173	9.02	0.771	56.0	26.0	18.0
Hassi-Messaoud	0.803	C ₅ -132	29.94	0.703	72.6	22.8	4.6
		C ₅ -173	36.45	0.725	65.7	26.1	8.2
		132-173	11.53	0.773	51.0	33.0	16.0

The first two columns give the original crude oil and its density, the third indicates the naphtha distillation range on the TBP curve, the fourth gives the volume yield of naphtha based on the crude, and the fifth column gives the density of the naphtha (at 15°C, similar to the crude). The right-hand part of the table gives the chemical composition of the naphtha expressed in paraffins (P), naphthenes (N) and aromatics (A).

(1) Specific gravity = 59.0/39.2

TABLE 2.4
NAPHTHA STEAM CRACKING YIELDS (% Wt)
OF PYROLYSIS PRODUCTS AS A FUNCTION OF SEVERITY

Severity	Medium		High		Very high	
	C ₂ H ₆ Recycle	Without	With	Without	With	Without
H ₂ CH ₄ }		14.9	15.5	0.8	0.9	17.8
C ₂ H ₄		18.3	24.4	23.5	28.5	30.0
C ₂ H ₆		7.5	—	6.2	—	4.2
C ₃ H ₆ } C ₃ H ₈ }		19.2	19.5	17.5	17.5	17.5
C ₄ H ₆		3.1	3.1	3.2	3.2	4.0
Other		9.1	9.6	7.2	7.2	5.7
Gasoline		24.9	24.9	22.6	22.6	16.1
Heavy products		3.0	3.0	4.1	4.1	4.7

hydrocarbon is an ideal raw material for the manufacture of ethylene, must be conducted in special furnaces in order to meet the optimal conditions required. Correlations between operating variables and yields of the main products are valid only for a specific type of furnace. However, although the absolute values of these models are not comparable from one installation to another, the trend of the variations remains the same.

Hence, for a given furnace, the influence of the pyrolysis temperature can be isolated by keeping the residence time and steam content constant. As the furnace exit temperature rises (Table 2.5), the ethylene yield also rises, while the yields of propylene and pyrolysis gasoline (C_5 -200°C cut) decrease. At very high temperature, residence time becomes the most important factor. With respect to ethylene yield, each furnace exit temperature corresponds to an optimum, as illustrated in Fig. 2.7. At present, the highest ethylene yields are achieved by operating at high severity, namely around 850°C, with residence time ranging from 0.2 to 0.4 s. However, operation at the very high severities is nonetheless limited by the prohibitive formation of coke, which increases the frequency of decoking operations.

TABLE 2.5
NAPHTHA STEAM CRACKING
INFLUENCE OF OUTLET FURNACE TEMPERATURE ON YIELDS

Outlet furnace temperature (°C)	815	835	855
H_2	0.66	0.74	0.81
CH_4	13.82	15.65	17.40
C_2H_4	24.71	27.06	29.17
C_3H_6	17.34	16.28	14.44
C_4H_6	4.18	4.17	3.99
C_6H_6	4.89	5.90	7.08
C_5 -200°C	22.64	20.89	20.01

Naphtha characteristics - distillation range, 35-160°C.

Chemical composition (% vol.) = paraffins 80, naphthenes 15, aromatics 5. Steam dilution ratio = 0.60.

Yields of various pyrolysis products are expressed in % Wt relating to feed.

At a given severity, the ethylene yield also decreases as the partial pressure of the hydrocarbons increases (Fig. 2.8a). This partial pressure is adjusted, in order to optimize the ethylene yield, by diluting the reaction mixture with steam. As shown in Fig. 2.8b, it is preferable to operate with steam to naphtha ratios higher than 2. For economic reasons, a value of 0.5 to 0.6 t of steam per ton of naphtha is generally adopted as the upper limit.

Yields of pyrolysis products also depend on the chemical composition of the naphtha feedstock. The thermal stability of hydrocarbons increases in the following order: paraffins, naphthenes, aromatics. It decreases as the chain becomes longer. Thus, it is usually observed that the ethylene yield, as well as that of propylene, is higher if the naphtha feedstock is rich in paraffins.

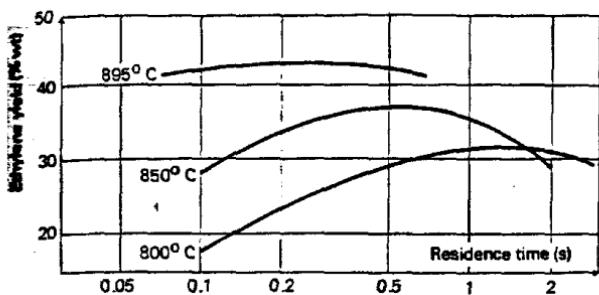


Fig. 2.7. Naphtha pyrolysis. Influence of temperature and residence time on ethylene yield.

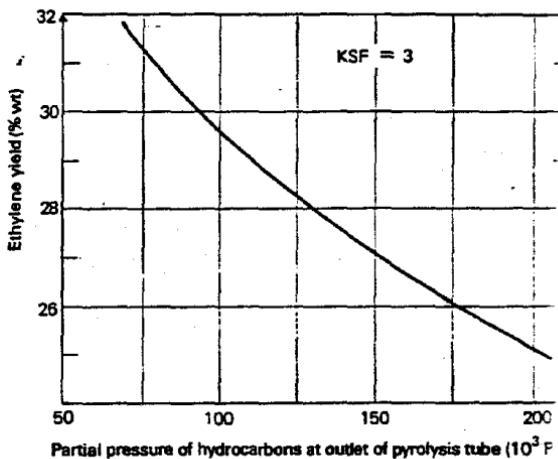


Fig. 2.8 a. Naphtha pyrolysis. Influence of partial pressure of hydrocarbons on ethylene yield (the results are obtained with a given feedstock and constant residence time and severity).

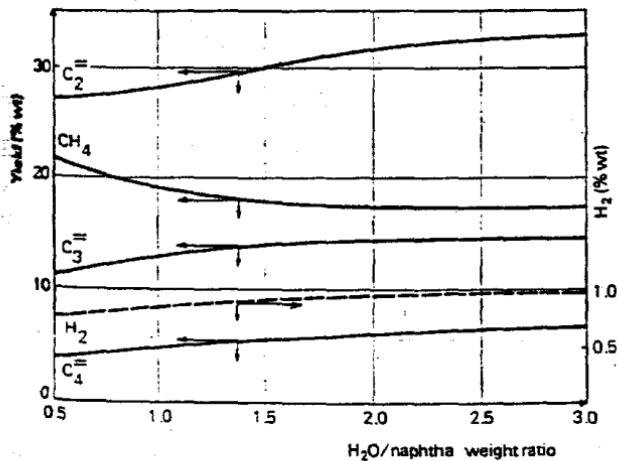


Fig. 2.8 b. Naphtha pyrolysis. Influence of $H_2O/naphtha$ weight ratio (dilution rate) on ethylene yield.

2.1.3.3 Gas oil steam cracking

Like naphthas, gas oils are liquid petroleum fractions characterized in particular by their distillation range. A distinction is drawn between light or "atmospheric" gas oils, which are distilled between 250 and 350°C, and heavy or "vacuum" gas oils, with boiling points ranging between 350 and 450°C, and even 500°C. Due to the shortage of naphtha and the growing surplus of heavier petroleum cuts, gas oil steam cracking, hitherto not very significant, now offers an increasingly popular solution to meet the needs of the petrochemical industry.

The distribution of compounds produced by this operation is quite different from that obtained from naphtha. The main reason for this is the pronounced "aromaticity" of gas oils, which affects the maximum ethylene yield. Moreover, this parameter may vary substantially from one gas oil to another, and in comparable operating conditions this partly explains the wide differences observed in the distribution of the hydrocarbons formed. The *Stone and Webster Company* established a correlation between the BMCI (*Bureau of Mines Correlation Index*) for gas oils and the maximum ethylene yield. The BMCI created in 1940, represents an "aromaticity index" defined by the following equation:

$$\text{BMCI} = \frac{87.552}{\text{VABP}({}^{\circ}\text{R})} + 473.5 \cdot (\text{sp. gr.}) - 456.8$$

where

VABP(${}^{\circ}\text{R}$) = Volume Average Boiling Point in degrees Rankin,
sp. gr. = Specific gravity 60/60°F (or density 15.6/15.6°C).

As shown by Fig. 2.9, ethylene and hydrogen production are lower with increasing aromaticity of the gas oil feedstock. By contrast, liquid fuel production increases (fraction above 200°C).

Table 2.6 shows a typical product distribution obtained by the steam cracking of gas oil and vacuum distillate, by a comparison with the distribution resulting from the conversion of a naphtha, while highlighting the influence of the treatment severity. This reveals a substantial decrease in ethylene production for gas oils which, depending on the operating conditions, amounts to 20 to 26 per cent by weight of the feed, and the very sharp increase in that of fuel oil, which reaches equally high percentages.

For the specific case of a naphtha of specific gravity $d_4^{15} = 0.713$ and an atmospheric gas oil with specific gravity $d_4^{15} = 0.841$, a Linde study compares the performance obtained in the same furnace with these two feedstocks, at different treatment severities, a concept defined in this case by the weight ratio of the propylene to ethylene produced (Fig. 2.10).

The comparison is made not in relative percentages, but in terms of the relative quantities of each of the products (including the feedstock), for a given production of ethylene and consequently propylene.

On the whole, these analyses show that gas oil steam cracking produces fewer light products than the treatment of naphtha, and more heavy products which display a higher aromatics content. Hence the C₅, 200°C cut boosts the BTX (Benzene, Toluene, Xylenes) (majority benzene) concentration. Similarly, fuel oil (fraction above 200°C) displays a more pronounced aromatic character. This feature makes it incompatible with straight-run distillation fuel oils. The mixture causes the deposition of asphaltenes and other

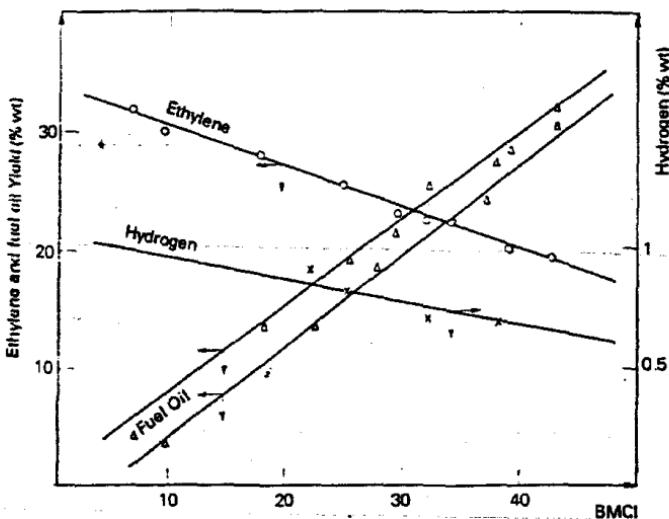


Fig. 2.9. Steam cracking of gas oils. Maximum ethylene yield (without ethane recycle) as a function of BMCI.

TABLE 2.6
TYPICAL YIELDS OF THE STEAM CRACKING OF LIQUID FEEDSTOCKS
AT LOW AND HIGH SEVERITY

Feedstock characteristics	Kuwait naphtha	Kuwait gas oil	Es Sider vacuum distillate			
$d_4^{15(1)}$	0.713	0.832	0.876			
Boiling point	30-170	230-330	300-540			
H ₂ (% Wt)	15.2	13.7	13.0			
Aromatics (% Wt)	7	24	28			
Yield (% Wt) severity	Low	High	Low	High	Low	High
CH ₄	10.3	15.0	8.0	13.7	6.6	9.4
C ₂ H ₄	25.8	31.3	19.5	26.0	19.4	23.0
C ₂ H ₆	3.3	3.4	3.3	3.0	2.8	3.0
C ₃ H ₆	16.0	12.1	14.0	9.0	13.9	13.7
C ₃ H ₈	4.5	4.2	4.5	4.2	5.0	6.3
C ₄ H ₈	7.9	2.8	6.4	2.0	7.0	4.9
BTX	10.0	13.0	10.7	12.6	18.9	16.9
C ₄ -200°C (Except BTX)	17.0	9.0	10.0	8.0	25.0	21.0
Fuel oil	3.0	6.0	21.8	19.0	2.5	1.4
H ₂ , C ₂ H ₂ , C ₃ H ₄ , C ₃ H ₈	2.2	3.2	1.8	2.5	1.4	1.8
Total	100.0	100.0	100.0	100.0	100.0	100.0

(1) Specific gravity, 59.0-39.2.

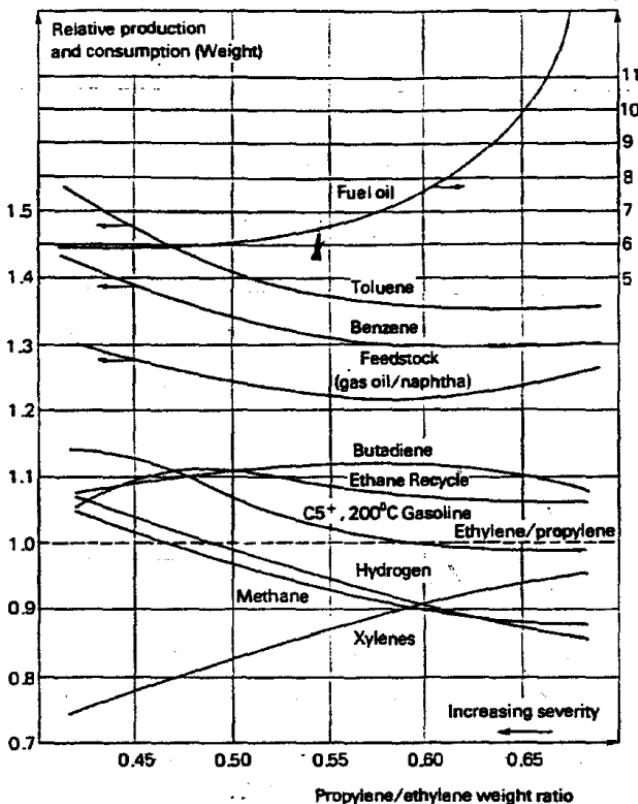


Fig. 2.10. Influence of severity on relative weight production and consumption of the steam cracking of gas oil and naphtha.

compounds with condensed aromatic rings. Thus, part of it is burned in the facility itself, since the production of methane is insufficient to guarantee the energy self-sufficiency of the unit. The remainder is used either as a fuel, or as a feed for the production of electrode grade coke or carbon black, but the quality of the products obtained often makes it unsuitable for these applications.

Another problem raised by gas oil steam cracking is the sulfur content, which is usually very high in this petroleum cut. During the operation, in fact, about one-third of the sulfur is removed as H_2S in the cold section of the process. The remainder is found in the $200^\circ C^+$ fraction at concentrations two to three times higher than those of the feed, which are incompatible with the pollution regulations in force today.

Furnaces with very short residence time (Short Residence Time technology developed by Lumus) adapt ideally to the cracking of gas oils on account of their tube diameter, which is larger than that of standard equipment, the low partial pressure of steam, and decreased coking.

2.1.3.4 Crude oil steam cracking

The rising price of naphtha has led a number of oil companies to consider the direct cracking of crude oil, without prior fractionation. This alternative is beset by many technological problems, due chiefly to the very great complexity of the feedstock. Hence the ash content, which is nil in petroleum cuts produced by straight-run distillation, varies in crude oils from 0.01 to 0.1 per cent weight, depending on their source. The asphaltene content becomes very high and may be as much as 20 per cent by weight. Sulfur, generally present in a concentration of 0.1 to 5 per cent by weight, necessitates prior desulfurization, which is not required in the case of naphthas. It should be added that the H:C atomic ratio of the crude oil (1.4 to 1.9) is low in comparison with that of naphtha (2 to 2.3). This means that the feedstock is poorly adapted to the production of ethylene. Furthermore, even by selecting more suitable paraffinic crudes, large quantities of coke are formed, requiring frequent decoking, as well as many by-products that make recycling necessary.

Despite these difficulties, three processes have been developed in recent years, designed to use either total crude oil, or heavy feedstocks such as wholly deasphalted crudes, for the manufacture of ethylene. These are the Carbide/Kureha/Chiyoda, Dow, and Kunigai/Kunii processes. Table 2.7 gives the yields of pyrolysis products of these three new processes.

TABLE 2.7
PYROLYSIS YIELDS OBTAINED BY NEW CRACKING PROCESSES

Yields (% Wt)	ACR process (Carbide/Kureha/ Chiyoda)	Dow process	KK process Mark I
Hydrogen	2.4	8	0.5
Methane	8.9	14.0	8.9
Acetylene	4.2	2.3	0.2
Ethylene	31.8	25.2	14.4
Ethane	1.7	1.9	2.3
Propylene	6.1	8.3	7.6
Other C ₃ -	2.3	1.0	0.2
C ₄	3.5	6.6	4.3
Naphtha pyrolysis gasoline	10.9	23.2	7.7
Fuel oil/tars	24.1	15.7	52.3
H ₂ S/CO CO ₂	4.1	1.8	1.6
Total	100.0	100.0	100.0
Feedstock	Light Arabian crude (whole)	Unidentified crude	Khafji vacuum residue

This table points out the low production of propylene in comparison with the steam cracking of naphtha, the high coproduction of acetylene ranging up to nearly 150 kg/t of ethylene instead of the 15 kg/t observed in naphtha steam cracking, and the substantial formation of fuel oil and tars.

The Kureha process, developed jointly with *Union Carbide* and *Chiyoda*, uses an elaborate cracking reactor (Advanced Cracking Reactor: ACR). The high-temperature plasma used in the reactor is generated by the combustion of a liquid or gaseous fuel in the presence of oxygen, followed by the injection of superheated steam into the combustion products. The steam cools the hot gases to an approximate temperature of 2000°C, and serves as a diluent for the hydrocarbon feedstock introduced into the reactor. The feedstock is preheated before injection into the high-temperature plasma, where adiabatic cracking takes place.

After a residence time of about 0.020 s, the reaction products leave the reaction zone at about 900°C and undergo rapid quench by the injection of a heavy oil in a quench cooler developed by the *Ozaki Company*, and which helps to produce high-pressure steam. The quench oil is recovered and recycled, while the cracking effluents are fractionated to separate the naphtha and tars. The gaseous products are then treated in a special compression and treatment system required to remove large amounts of acetylene, CO₂ and H₂S obtained in the process. The rest of the recovery section is conventional.

The Dow process also uses a high-temperature plasma. The ethylene yield varies between 22 and 25 per cent weight depending on the operating conditions and feeds.

The KK (Kunigi/Kunii) process uses a fluidized bed raised to high temperature to crack vacuum residues. The facility is closely similar to that of fluidized bed coking units and catalytic cracking units. In the basic process, called Mark I, coke raised to 750°C was employed. The ethylene yield was only 14 per cent weight, while that of tars and coke, which had a high sulfur content, reached 52 per cent weight. The Mark II process uses hot ceramic spheres to raise the temperature to 800°C. This yields far fewer tars, but the enormous amounts of hydrogen and CO formed make ethylene purification uneconomical. Changes in this process finally culminated in the KK/Idemitsu Syngas process currently planned for the manufacture of synthesis gas.

2.1.4 Industrial steam cracking

The complexity of the steam-cracking plant is largely connected with the type of feedstock treated. Among the various alternatives, however, the choice of naphtha offers the most complete, and hence the most representative case study. This is because this petroleum cut constitutes one of the most widely used raw materials for the manufacture of ethylene, and also because its treatment includes that of ethane, by recycling in special furnaces.

On the whole, a steam-cracking facility comprises two main sections: a so-called hot section, where the feedstock is pyrolysed and the effluent conditioned, and a so-called cold section, where the products formed are separated and purified.

Figure 2.11 shows a highly simplified flow sheet of such a facility for the case of naphtha feedstock. It features a number of furnaces, quench boilers, and a highly complex fractionation train. The hydrocarbon feedstock enters the hot section of the unit through the convection zone of the furnace, where it is preheated (part 1) and is then mixed with steam that is also preheated in this zone. The hydrocarbons and water pass through the radiation zone of the furnace (part 2), where the rapid temperature rise and pyrolysis reactions take place. At the furnace exit, in order to avoid any subsequent reaction, the

effluents are fixed in their kinetic development possibilities by a sudden quench generally carried out in two steps: a first indirect quench with water, followed by a second direct quench using the heavy residue by-product of pyrolysis (parts 3, 4 and 5).

The effluents are then transferred (part 6) to a primary fractionation column (part 8), which separates a heavy residue at the bottom (part 7) and a fraction of pyrolysis gasoline and water on sidestreams, while the light pyrolysis products leave at the top in gaseous form.

After compression (part 9), caustic scrubbing and drying, these light effluents enter the cold section of the unit, which can be designed in various ways, and which performs the following separations:

- Hydrogen, concentrated to various degrees.
- Ethylene containing 99.9 per cent by weight.
- 95 per cent propylene, which can be raised to 99.5 per cent by weight entirely or partly.
- A C₄ cut containing 25 to 50 per cent butadiene.
- The complementary fraction of pyrolysis gasoline which is rich in aromatic hydrocarbons.

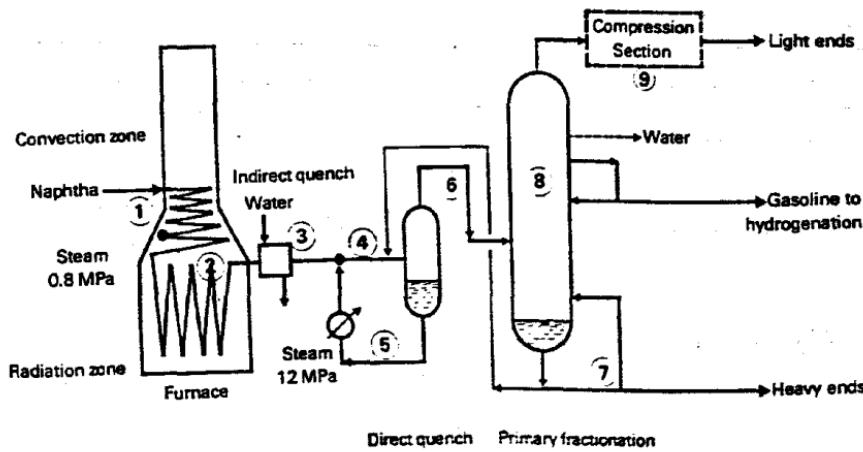


Fig. 2.11. Base scheme of a naphtha steam-cracking unit (hot section).

2.1.4.1 Furnaces

Pyrolysis furnaces are designed to provide a rapid temperature rise of the feedstock, a high exit temperature, and very short residence time. In solving these problems, the design of the pyrolysis tubes and furnaces are of decisive importance.

A. Pyrolysis tubes

The basic equations required to design the tubes essentially deal with the determination of the following characteristics:

- (a) Heat exchange area required, calculated from the feasible heat fluxes and energy needs of the system.
- (b) Severity of the operation, according to the kinetic equation expressing the KSF.
- (c) Residence time, determined from the mass flow rate of the reaction mixture and its average specific weight in the tube.
- (d) The quantity of heat to be transferred to raise the temperature and compensate for the endothermic character of the pyrolysis reactions, based on the thermodynamic properties (specific heats, temperature increases, heats of reaction etc.).
- (e) The heat flux that can be achieved across the tube wall, determined from the overall heat transfer coefficient, the maximum allowable wall temperature, limited by the stresses in the metal, and that of the reaction mixture, which varies along the tube. The highest heat fluxes currently achieved are in the range of $350,000 \text{ kJ/m}^2 \cdot \text{h}$.
- (f) Pressure drop from the length and diameter of the tubes selected.
- (g) Rate of coke accumulation on the inside wall of the pyrolysis tube, which alters the overall heat transfer coefficient.

These equations can be used to point out the direct proportionality between residence time and the inside diameter of the tube selected. Thus, heat transfers are adjusted to the requisite level by adjusting the number of tubes and their length.

Based on the foregoing considerations, it can therefore be inferred that a decrease in the tube diameter, which causes a reduction in residence time, results in a higher ethylene yield (diagram a in Fig. 2.12) in industrial naphtha steam cracking conditions. Simultaneously, a drop in the propylene yield (diagram b in Fig. 2.12) is observed in the normal

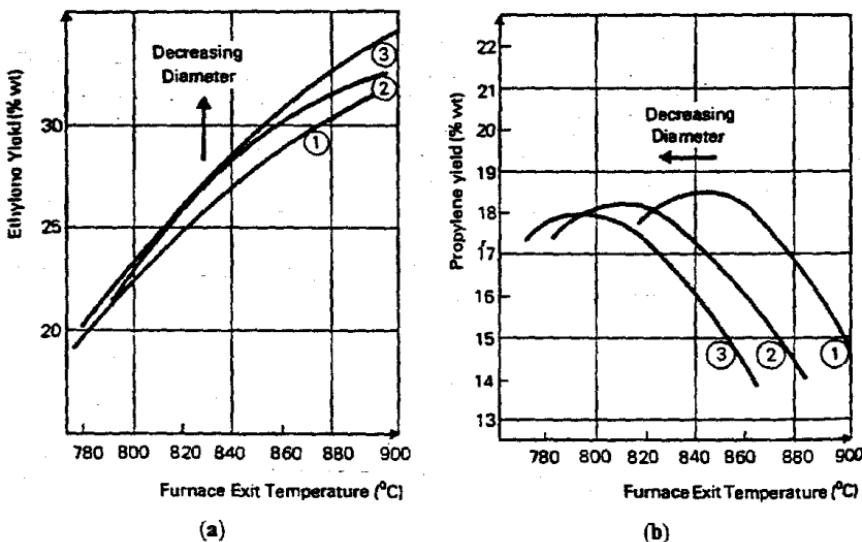


Fig. 2.12. Steam cracking of naphtha. Effect of pyrolysis tube geometry on olefin yields.

zone of furnace exit temperatures, and consequently, an increase in the ratio of ethylene to propylene output.

Reducing the diameter nevertheless raises a number of problems, associated with the need to limit pressure drops, prevent excessive erosion of the tube interior by the gases, and to avoid sharply increasing the capital investment, which rises with the number of tubes employed.

Furthermore, short residence time entails the highest possible heat transfer fluxes. The layout of the tubes, their metallurgy, the distribution of the burners, and the arrangements in the furnace itself are designed to meet this objective. The chief limitation to a high heat transfer flux resides in the highest metal "skin" temperature that the tube can withstand. For example, Table 2.8 shows the influence of skin temperature on the geometry and operating conditions of a pyrolysis tube of fixed diameter operating at constant severity.

TABLE 2.8
NAPHTHA STEAM CRACKING. TUBE PERFORMANCE

Maximum skin temperature (°C)	Tube length (m)	Pressure drop (10^6 Pa)	Average heat flux (kJ/h · m ²)	Minimum residence time (s)
925	55	0.115	190,000	0.46
980	40	0.090	250,000	0.35
1,040	35	0.070	315,000	0.27

Characteristics of pyrolysis tubes: the operation is conducted at a feedstock flow rate set for constant tube outlet pressure and dilution rate in tubes 0.105 m in diameter. The rise in the tube skin temperature is offset by a decrease in their length and hence in contact time, to ensure operation at constant severity in the neighborhood of the maximum ethylene yield.

In practice, tubes with inside diameter from 65 mm (*Stone and Webster*) to 120 mm (*Lummus, Selas*) and 7 to 8.5 mm thick are employed for naphtha steam cracking. The gases flow within these tubes at a linear velocity of about 300 m/s. The pressure drop recorded between the furnace inlet and outlet may reach 0.4 to $0.7 \cdot 10^6$ Pa in these conditions. The tubes are fabricated by extrusion or centrifugal casting. Cast tubes are made of medium alloy steels (25 to 30 per cent chromium and 20 to 30 per cent nickel) containing 0.5 per cent carbon. If they are positioned vertically, their sagging strength allows for metal skin temperatures of 1000 to 1100°C.

At this stage, it should be observed that the internal surface of the tube exerts a significant influence on the pyrolysis process. Iron and nickel catalyze dehydrogenation reactions and accordingly favor the formation of heavy side products and coke. This catalytic action can be diminished by superficial sulfurizing of the steel. In addition, the oxidizing effect of steam on alloy steels also tends to reduce the extent of these undesirable dehydrogenations. It is also recommended to hone the irregularities in the internal surface of pyrolysis tubes carefully to prevent the adhesion of coke particles on the surface and the carburization of the metal at possible failure locations. The tubes are delivered U-shaped, with branches up to 9 to 10 m long and interconnected to form coils. They may exhibit a uniform or tapered profile, or comprise elements of different diameters, designed to minimize pressure drops and optimize yields (split tube design).

Millisecond technology requires a straight tube of approximately 30 mm in diameter and 11 m long.

B. Furnace design and internal arrangements

Until 1960, furnaces were designed to operate with long residence times (about 1 s) and relatively low severities. Coils with an inside diameter of 90 mm were laid out horizontally.

The second generation of furnaces emerged in late 1960 with vertical tubes, thus eliminating problems of sagging and expansion. These furnaces were originally developed to allow for higher exit temperatures and shorter residence times (0.4 to 0.5 s), but their inside diameter remained similar to the earlier tubes. Since then, the tendency is to reduce the tube diameter, while retaining the vertical position in the furnace, and several systems have been proposed, which are shown schematically in Fig. 2.13.

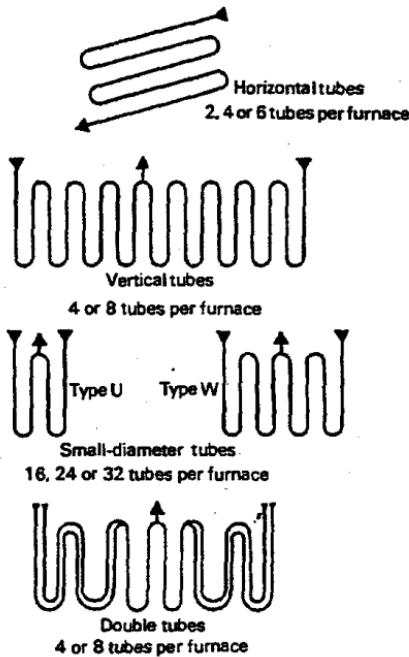


Fig. 2.13. Design of pyrolysis tubes.

The coils are hung at the top from an articulated rod provided with a counterweight or a system of springs. They are fitted at the bottom with guides enabling them to move in slides provided in the refractory of the furnace hearth. In this way, the supports are not directly exposed to the radiant heat, and the tubes assume a position in which the stress is a minimum and where sagging cannot cause substantial deformation. Expansion is allowed for, and thermal shocks are easier to withstand, thus lengthening coil life.

Depending on its length and diameter, a furnace contains 4 to 16 tubes laid out in one or two staggered rows. Certain arrangements (*Linde*) strike a compromise between relatively large diameter tubes and tubes of small inside diameter. They comprise two parallel coils at the furnace inlet, which then merge in a tube of larger diameter near the outlet end. This system offers the advantage of allowing an increase in total length, in other words the time interval between two successive decokings. In this system with two tube diameters, the small-dimension portion provides the optimal area/volume ratio and short residence time. Furthermore, since it is located on the inlet side, where the side reactions producing coke are still insignificant, fouling, which is inevitable in the terminal zone of the tube, remains very moderate at this level.

In the Millisecond technology each tube is independently suspended, so that any growth occurs without affecting the adjacent tube.

Figure 2.14 shows the tube layout in the furnace, according to the earlier arrangement of coils laid out horizontally (diagram a) and with the modern design of horizontal tubes in the convection zone and vertical tubes in the radiation zone (diagram b of the same figure). This shows a two-cell furnace with offers the advantage, over single-cell units, of lower heat losses thanks to the common wall. Heating is provided by "radiant" burners (Fig. 2.15) which avoid a direct flame on the tube and generate radiation by heating the refractory. The refractory brick can withstand temperatures up to 1700 to 1800°C. The burners are usually located on either side of the coils in the sidewalls of the furnace, and use steam-cracking by-products, essentially methane, as a fuel.

Diagram c in Fig. 2.14 gives the metal skin temperatures of the vertical tubes for a terrace wall furnace, as well as the temperatures reached by the walls and supports. The top part of the figure shows the suspension of the coils by hangers, rod and counterweight. Heating is provided in this case by combination burners running both on gas and fuel oil atomized with steam, in the form of a line burner for the gas, and a tunnel burner for the fuel.

Some systems make use of auxiliary short-flame fuel oil burners, placed in the floors or roofs of the cells.

As a rule, the feed is preheated to about 400°C in the convection zone, by the heat from the hot gases leaving the furnace. It is then mixed with diluent steam, and then enters the radiation zone, where it is raised to over 800°C in three to four tenths of a second. The energy efficiency of a furnace is about 85 per cent, and the quantities of heat supplied in the convection and radiation zones are 47 and 53 per cent respectively. In the radiation zone, the temperature profile of the steam/hydrocarbon mixture is regulated by adjusting the heating intensity of the rows of burners.

In the current state of the technology, the production capacity of a two-cell pyrolysis furnace is about 40,000 t/year of ethylene. Thus, a 400,000 t/year steam cracker comprises ten furnaces on naphtha and one or two used to pyrolyse recycled ethane. One or two spare furnaces (10 to 15 per cent of the theoretical production capacity) are also normally provided, in order to compensate for the production deficit due to decoking operations.

The furnaces obviously constitute the essential equipment of the hot section of the steam-cracking process, and they condition the satisfactory running of the overall installation. However, their optimal operating conditions and the flexibility of the process to operating parameters can often only be evaluated on the completion of full-scale experiments on a pilot furnace.

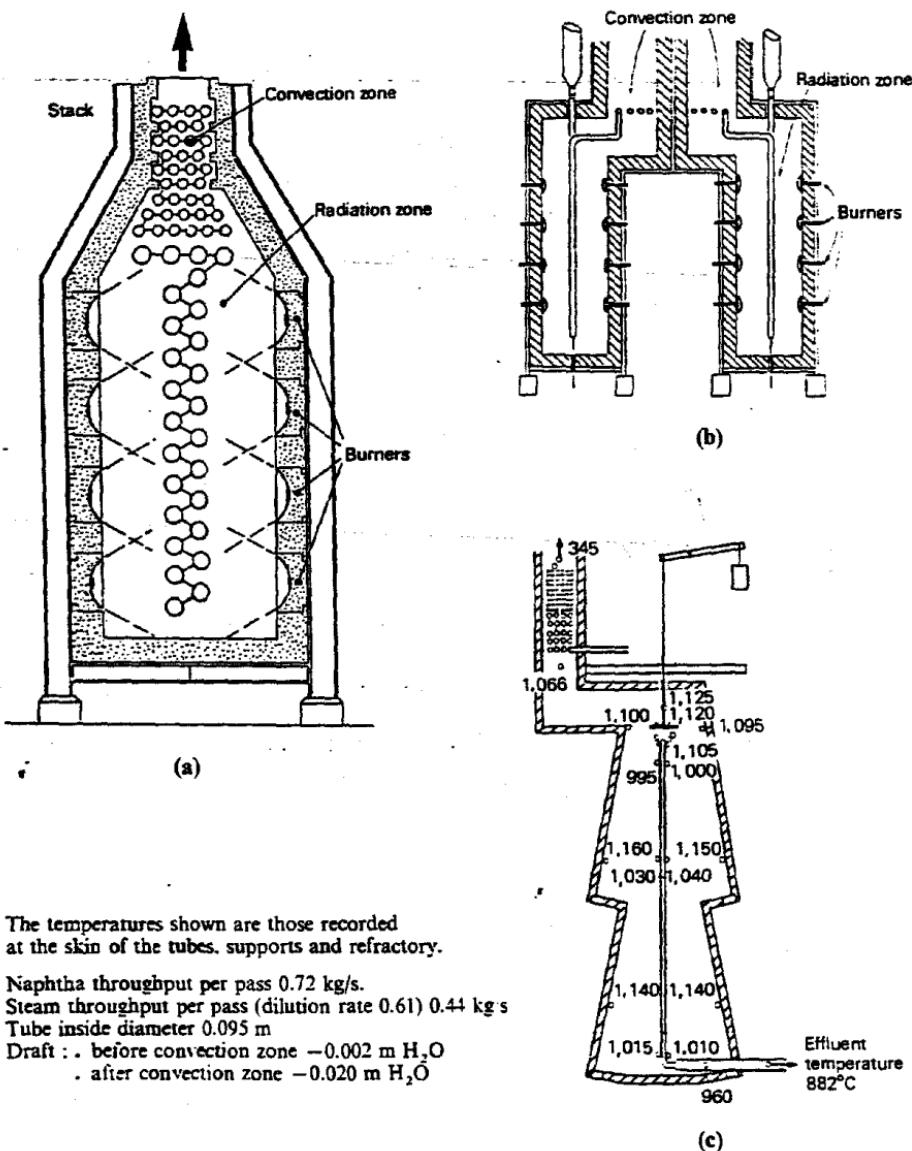


Fig. 2.14. Examples of steam-cracking furnace design.

- Furnaces with horizontal pyrolysis tubes.
- Double cell furnaces with vertical tubes.
- Terrace furnaces with vertical tubes.

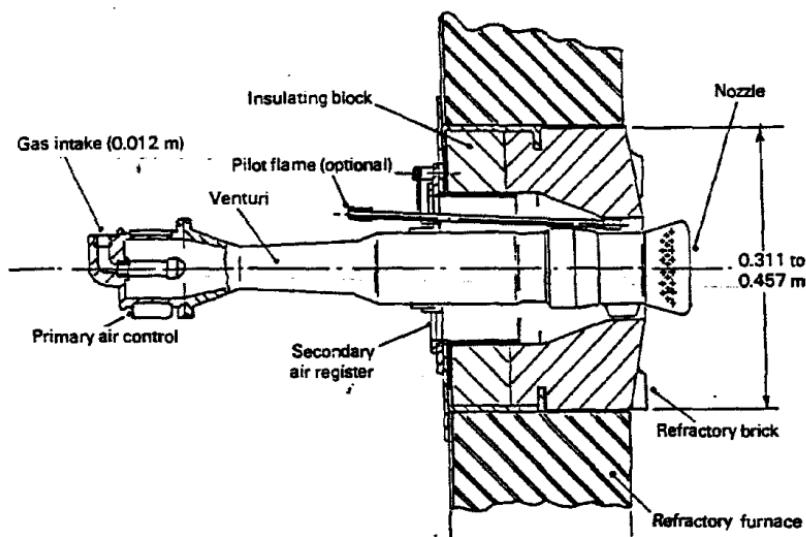


Fig. 2.15. Schematic section of a radiant burner.

This body of data represents a large share of the know-how of the firms that market steam crackers. These companies are usually engineering firms that own their own technology (*Stone and Webster, Lummus, Kellogg, Mitsubishi etc.*), furnace specialists (*Selas, Foster Wheeler, KTI(Kinetics Technology International etc.)*), or applied research centers (*Institut Français du Pétrole: IFP etc.*).

2.1.4.2 Quench

The products leaving the furnace radiation zone must be cooled as quickly as possible. This operation is designed in particular to prevent the effluent composition from changing by the formation of heavy polymerization products and the increase in the gasoline content. It is important for the transfer line between the furnace and the quench boiler to be as short as possible to avoid additional residence of the effluents at elevated temperature. The heat of the furnace is first recovered by indirect cooling in the quench boilers, and directly by the introduction in-line of a recycle using a heavy hydrocarbon cut called quench oil (Fig. 2.11).

For naphtha feedstocks, quenching is essentially performed in boilers, which generate high-pressure steam by heat exchange between the effluents and water. This steam is then used to drive the compressors of the gaseous fraction treatment installations. The gas temperature is accordingly lowered to 400 to 450°C, and 50 per cent of the heat supplied by the furnaces is recovered at this level. In the steam cracking of heavy naphthas and gas oils, the quantity of heat absorbed by the quench boiler is reduced by diminishing the heat exchange area. In the extreme case of vacuum gas oils, the quench boiler is

totally eliminated and supplanted by direct quench. The higher the heavy fraction content of the effluent, the more it tends to cause fouling in the boiler heat exchanger tubes, entailing frequent shutdowns for decoking.

These indirect quench boilers are actually in-line heat exchangers (Transfer Line Heat Exchangers : TLX), normally placed vertically at the outlet of the pyrolysis tubes. The tube bundle, which conveys the pyrolysis gases, consists either of double pipes (*Stone and Webster, Schmidt'sche, Mitsubishi*) or a set of rows of tubes and baffles (*Borsig*) designed to guarantee the mechanical strength of the system with high vapor pressures. Table 2.9 lists the performance characteristics of quench boilers in accordance with the type of feed.

To provide an example, Fig. 2.16 shows a simplified isometric view of a cell of a steam cracker with vertical tubes in the radiation zone and horizontal tubes in the convection zone. It also shows the positions of the sidewall burners, quench boilers, steam drum, and the injection device of the heavy cut which performs the supplementary direct quench.

2.1.4.3 Decoking and run length

Despite all the precautions observed to minimize the formation of coke in the furnace tubes and in the quench boiler it is impossible to eliminate this completely. Furnace operation must therefore be interrupted periodically to remove the coke: this is the decoking operation.

Run length between two successive decokings varies according to the installation and the type of feedstock, but can be estimated at a few weeks on the average. For a steam cracker producing 200,000 t/year of ethylene in five furnaces, this means that one furnace is always undergoing decoking, so that production is carried out by four furnaces only.

In ideal conditions, a furnace operating on naphtha can run for 90 days without decoking. However, the run length is always shorter due to the inevitable fouling of the quench boiler. Progressive coke deposition in the pyrolysis tubes results in an increase in their metal skin temperature, connected with the growing inefficiency of heat transfer, and in an increase in the pressure drop caused by the reduction of the open cross-section of the tube.

For small-diameter tubes which are fouled more rapidly, the increase in pressure drop is the decoking criterion, whereas, for larger-diameter tubes, which are less affected by coke deposits, it is the actual skin temperature of the tube in the radiation zone which indicates the degree of fouling.

Run length is hence given by the equation :

$$t_c = \frac{(Tm)_c - (Tm)_p}{\Delta T}$$

where

t_c = run length,

$(Tm)_c$ = maximum allowable skin temperature on a coked tube,

$(Tm)_p$ = skin temperature on a clean tube,

ΔT = daily increase in tube skin temperature due to coking.

TABLE 2.9
NAPHTHA STEAM CRACKING, QUENCH BOILER PERFORMANCE

Feedstock treated	Cracked gas temperature (°C) at boiler exit	Properties of steam produced	
		Pressure (10 ⁶ Pa)	Temperature (°C)
Ethane	320-370	4.0-4.5	252-260
Naphtha	425-450	8.0-10.0	297-313
Light atmospheric gas oil	450-500	8.0-12.5	297-329
Heavy atmospheric gas oil	500-550	10.0-13.5	313-335

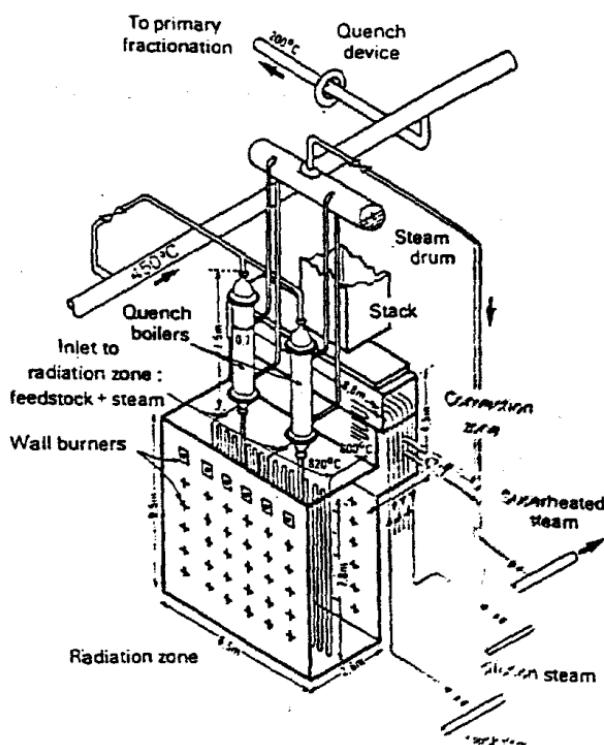


Fig. 2.16. Isometric view of a steam-cracking furnace cell.

In practice, run length is as long as 90 days on an ethane feedstock, 65 with naphtha, and 40 with gas oil.

Pyrolysis tubes and quench boilers are normally decoked by slow burning of the coke in the presence of a mixture of steam and air at temperatures ranging from 600 to 800°C. The operation begins in the presence of a mixture that is very poor in air (1 per cent volume), which is progressively enriched to 15 per cent. Steam can also be used alone, but this requires higher temperatures (900 to 950°C) to activate the reaction. To provide an indication, at 950°C, decoking time using steam only is 30 hours. By adding 10 per cent air, it can be cut to 10 hours, and to 5 hours with 20 per cent air. Further decoking of the quench exchanger can be carried out mechanically by means of high-pressure water jets (30 to 70 . 10⁶ Pa). If the coke formed is very hard, it can be removed by sand blasting with water.

2.1.4.4 Primary fractionation

The effluents from the different quench boilers are first collected together. They undergo supplementary in-line cooling, and are then sent to a so-called primary fractionation column, whose bottom stream, itself previously cooled, serves for the direct quench operation. This column also separates the gases at the top that are sent to the compression section, and a gasoline sidestream. The diluent steam, which is condensed at various levels, is purified and re-used in a closed circuit, with make-up process water.

The gaseous mixture recovered contains a large number of compounds which must be isolated and purified. This is because, whereas the basic steam cracking product is ethylene, the upgrading of the other hydrocarbons formed, particularly in the treatment of liquid petroleum fractions, is indispensable for sound installation management. This trend received a strong impetus from the increase in crude oil prices.

Furthermore, while the quest for a maximum ethylene yield gave rise to a highly advanced technology in pyrolysis furnaces, it was also necessary to develop and improve separation techniques, both to optimize the uses of the different cracked products, and to meet increasingly stringent commercial requirements. Owing to downstream applications, and especially polymerization processes, the basic petrochemical hydrocarbons demand a very high degree of purity. The specifications required for contents of acetylene derivatives, total sulfur and oxygen compounds are thus especially low.

2.1.4.5 Separation and purification of cracked products

These operations essentially involve low-temperature distillation in the cold section of the facility, after compression, desulfurization and drying of the light gaseous effluents. This section also includes the intermediate chemical purification treatment of ethylene and propylene which contain acetylene impurities, compounds which are especially detrimental to the subsequent uses of these olefins. They are eliminated by selective hydrogenation on metallic catalysts. The final arrangement is therefore a series of very complex operations designed to furnish the different products separately at the requisite specifications, including ethylene, propylene, C₄ cut, C₅- cut etc.

A. Compression, desulfurization and drying

The distillation of the effluents that leave primary fractionation in gaseous form first requires their condensation to the liquid phase. Given the high volatility of some com-

pounds (the boiling points at atmospheric pressure of methane, ethane and ethylene are -161.6 , -88.9 and -103.7°C), this operation, conducted at standard pressure, would require extremely low temperatures. Condensation is therefore carried out under pressure to limit the technological difficulties encountered in cryogenic separation.

The gases are compressed in several steps (four to five) with intermediate cooling to prevent any heating that could induce undesirable polymerizations. Between the different compression steps, the liquid or liquefied fractions are collected and cleared by stripping of the lighter components, which are recycled. At this level, one of the major advances in steam cracker technology was achieved by the use of centrifugal compressors, which superseded reciprocating compressors. Their main advantages reside in their smaller investment and lower maintenance costs, as well as their compact size. They are available today in capacities of 20,000 kW or more.

The gases are desulfurized before the final compression stage. By this time, the sulfur contained in the feed is in the form of H_2S , COS and light mercaptans. These derivatives, as well as the CO_2 , are removed by caustic scrubbing, sometimes preceded by scrubbing with ethanolamines. The gases are then dried on alumina or molecular sieves to a residual moisture content lower than 5 ppm. This is done to prevent the formation of ice crystals during subsequent cooling stages.

B. Features of the cold separation section

Operations involving the distillation of hydrocarbons and the hydrogenation of acetylene impurities can be combined in different ways. The final decision depends on the pyrolysis feedstock, the degree of recovery desired for the different products, and economic data. Figure 2.17 offers an illustration of a classic system. The effluents, which make up a combined liquid/gas phase, are sent to a demethanizer normally operating at a pressure of about $3.2 \cdot 10^6 \text{ Pa}$, and where the methane is condensed at the top around -100°C .

However, some installations operate at lower pressures and temperatures of -140°C , implying thorough familiarity with cold technology and virtually perfect thermal insulation. By Joule-Thomson expansion, the overhead fraction can supply fairly pure hydrogen, containing 85 to 90 per cent volume depending on the final pressure. The bottom product from the demethanizer is sent to a second column, or de-ethanizer, which separates the C_2 cut (ethylene + ethane) at the top from the heavier products.

The acetylene derivatives of the C_2 cut are eliminated by selective hydrogenation. The hydrogen employed is obtained from the demethanizer, so that some methane is reintroduced into the C_2 cut, which is therefore usually sent to a secondary demethanizer after hydrogenation. The palladium (or nickel) based catalysts are placed in one or two reactors, sometimes featuring several beds with intermediate cooling. The temperature rises from 40 to 80°C between the inlet and outlet of a bed, and the operating pressure is about $3 \cdot 10^6 \text{ Pa}$.

At the exit of the selective hydrogenation section, the ethylene is separated from the ethane in a column with 110 to 120 trays operating at $1.9 \cdot 10^6 \text{ Pa}$ with an overhead temperature of about -35°C . The refluxes from these different columns are condensed by cooling and, given the temperature levels required, it is necessary to use refrigerant fluids operating in a closed circuit of compressions and expansions. Since steam cracking produces ethylene and propylene, these two components naturally serve as the refrigerant fluid, possibly with methane. For technical as well as economic reasons, it is important

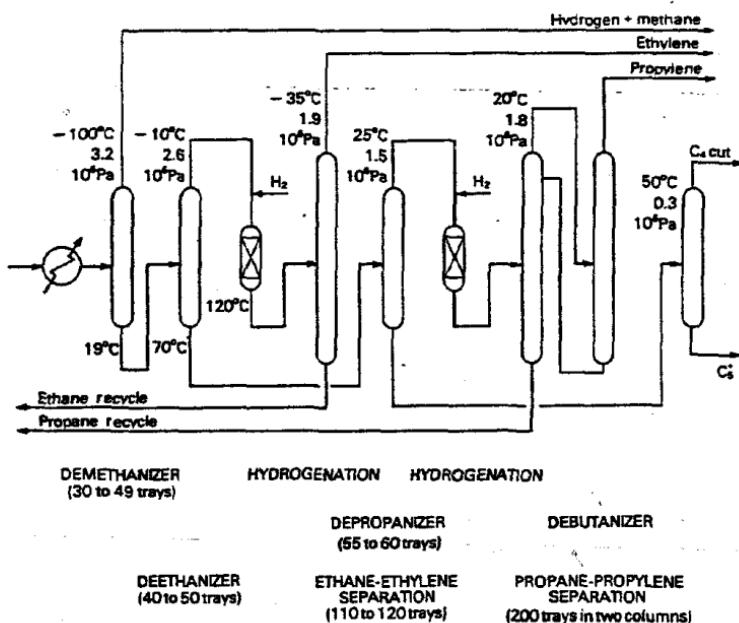


Fig. 2.17. Cold separation section of a naphtha steam-cracking unit.

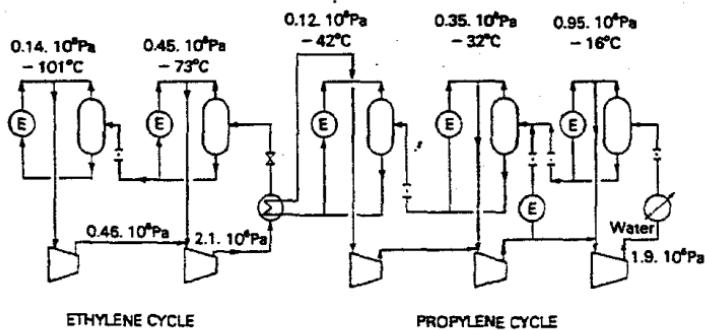


Fig. 2.18. Design of refrigeration cycles in a steam cracker.

to produce the refrigeration capacity required at a temperature close to that of the operation, and this may require several compression stages. As a rule, the temperature levels set are +15, -30 and -40°C for the propylene cycle, and -50, -75 and -100°C for the ethylene cycle.

Figure 2.18 illustrates the operation of a refrigeration cascade with propylene and ethylene. The starting point is propylene, which can be condensed at moderate pressure by water at 20 to 30°C. The liquid phase produced is cooled by expansion, causing partial vaporization. The rest can then provide refrigeration by vaporization in one of the condensers of the installation, or can be expanded again to create a lower temperature level. This allows new heat exchanges, or serves to prolong the cascade. The intermediate vapor phases are recompressed and recondensed by propylene from the previous stage or by water. At a pressure close to atmospheric, the propylene condenses the ethylene which, by successive expansions, serves to lower the temperature to -101°C and hence to create the demethanizer reflux.

Most of the compression capacity is absorbed by the propylene cycle (80 to 90 per cent). This is because the initial condensation of the propylene ensures the operation of the cascade. For the demethanizer, Fig. 2.19 also shows the practical production of the reflux created by the vaporization of ethylene from the refrigeration loop.

At the bottom of the deethanizer, a C_{3+} cut is collected, which is fractionated in more conventional columns. The C_3 cut collected at the top of the depropanizer is selectively hydrogenated to remove methylacetylene and propadiene. Since its propylene content may be as high as 95 per cent weight, depending on the severity, this cut is often

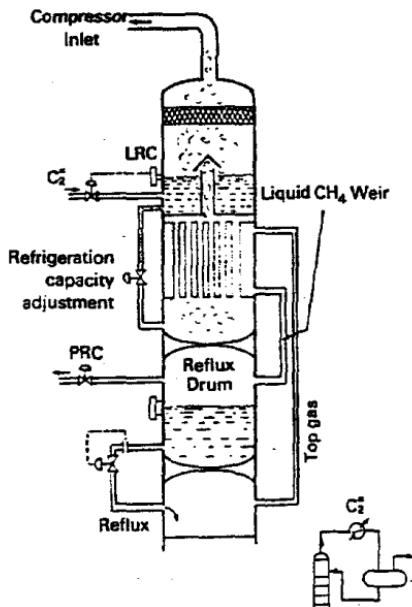


Fig. 2.19. Arrangements in the top of a demethanizer.

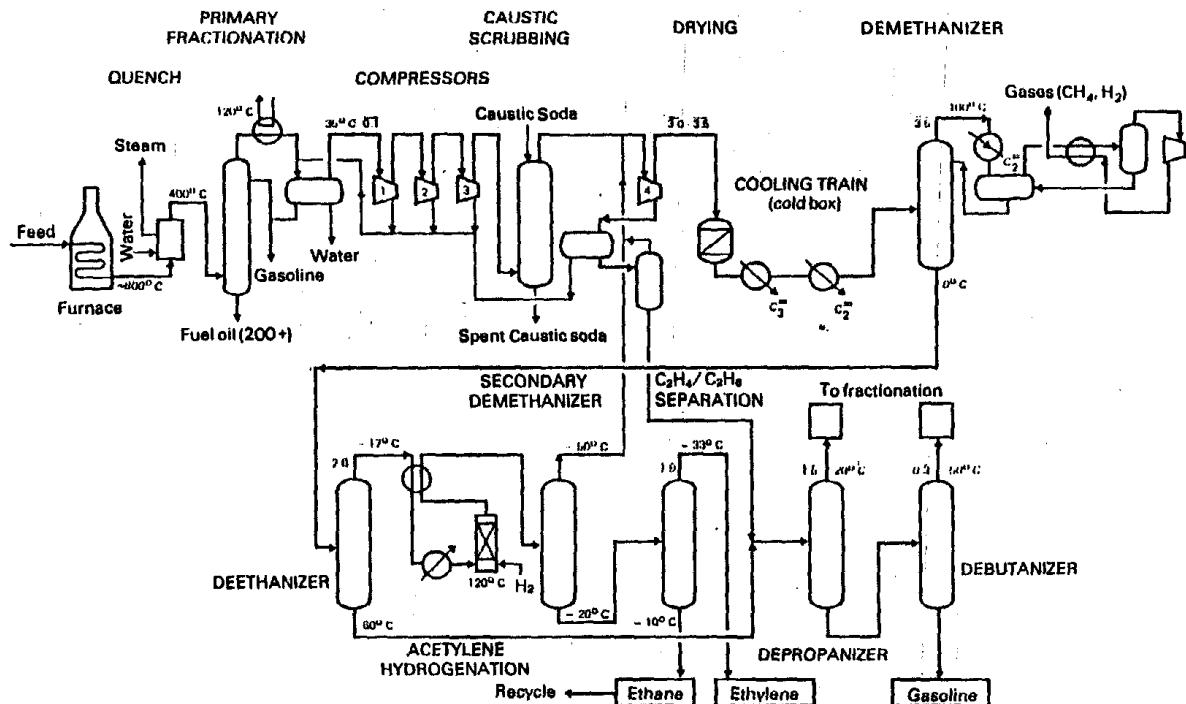
used directly. To obtain very pure propylene (99.5 per cent weight), however, it is necessary to remove the propane in a supplementary column. Table 2.10 offers a glance at the specifications that the ethylene and propylene thus separated are required to meet. The heavier hydrocarbons obtained at the bottom of the depropanizer are treated in a debutanizer, which produces a 1,3-butadiene-rich C₄ cut at the top. In accordance with the severity, Table 2.11 provides a typical example of the composition of this effluent for a naphtha feedstock. The pyrolysis gasoline drawn off at the bottom may, depending on the severity, contain 50 to 85 per cent weight of aromatic hydrocarbons, of which more than half is benzene. Its composition and treatment are discussed separately in Section 2.15.

TABLE 2.10
COMMERCIAL SPECIFICATIONS OF ETHYLENE AND PROPYLENE

Product	Ethylene	Crude propylene	Pure propylene
Ethylene min.	99.9% Wt	300 ppm	50 ppm
Propylene max.	50 ppm	91% Wt	99.5% Wt
Saturates (ppm) max.	1,000	Ethane 1,500 Higher HC 500	5,000
Acetylenics (ppm) max.	2	10	5
Propadiene (ppm) max.	—	20	10
Butadiene (ppm) max.	—	—	20
Oxygen (ppm) max.	1	2	2
Sulfur (ppm) max.	(H ₂ S) 1	(Total) 5	(Total) 1
CO (ppm) max.	5	—	5
CO ₂ (ppm) max.	5	—	5
Water max.	Dew-point - 60°C	20	10
Hydrogen (ppm) max.	1	—	1
Nitrogen oxides (ppm) max.	5	—	5

TABLE 2.11
TYPICAL COMPOSITIONS OF C₄ CUTS (% WT)

Components	Average	High
C ₃ s	0.3	0.3
n-butane	5.2	2.8
Isobutane	1.3	0.6
1-butene	16.0	13.7
Cis 2-butene	5.3	4.8
Trans 2-butene	6.6	5.8
Isobutene	27.4	22.2
Butadiene	37.0	47.5
Acetylenics	0.4	1.8
C ₃ s	0.5	0.5
Total	100.0	100.0



Figures with a bar indicate the service pressures at different points of the unit in 10^6 Pa.

Fig. 2.20. Simplified flow scheme of a complete naphtha steam-cracking unit.

The operating conditions in the cold separation section are essentially shown in Fig. 2.17. The choice of the gradation in the decreasing operating pressures between the demethanizer and the debutanizer is designed to ensure that the corresponding column bottom temperatures are sufficiently low to prevent any undesirable polymerization.

Figure 2.20 summarizes the complete arrangements of the different units of the hot and cold sections of an industrial steam cracking plant.

2.1.5 Pyrolysis gasolines

Due to their high content of aromatic hydrocarbons, especially benzene, C₅-gasolines produced by the steam cracking of liquid petroleum fractions, or the cuts to which they give rise by simple distillation, constitute a highly valuable product for both gasolines as well as petrochemicals.

2.1.5.1 Composition of pyrolysis gasolines

Table 2.12 shows the typical analyses of a C₅-gasoline and of aromatic cuts, obtained by naphtha steam cracking. As may be observed, these effluents contain non-negligible amounts of diolefins and alkenylaromatics, which make those employed in the refinery (C₅-fraction) unsuitable for direct use as a gasoline. These thermally unstable components cause gumming in motors, and therefore must first be removed.

In petrochemical applications, dienes also hamper the normal running of the installations and catalysts. In these uses, however, olefins and sulfur compounds also present a number of drawbacks, with respect to extraction solvents, for example. Given the

TABLE 2.12
TYPICAL COMPOSITIONS OF C₅-GASOLINE AND AROMATIC CUTS
PRODUCED BY NAPHTHA PYROLYSIS

Components	Composition (% Wt)		
	C ₅ -gasoline	C ₆ -200°C cut	C ₆ -C ₈ cut
Paraffins and naphthenes	11.8	7.8	9.7
Olefins	5.5	2.4	3.0
Diolefins	18.1	8.7	5.9
Aromatics			
Benzene	28.0	35.2	43.7
Toluene	13.9	17.4	21.7
C ₈	7.2	9.0	11.3
Alkenylbenzene (styrene)	3.0	3.8	4.7
C ₉ -.....	12.5	15.7	-
Total aromatics.....	64.6	81.1	81.4
Total	100.0	100.0	100.0
Sulfur content (ppm)	220	180	150

increasing severity of commercial specifications concerning the sulfur content of benzene, supplementary purification of aromatic pyrolysis effluents is therefore indispensable in this case. Since the ideal technique for this purpose is hydrotreating, and in view of the very stringent specifications on the residual amounts of non-aromatics in benzene, this operation can only be considered a pretreatment.

It must also be highly selective and convert the least possible aromatic hydrocarbons, whose contents, in steam cracking, depend essentially on the feedstock treated and the operating conditions. Based on naphtha feedstock, Table 2.13 indicates the variation in the composition of C₅- gasolines as a function of the treatment severity. On the whole, for a given feedstock, the higher the ethylene yield, in other words the greater the severity, the less pyrolysis gasoline is produced, and the higher its benzene concentration. The C₆ and C₈ aromatics contents also tend to rise, while the toluene content remains relatively constant.

2.1.5.2 Pyrolysis gasoline hydrotreating

On account of their excessive thermal instability, dienic compounds cannot be eliminated at the same time as olefins and sulfur compounds. Two successive operations are therefore necessary in this case:

- (a) Selective hydrogenation of diolefins, also called hydrodedienization or first step hydrogenation.
- (b) Fairly severe hydrotreating to convert nearly all the sulfur compounds, but sufficiently selective to avoid significantly hydrogenating the aromatics: this is hydrodesulfurization, also called second step hydrogenation.

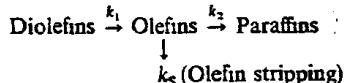
Only first step hydrogenation is necessary if all the pyrolysis gasolines are used as gasolines.

A. Hydrodedienization or first step hydrogenation

This hydrogenation must avoid:

- (a) The formation of gum by the polymerization of diolefins during the operation.
- (b) The hydrogenation of olefins.

In the sequence of catalytic reactions:



where k represents a conversion rate constant, it is necessary for the first reaction to be rapid and for the olefins to diffuse easily once they have been stripped. Accordingly, k_1/k_2 must be large, and this is achieved by using an active element with high selectivity: k_3/k_2 must also be large, requiring the use of a catalyst whose pores are at least 100 Å in diameter.

TABLE 2.13
NAPHTHA STEAM CRACKING. VARIATION IN COMPOSITION OF PYROLYSIS GASOLINES WITH SEVERITY

Components	Severity: % ethylene (with ethane recycle)					
	Low 24.4		High 28.5		Very high 33.4	
	Gasoline					
	% Feedstock	Composition (% Wt)	% Feedstock	Composition (% Wt)	% Feedstock	Composition (% Wt)
C ₅		28.7		20.5		5.9
Benzene	5.4	21.6	6.3	28.0	7.1	43.7
Other C ₆		9.7		7.0		1.9
Toluene	3.4	(3.5)	3.1	13.9	2.4	15.0
Other C ₇		4.8		3.1		0.7
Xylenes, ethylbenzene	0.9	3.5	1.6	7.2	1.7	10.7
Styrene	0.4	1.6	0.7	3.0	0.7	4.2
Other C ₈		3.2		1.8		0.9
C ₉ aromatics		9.3		12.5		14.1
Other C ₉₊		4.1		3.0		2.9
Total	24.9	100.0	22.6	100.0	16.3	100.0
% aromatics in gasolines		49.5		64.6		87.7

Hydrogenation can also be carried out at the lowest possible temperature, by increasing the amount of catalyst. The hydrogen pressure must also be sufficiently high to accelerate the reaction:



Accordingly, two types of process are available in practice.

a. Processes with nickel catalyst

The catalyst, distributed in one or two beds, consists of nickel or nickel sulfide on alumina. The reaction takes place at about 120 to 160°C, at a pressure of about 2 to $6 \cdot 10^6$ Pa. The pressure actually depends on the purity of the hydrogen, whose partial pressure must be 1 to $2 \cdot 10^6$ Pa, and corresponds in practice to an H_2/C_4 -mole ratio of about 0.05 to 0.6 at the reactor exit. The LHSV (Liquid Hourly Space Velocity) is normally between 1 and 3 h^{-1} . The maintenance of a large fraction of the feed in the liquid phase helps to remove the polymers formed by continuous washing of the catalyst, improving its life, which is 2 to 4 years, with run lengths of 2 to 9 months, depending on each specific case. The catalysts are regenerated by removing the gums deposited on the beds by treatment with steam or controlled combustion at about 400°C.

The principal processes of this type are commercialized by *BP (British Petroleum)* and *IFP*. Similar technologies have also been developed by *Gulf (HPG)* and *Houdry Kellogg, Shell* etc. On the whole, their flow sheets (Fig. 2.21 a) comprise preheating of the feedstock and hydrogen by heat exchange with the reactor effluent, introduction into this reactor and flash of the product under pressure, in order to separate the hydrogen and light components by vaporization, part of which is recycled by a compressor and the remainder purged. The liquid fraction is stabilized and rid of the heavier components in two distillation columns.

b. Processes with palladium-based catalysts

The catalyst systems employed contain about 0.3 per cent weight of palladium as well as various additives. They have a low specific surface area and high activity. They operate at an average temperature between 80 and 160°C, at 2 to $3 \cdot 10^6$ Pa, and with a LHSV of 3 to 8 h^{-1} . Polymer formation is very slight.

The foremost licensors of these processes and of palladium catalysts are *Amoco (American Oil Co.)*, *BASF (Badische Anilin und Soda Fabrik)*, *Bayer-Lurgi*, *Engelhard (HPN)*, *IFP*, *Lummus (DPG Hydrotreating)*, *Mitsubishi*, *UOP (Universal Oil Products)* etc. The industrial unit scheme is substantially the same as for selective hydrogenation in the presence of nickel. However, the technology selected by *Bayer* differs in so far as the feedstock is cooled and the temperature maintained at the desired level by means of a refrigerant fluid or water.

Tables 2.14 a and 2.14 b provide an idea of the effectiveness of deoxygenation and the characteristics of the effluents obtained, concerning the entire gasoline fraction, and also concerning a C₆-C₈ cut. In the former case, the presence of aromatics and olefins ensures a product with good octane numbers, which can therefore be upgraded as a gasoline. However, its volatility curve and its (excessively high) density preclude its direct use, and it must first be mixed with other gasolines. In the second case, despite the virtually complete disappearance of diolefins and styrene, the remaining high concentrations of

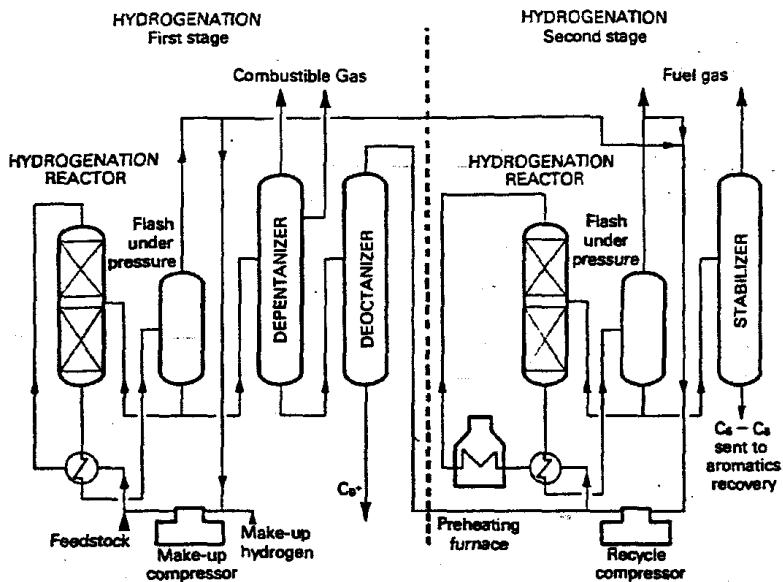


Fig. 2.21 a. Hydrogenation of pyrolysis gasolines. Separate stages on C₅-C₉ cut with intermediate fractionation.

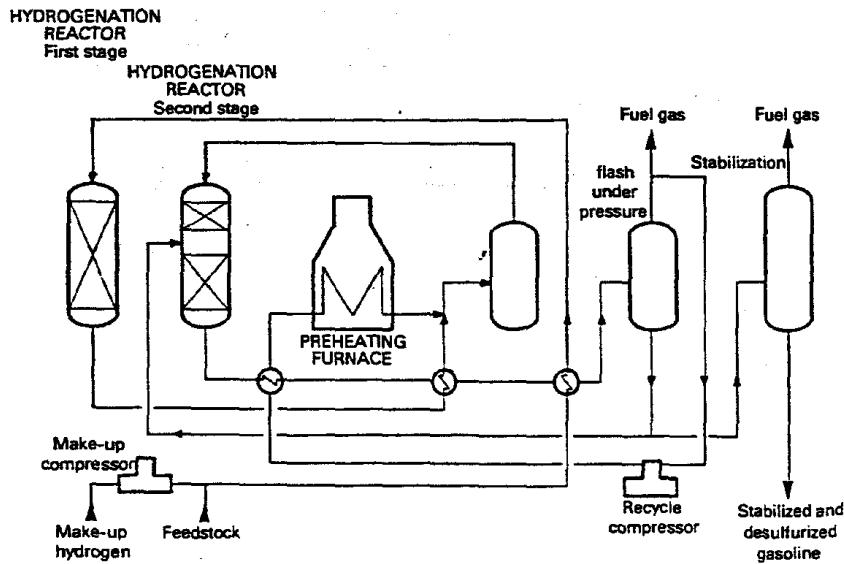


Fig. 2.21 b. Hydrogenation of pyrolysis gasolines. Integrated stages on C₅-C₉ cut.

TABLE 2.14a
DEDIENIZATION OF A C₅-200°C PYROLYSIS GASOLINE

Gasoline characteristics	Crude gasoline	Hydrotreated gasoline
<i>d</i> ₄ ²⁰⁽¹⁾	0.821	0.819
ASTM distillation (°C)		
LP	30	40
5 %	42	42
10 %	49	48
50 %	98	100
90 %	164	166
95 %	174	179
FP	195	204
Diene value (g I ₂ /100 g)	27	0.3
Bromine number (g Br ₂ /100 g)	75	47
Total sulfur (ppm)	400	380
Mercaptan sulfur (mg/l)	18	< 5
Octane Number		
Research clear	97	97
Research Pb 0.15 g/l	98	98
Motor clear	86	85
Motor Pb 0.14 g/l	87	87

(1) Specific gravity, 68.0/39.2.

TABLE 2.14b
HYDROGENATION OF A PYROLYSIS C₆-C₈ CUT, WEIGHT BALANCE

Composition cut	Crude cut	Dedienized cut	Dedienized and desulfurized cut
Diolefins and styrene	10.6	0.3	≈ 0
Olefins	3.0	2.4	≈ 0
Benzene	43.7	43.7	43.6
Toluene	21.7	21.7	21.5
Xylenes and ethylbenzene	11.3	11.3	11.3
Aromatics ⁽¹⁾	64.6	64.6	64.3
Total sulfur (ppm)	150	145	0.5
Thiophenic sulfur (ppm)	120	120	0.2

(1) Aromatics content of C₅-₈ gasoline (see Table 2.13).

olefins, and especially sulfur, prevents the direct use of the hydrotreated cut as a petrochemical base.

B. Hydrodesulfurization or second step hydrogenation

This differs from conventional hydrodesulfurization by the small amounts of sulfur compounds initially present and the even lower contents required in the product, both of sulfur (1 ppm for the 60 to 150°C cut) and olefins (50 ppm). Moreover, the components to be removed are thiophenic, entailing relatively severe operating conditions (elevated temperature and high hydrogen pressure) due to their poor reactivity. However, the existence in the feed of residual amounts of certain diolefins which resist dedienization, and especially of olefins, tends to make the medium extremely reactive.

To control the exothermicity of the reaction, a number of technological arrangements are indispensable, such as intermediate quenches in the reactor. To maintain a satisfactory desulfurization rate, this must therefore be compensated by a lower space velocity or better activity of the catalyst system, especially since the risks of polymerization attributable to the residual diolefins and olefins, which are hydrogenated first, require operation at the top of the reactor at the lowest possible temperature and with a high partial pressure of hydrogen.

The usual catalysts are based on cobalt, nickel, molybdenum and tungsten sulfides, generally combined and deposited on alumina. The most widely used formula is a composite sulfide of molybdenum and cobalt on alumina. Run length and catalyst life are longer than those of the catalytic systems employed in first step hydrogenation, i.e. 6 to 12 months and 3 to 5 years, and the regeneration method is identical.

The conversion takes place at an average temperature between 280 and 350°C, and with a partial pressure of hydrogen of about $1.5 \cdot 10^6$ Pa.

The patent holders are the same as those who practice dedienization. The flow sheet (Fig. 2.21 a) comprises the preheating of the feedstock and hydrogen by heat exchange with the reactor effluent and passage through a furnace, the reactor itself, containing catalysts placed in fixed beds between which a quenching fluid (cold product recycle) is injected, flash under pressure of the effluent to separate the light products, part of which is recycled by means of a compressor, and the stabilization of the liquid fraction by distillation.

Hydrodesulfurization and dedienization can be set up side by side, requiring intermediate fractionation (C_5 -200°C cut, Fig. 2.21 a) or incorporated (C_6 - C_8 cut, Fig. 2.21 b). The characteristics of a dedienized and desulfurized C_6 - C_8 cut are presented in Table 2.14 b. Losses of aromatic hydrocarbons by hydrogenation to naphthenes are low (about 0.5 per cent).

2.1.6 Steam cracker economics

Although steam cracking was initially designed for ethylene manufacture, it is only economically justified if the different hydrocarbons which it produces are properly upgraded as petrochemical intermediates. Hence although ethane only produces ethylene as an upgradable product, in the case of propane an attempt is made to profit from the sale of ethylene and propylene, and, in the case of the liquid petroleum fractions (naphtha

and gas oil), that of ethylene, propylene, butenes, butadiene and aromatic gasoline. With the exception of hydrogen, which is used directly in a blend with methane in selective hydrogenation treatments, and sometimes purified by cryogenic methods, the remaining effluents are employed as fuels on the unit itself (methane and residual hydrocarbon sent to a pool (fuel oil).

The average size of steam cracking units has grown from about 50,000 t/year of ethylene in 1950 to about 450,000 t/year today. In fact, recent advances in metallurgy, and developments in engineering and applied chemistry, now allow the construction of steam crackers capable of producing 750,000 t/year of ethylene. The limiting parameters are essentially related to the economic situation (market size, costs and means of transport, instability of demand etc.). It is generally assumed that the optimal size of a pyrolysis facility is that for which a utilization (or load) factor of 100 per cent is reached three years after startup. This is because this factor is vitally important for the economics of a steam cracker, given the scale of the investments concerned.

From this standpoint, Tables 2.15 and 2.16 give, for different feedstocks, a percentage distribution of the battery limits investments between the different sections of the facility, with their relative scale. For a basic case related to a production capacity of 450,000 t/year of ethylene, Table 2.17 gives investment data (France, conditions in mid-1986), together with the consumption of chemicals, catalysts, utilities, etc., which, as a first approximation, are independent of the treatment severity, but vary with the feedstock and, to a lesser degree, with capacity.

The investments mentioned do not include off sites or storage facilities, which together account for 40 to 50 per cent of the battery limits investments. They are related to the complete steam cracking unit, to the exclusion of the treatment of the C₄ cut (butadiene extraction in particular) and the C₃₊ cut (selective hydrogenations). Hence they account for the different separations and selective hydrogenations of the C₂ and C₃ cuts. The consumption figures are net values. Residual combustible gases are presumed to be

TABLE 2.15
STEAM CRACKING. DISTRIBUTION OF BATTERY LIMITS INVESTMENTS
BETWEEN THE DIFFERENT SECTIONS OF THE INSTALLATION

Sections	Feedstock		
	Ethane	Naphtha	Gas oil
Pyrolysis furnaces	30	35	40
Primary fractionation	8	10	12
Compression/scrubbing/drying	20	18	16
Demethanization	10	8	7
C ₂ separation and treatment	10	7	7
C ₃ separation and treatment ⁽¹⁾	2	4	4
Refrigeration	20	18	14
Total	100	100	100

(1) Production of chemical grade propylene.

TABLE 2.16
STEAM CRACKING, BATTERY LIMITS INVESTMENTS, RELATIVE AMOUNTS
ACCORDING TO FEEDSTOCK

Feedstock	Relative investments
Ethane	80 to 85
Ethane/propane (50/50)	82 to 87
Propane	85 to 90
Butane	90 to 95
Naphtha/LPG (50/50)	90 to 95
Light and medium-range naphtha	100
Kerosene, full-range naphtha	100 to 105
Naphtha/gas oil (50/50)	115 to 120
Naphtha/gas oil/butane	120 to 125
Atmospheric gas oil	110 to 115
Vacuum gas oil	120 to 125

TABLE 2.17
STEAM CRACKING, ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 450,000 t/year ETHYLENE STREAM FACTOR 8,000 h/year

Feedstock	Ethane	Ethane/ propane (50/50)	Medium-range naphtha	Atmospheric gas oil
Battery limits investments (10^6 US\$) ⁽¹⁾	230	250	280	350
Consumption per ton of ethylene				
Chemicals				
Caustic soda (100%) (kg)	2	3	0.5	2
Monooethanolamine (kg)	—	—	0.2	1
Miscellaneous (US\$)	0.4	0.4	0.4	0.4
Catalysts (US\$)	0.4	0.4	0.9	0.9
Utilities				
Steam (t)	1	2	(-)0.15	0.9
Fuel (10^6 kJ) ⁽²⁾	$10^{(2)}$	4	—	—
Electricity (kWh)	$30^{(2)}$	40	80	100
Cooling water (m^3)	$200^{(2)}$	220	280	300
Process water (m^3)	2	2	2	2
Labor (Operators per shift)	8	9	12	12

(1) The extrapolation exponent, about 0.7 for medium-sized installations, tends towards 0.8 for large units and 0.6 for small capacities.

(2) For 100,000 t/year, utilities consumption is as follows: fuel $8 \cdot 10^6$ kJ, electricity 650 kWh, cooling water $250 m^3$.

(3) Methane and residual hydrogen are burned in the furnaces. Liquid fuel oil is a by-product.

TABLE 2.18
SELECTIVE HYDROGENATION OF PYROLYSIS GASOLINES. ECONOMIC DATA
(France conditions, mid-1986)

Process	Hydrodeindienization	Total hydrogenation	
Characteristic of the installation	Separation of light and heavy compounds	Intermediate separation of C ₅ and C ₉₊	Final stabilization of light compounds
Feedstock	C ₅₊ cut	C ₅ -C ₉ cut	C ₆ -C ₈ cut
Feedstock capacity (t/year) ..	200,000	200,000	140,000
Battery limits investments (10 ⁶ US\$)	2.80	4.60	2.85
Initial catalyst loads (10 ⁶ US\$)	0.15	0.35	0.25
Material balance per ton of feedstock			
H ₂ consumed (kg) 80 to 100%	5-17	15-50	30-100
Fuel-gas (kg)	12	35	70
C ₅ (t)	—	0.2	—
C ₆ -C ₈ cut (t)	0.97	0.7	1.0
C ₉₊ and heavier (t)	0.03	0.1	—
Consumption per ton of feedstock			
Catalyst (US\$)	0.1	0.2	0.2
Utilities			
Steam (MP) (t)	0.3	0.45	0.1
Electricity (kWh)	6	15	20
Fuel (10 ⁶ kJ)	—	0.12	0.25
Cooling water (m ³)	15	25	15
Labor (Operators per shift) ..	0.5	1	1
Feed composition (% Wt)			
Diolefins		38	27
Olefins		16	14
Aromatics		36	53
Paraffins		10	6
Total sulfur (ppm)		500	1,500
Acid sulfur (ppm)		20	50

(1) Including 0.05 · 10⁶ US\$ of recoverable precious metals.

(2) Including 0.04 · 10⁶ US\$ of recoverable precious metals.

TABLE 2.19
ETHYLENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
HDPE	16	22	20	18
LDPE	38	26	31	33
Polystyrene and derivatives	7	7	9	7
PVC	18	14	15	15
Acetaldehyde	3	1	5	3
Ethanol	2	2	1	3
Ethylene oxide	11	17	11	14
Vinyl acetate	1	2	3	2
Miscellaneous ⁽¹⁾	4	9	5	5
Total	100	100	100	100
Production (10 ⁶ t/year)	12.4	14.1	4.4	42.5
Capacity (10 ⁶ t/year) ⁽²⁾	14.7	15.9	4.6	50.0
Consumption (10 ⁶ t/year)	12.6	14.1	4.4	42.5

(1) Chlorinated solvents, ethylchloride, ethyldibromide, ethylene-vinyl acetate copolymers, linear olefins, linear alcohols, *p*-methylstyrene, propionaldehyde...

(2) In 1986 the worldwide production capacity of ethylene was 52.3 · 10⁶ t/year with the following distribution:

United States	16.0	Western Europe	13.9	Middle East	2.4
Canada	2.2	Eastern Europe	6.6	Japan	2.4
Latin America	2.9	Africa	0.5	Asia and Far East	3.2

TABLE 2.20
PROPYLENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
Acrylonitrile	17	18	20	18
Cumene	9	9	5	9
Isopropanol	6	6	3	5
Oxo alcohols	13	8	10	11
Polypropylene	34	35	47	36
Propylene oxide	10	11	6	9
Oligomers	7	7	1	4
Miscellaneous ⁽¹⁾	11	6	8	8
Total	100	100	100	100
Sources (% product)				
Steam cracking	86	53	89	75
Catalytic cracking	14	47	11	25
Total	100	100	100	100
Production (10 ⁶ t/year)	7.2	7.0	3.0	22.5
Capacity (10 ⁶ t/year) ⁽²⁾	8.7	9.9	3.0	28.5
Consumption (10 ⁶ t/year)	7.1	6.8	2.9	21.5

(1) Acetone, acrolein, acrylic acid, allyl chloride, carbon disulfide, chlorinated solvents, cresols, dichloropropadiene, epichlorohydrin, ethylene-propylene rubber, glycerin, 4-methyl-1-pentene, oxalic acid, polymethyl methacrylate, paramins...

(2) Steam cracking and catalytic cracking. In 1986 the worldwide production capacity of propylene was 28.3 · 10⁶ t/year with the following distribution:

United States	9.7	Western Europe	8.2	Middle East	0
Canada	0.7	Eastern Europe	3.3	Japan	0
Latin America	1.3	Africa	0.1	Asia and Far East	1

burned in the furnaces, while liquid fuel oil is not. This points out the virtual energy self-sufficiency of steam crackers running on naphtha.

In contrast to the lighter effluents, the C₄ cut, especially that from the steam cracking of naphtha or gas oil, does not require systematic supplementary stabilization treatment. Hence it is utilized as required in the installations distinct from the actual pyrolysis unit. On the other hand, the C₅-gasoline must be selectively hydrogenated before any subsequent use. This operation should normally be incorporated with steam cracking, but is technologically and economically distinct owing to the two available possibilities of utilization, as a gasoline and as a petrochemical base. These two alternatives in fact entail different supplementary treatments. Accordingly, Table 2.18 lists the related economic data separately.

Steam cracking facilities manufacture nearly all the ethylene produced worldwide, and a large share (57 per cent) of the propylene utilized for petrochemicals. As shown by Tables 2.19 and 2.20, these olefins offer many applications and represent very high consumption tonnages. They are essentially employed captively, so that, to limit transport and storage costs, this factor tends to encourage the installation of production and utilization centers at the same location, as well as the creation of highly diversified petrochemical complexes around the steam crackers. With the growing size of pyrolysis units, the vastness of these complexes is growing accordingly, and any production incident has considerable economic repercussions in such situations. To overcome this drawback, appropriate pools of ethylene (and propylene) have been created by connecting the steam crackers of a given geographic area by a network of pipelines, and by building large underground storage facilities. In the United States, this is the case of the Ethylene Texas Spaghetti Bowl. Intensive interconnections also exist in Western Europe: in the United Kingdom, along the Rhine Valley (Eastern France, West Germany, Benelux), in France (Midi/Rhône-Alpes regions) and in Italy (Po Plain).

2.2 CATALYTIC REFORMING

Catalytic reforming was originally practised in two different types of installation, depending on whether it was used in refining or for petrochemicals. This distinction, related to the severity of operating conditions, subsequently blurred, due to the growing need for high-performance gasolines, which was more rapid than that of benzene, toluene and xylenes for the chemical industry, and because of the requirement for a high octane number, in other words an increase in the aromatics content of the reformates. This trend was initially accentuated by pollution regulations and the partial removal of lead from gasolines, and also by energy conservation measures that encouraged a better upgrading of petroleum cuts.

At present, to contend with increasingly stringent energy requirements, the manufacturers are again trying to develop more specific processes.

Thus, in refining, they employ reformers operating at high severity, but with greater operating stability and improved gasoline yields, and in petrochemicals, the optimization of the production of BTX aromatics by the use of high-temperature reactors.

On the whole, catalytic reforming remains a refining process, which is extensively described in specialized works. We shall only dwell here on the main aspects and specific applications designed to produce petrochemical feedstocks.

2.2.1 Physico-chemical characteristics of reforming

2.2.1.1 Reactions involved

Similar to the attempt to obtain a high octane number from a mixture of hydrocarbons, aromatics production results from the following reactions:

- (a) Dehydrogenation of naphthalenes (alkylcyclohexanes) to aromatics.
- (b) Dehydrocyclization of paraffins and isoparaffins to aromatics.

Added to these are the isomerization of paraffins to isoparaffins and of alkylcyclohexanes, conversions which supply the foregoing reactions.

A number of side reactions also takes place, the most important of which are the following:

- (a) Coke formation.
- (b) Hydrocracking of paraffins and naphthalenes.
- (c) Demethanation.

2.2.1.2 Thermodynamic and kinetic considerations

The stability of aromatics in comparison with other hydrocarbons increases with temperature (Fig. 2.1), so operations are conducted above 300°C. However, the kinetic competition between the desired and side reactions gives rise to the selection of specific operating conditions for the required conversions:

- (a) The dehydrogenation of naphthalenes to aromatics is highly endothermic ($\Delta H = 210 \text{ kJ/mol}$) and exentropic. It is favored by raising the temperature and lowering the pressure. The reaction rate decreases with an increase in the number of carbon atoms in the feedstock, but remains substantially higher than that of the other reactions, which increases with the number of carbon atoms.
- (b) The dehydrocyclization of paraffins is even more endothermic and exentropic than dehydrogenation ($\Delta H = 250 \text{ kJ/mol}$). Hence it is favored by higher temperature and lower pressure. However, it is much slower than dehydrogenation, and, due to its low reaction rate, it only becomes important if the operating conditions are severe (elevated temperature and low pressure).
- (c) The isomerization of *n*-paraffins to isoparaffins and of alkylcyclopentanes to alkylcyclohexanes is slightly exothermic (ΔH between -10 and -20 kJ/mol) and very fast in the usual operating conditions. Hence it is relatively unaffected by a variation in temperature and by pressure, but is inhibited by the aromatics formed by dehydrocyclization. The thermodynamic equilibrium of isomerization is constantly shifted by the two foregoing reactions.
- (d) Coke formation, which results from intensive cracking of hydrocarbons, is favored by high temperature and low pressure. This is one of the most disturbing side

reactions, because it leads to a decrease in the activity of the catalysts employed. It is minimized by maintaining a hydrogen pressure that pushes the reaction towards hydrocracking.

- (c) Hydrocracking is an exothermic reaction ($\Delta H = -40 \text{ kJ/mol}$) that is thermodynamically complete in the usual operating conditions, but is limited by a slow reaction rate. At a higher temperature, this conversion may become more important than isomerization and dehydrogenation. Moreover, it increases in extent with a rising aromatics concentration.

These considerations are illustrated by thermodynamic calculations, of which some results are given in Table 2.21.

In theory, favorable conditions correspond to a pressure of $0.1 \cdot 10^6 \text{ Pa}$ and temperatures not exceeding 350°C . However, cracking reactions (coke formation) are excessive in this case, and the selectivity of the operation is reduced. Hence the reactions producing aromatics must be activated selectively, and operations conducted at a sufficiently high partial pressure of hydrogen.

TABLE 2.21
CATALYTIC REFORMING. THERMODYNAMIC DATA

Reaction	Equilibrium temperature ($^\circ\text{C}$) for 90% conversion			
	$0.1 \cdot 10^6 \text{ Pa}$	$1 \cdot 10^6 \text{ Pa}$	$2.5 \cdot 10^6 \text{ Pa}$	$5 \cdot 10^6 \text{ Pa}$
Cyclohexane \rightarrow benzene + 3H_2	294	355	443	487
Methylcyclopentane \rightarrow benzene + 3H_2 ..	315	391	492	540
<i>n</i> -hexane \rightarrow benzene + 4H_2	354	487	562	623
Methylcyclohexane \rightarrow toluene + 3H_2 ...	248	320	356	385
<i>n</i> -heptane \rightarrow toluene + 4H_2	305	428	496	550

2.2.1.3 Catalytic activation of reactions

A. Catalyst types

The reactions are activated by catalysts capable of favoring isomerization and cyclization as well as dehydrogenation. This means that the catalytic systems used are multifunctional, and that they theoretically possess the following:

- (a) A hydrogenation/dehydrogenation function, provided by the presence of a metal. This element must be active and stable at the reaction temperatures ($\geq 500^\circ\text{C}$) and its content must be controlled to prevent or minimize demethanation reactions.
- (b) An acid function, provided by the support, with or without the addition of a halogenated compound, which favors isomerization and cyclization reactions to varying degrees. The acidity must be controlled to moderate hydrocracking.

Two types of catalyst can be considered in practice:

- (a) Catalysts containing oxides or sulfides of Cr, Mo, Ni and W.

- (b) Catalysts containing noble metals, usually platinum alone or combined with other metallic substances.

Oxides and sulfides were the first to be employed because they were unaffected by the sulfur compounds in the feedstock. Due to their low selectivity, however, they have been superseded by noble metal based catalysts. For conventional systems, these catalysts exhibit the following characteristics:

- (a) The support usually consists of a γ alumina, containing a halogenated compound, which is a chloride, a fluoride, or a combination of both: the finished product is in the form of extrudates about 1.5 mm in diameter, with a specific surface area of $200 \text{ m}^2/\text{g}$, or spheres for regenerative systems.
- (b) The noble metal (platinum) content ranges from 0.2 to 0.8 per cent by weight.

New bi- and multimetallic catalysts have been marketed more recently:

- (a) To begin with, the introduction of rhenium helped to achieve greater performance stability with time, connected with an apparent tolerance to coke deposits. This results in the possibility of longer run lengths, or of operation in more severe conditions (lower pressure, lower hydrogen ratio, higher temperature).
- (b) Subsequently, the use of various other promoters also resulted in better intrinsic selectivity (ratio of *n*-heptane aromatization and cracking rates). This improvement is accompanied by a drop in activity, offset by a rise in temperature, with comparable stability, and correspondingly higher yields.

The role of these additives, which may be used in bi- or multimetallic combinations (Re, Ir, Ru, Ag, Au, Ge etc.) is poorly understood. They help to enhance the properties of platinum by keeping it in a suitable state of dispersion, and to modulate the acidic character of the support. They appear to oppose the sintering of metallic crystallites by the formation of alloys or polymetallic clusters.

B. Catalyst activity

Catalyst activity is reduced by two factors:

- (a) The formation of coke deposits during treatment, which are removed by regeneration.
- (b) The presence in the feedstock of poisons which are partly removed by pretreatment.

a. Coke formation

The formation of coke is due to the olefin and diolefin compounds whose appearance may be limited by lowering the temperature, raising the pressure, and increasing the hydrogen hydrocarbon ratio in the reactor.

It also depends on the type of feedstock, and on the content of polycyclic hydrocarbons and long molecules. Coke exerts the effect of reducing the active surface area of the catalyst, causing a progressive drop in conversion. To overcome this drawback, the temperature is first raised. When the maximum temperature supportable by the catalyst has been reached, the operation must be stopped for regeneration.

The amount of coke may vary from 1 to 14 per cent by weight of the catalyst according

to the conditions and the type of reactor. Regeneration by burning is carried out gradually below 500°C, to avoid local hot spots that are detrimental to the catalyst system. After nitrogen flushing, this is done using a gas whose oxygen content is gradually raised from 2 to 15 per cent by volume. The coke content is thus lowered to a maximum of 0.2 per cent by weight.

This operation is even more delicate with multimetallic catalysts, where the removal of additives by sublimation or destruction must be prevented.

b. Catalyst poisons

Platinum catalysts are especially sensitive to poisoning which can be caused:

- (a) Permanently by metals: arsenic, lead, copper and mercury.
- (b) Reversibly by sulfur, nitrogen, water and halogenides.

This makes prior purification of the feedstock necessary. To provide an example, the maximum impurities contents before and after feedstock treatment are listed in Table 2.22:

- (a) Sulfur and sulfur compounds lead to the formation of H₂S, which inhibits the hydrogenation/dehydrogenation function of the catalyst system by adsorption on platinum. This temporary inhibition is exploited with new conventional catalysts, whose excessive activity is temporarily limited by the injection of 0.2 to 0.4 per cent weight of H₂S in the feedstock, to prevent the premature formation of coke. Bimetallic systems are more sensitive on the whole than platinum alone to the presence of poison in the feedstocks (particularly sulfur). The specification demanded is normally less than 3 ppm, but some catalysts can operate with a higher content (5 ppm).
- (b) Nitrogen and its derivatives act by the production of ammonia, which inhibits the catalyst's acid function.
- (c) Water and halogenated compounds play complementary roles. Water present in excess causes halogen stripping and a decrease in the isomerizing and cracking activity of the catalyst. Too little water facilitates the formation of methane. The optimal moisture content of the recycle gas must lie between 5 and 60 ppm.

TABLE 2.22
MAXIMUM IMPURITIES CONTENTS OF CATALYTIC REFORMING FEEDSTOCK

Impurity	Content	
	Before pretreatment	After pretreatment
Arsenic (ppb)	50	20
Lead (ppb)	50	20
Copper (ppb)	50	20
Nitrogen (ppm)	2	1
Organic chlorine (ppm)	2	0.1
Water (ppm)	30	4
Sulfur (ppm)	200 to 1,000	10 or 5 depending on NO

according to the type of catalyst employed. The proportions can be adjusted by the injection of water or halogens (for example, in the form of CCl_4) in line with each specific case.

- (d) The sensitivity to permanent poisons is the same for the different types of catalyst (As < 0.001 ppm, Pb, Cu or Hg < 0.05 ppm each at the reactor inlet).

Pretreatment is chiefly designed to remove sulfur compounds, usually by hydrodesulfurization of the feedstock, followed by a stabilization, to separate the H_2S formed. This operation offers the advantage of simultaneously removing the other contaminants.

2.2.2 Industrial catalytic reforming

2.2.2.1 Main types of installation

Two types of unit were available until 1971:

- (a) Semi-regenerative units, with *in situ* catalyst treatment, during periodic shutdowns every six months to one year.
- (b) Cyclic regenerative units, with the use of an additional "swing" reactor, to replace each of the other reactors in succession during regenerations, thus ensuring uninterrupted production.

A new generation of so-called regenerative processes emerged with the development of multimetallic catalyst systems. They operate by continuous withdrawal and regeneration of the catalyst, which is then recycled to the reactors. This technology applies to the manufacture of gasoline, and specifically to that of aromatics. This is because it can withstand more severe treatment conditions, which allow intensive cyclization of the paraffins, the removal of those that subsist by hydrocracking, and the hydrodealkylation of the heavier compounds.

2.2.2.2 Operating conditions

Three or four reactors are laid out in series, according to requirements, with prior heating of the feedstock and intermediate heating of the effluents. Table 2.23 offers an indication of the average operating conditions.

For conventional reforming with three reactors in series, the variations in temperature between the inlet and outlet are as follows:

- (a) -30 to -70°C for the first, with an effluent at about 440 to 450°C.
- (b) -5 to -40°C for the second, with an effluent at about 480 to 490°C.
- (c) -10 to +10°C for the third, with an effluent at about 490 to 510°C.

2.2.2.3 Catalysts

The oxides and sulfides formerly used in fluidized beds have been abandoned in favor of the following categories of dual-function catalysts:

- (a) Conventional systems with:
- High platinum content (0.6 per cent): R 12 by *UOP*, RD 150 by *Engelhard*, RG 101, 402 and 404 by *IFP* etc.
 - Low platinum content (0.2 to 0.4 per cent): R 11 by *UOP*, RD 150 by *Engelhard*, 3 L by *Houdry*, RG 412 and 414 by *IFP* etc.
- (b) Bimetallic catalysts: R 16 (Pt/Re), R 20, R 22 (Pt/Ge) and R 50 by *UOP*, series E 500 by *Engelhard*, Pt/Re by *Chevron*, HR 51 by *Houdry*, Esso catalysts, RG 422 and 424 (Pt 0.6 per cent), RG 432 and 434 (Pt 0.35 per cent) by *IFP* etc. The catalysts R 15 and R 18 by *UOP* and RG 442 by *IFP* containing 0.35 per cent weight platinum serve to optimize the production of C₃/C₄ by enhancing the acid function of the support by the addition of growing amounts of halogenated compounds (chlorine, fluorine).
- (c) Multimetallic catalysts: series R 30 and R 60 by *UOP*, series E 600 by *Engelhard*, KX 130 (Pt/Ir) by *Esso*, Asahi's Pt/Pb catalyst, Amoco's specialty catalyst, RG 451 (Pt 0.35 per cent) and RG 461 (Pt 0.6 per cent) by *IFP* etc.

TABLE 2.23
CATALYTIC REFORMING. OPERATING CONDITIONS

Process	General variation range	Semi-regenerative	Cyclic regenerative	Regenerative	Specific production of aromatics
Pressure (10 ⁶ Pa)	0.7 to 4	1.5 to 2.5	0.7 to 1.5	1	0.7 to 1.5
Temperature (°C) at start and end of run	480 to 550	510 to 540	510 to 540	510 to 540	520 to 550
H ₂ /hydrocarbon mole ratio in feedstock	3 to 10	5 to 6	4 to 5	3 to 4	≈ 5
LHSV (h ⁻¹)	1 to 4	2 to 3.5	3.5 to 4	1.5 to 4	≈ 2

2.2.2.4 Equipment

Through the years, equipment design has adapted to developments in catalysts, in other words more severe operating conditions, particularly at very low pressures. This situation has resulted in a substantial decrease in the maximum allowable pressure drop in the furnaces, exchangers and reactors. In fact, at a given pressure, the pressure drop conditions the dimensioning of the hydrogen recycle compressor, and hence its cost.

Attempts were first made to reduce the thickness of the catalyst bed, by considering axial or radial gas flow in succession. With an axial stream, the reactor is cylindrical or, even better, spherical, allowing a gain in equipment weight. With radial flow, thin cylindrical rings of catalyst are prepared, with a scallop type of distribution for peripheral feed, and a central collector designed to gather the product. Efforts were then directed toward improvements in furnaces (of the box type with double heating and a large number of passes) and in heat exchangers (pure countercurrent and expansion bellows, preferably laid out vertically for maintenance and space considerations).

Low-pressure operation presents the drawback of incomplete recovery by flashing of liquefiable products such as propane and butanes, which are partly lost in the purge. These losses can be reduced by a supplementary separation step (absorption or cryogenics).

The marketing of regenerative processes has completely altered the inherent design of the facilities by the introduction of lift-type units.

2.2.2.5 Main reforming processes

The many processes implemented today include the following:

- (a) Specific reforming techniques : Ultraforming (*Standard Oil*), Houdriforming (*Houdry*), Powerforming (*Esso*), Platforming (*UOP*), Magnaforming (*Engelhard, ARCO : Atlantic Richfield Co.*), Rheniforming (*Chevron*), Catalytic reforming (*IFP, Engelhard, Kellogg, Asahi, Amoco*) etc.
- (b) Variants obtained by combination with other processes, or intended for specific applications : Iso-plus Houdriforming (*Houdry*), Selectoforming (*Mobil*, marketed by *UOP, Chevron* and *IFP*), Aromizing (*IFP*), aromatic reforming (*Chevron*).

In the first analysis, the flow sheet of the different types of semi-regenerative or cyclic regenerative reforming is substantially the same (Fig. 2.22 a). It comprises a series of three or four alternating reactors and furnaces. As a rule, the feedstock is first preheated by heat exchange with the effluent : the latter is then cooled, flashed to allow recovery and partial recycling after recompression of the hydrogen, and finally stabilized by the removal of the light constituents (C_2 , C_3) it contains. An additional "swing" reactor is provided for cyclic regenerative systems.

The principle of the regenerative technologies introduced by *UOP* and *IFP* is completely different. In the *UOP* process (Fig. 2.22 b), the reaction section consists of four radial-flow reactors laid out in series. The first three are stacked, while the fourth, which contains half of the total amount of catalyst of the unit, is separate. Specially fitted furnaces guarantee minimum pressure drop. The catalyst system, introduced at the top of the elements 1 and 4, flows by gravity. It is withdrawn from the bottom of reactors 3 and 4, purged of hydrocarbons and sent by two inert gas lifts to the regeneration section. This section comprises a disengaging hopper, the regeneration tower and a surge hopper with gravity flow. The catalyst is returned to the reaction section by two new lifts. A very elaborate electronic system allows accurate control of the progress of the different phases in the operation.

The *IFP* process (Fig. 2.22 c) is more similar to conventional schemes with four separate reactors and with intermediate passage of the feedstock through a furnace. The catalyst flows by gravity in each of these items of equipment. It passes from one to the next by means of lifts, in which the lift gas is taken from the discharge of the hydrogen recycle compressor. At the bottom of the last unit, it is picked up by a new lift and sent to the regeneration section. This consists of two holdup drums placed above and below the actual regenerator, and an appropriate valve system. The regenerated catalyst is sent again by lift, to the top of the first reactor. The different operating sequences are programmed and are fully automated. In the case of aromatics production, reforming is followed by fractionation (particularly a depentanizer), in order to retain only the cut containing the desired hydrocarbons.

2.2.2.6 Pretreatment

All reforming processes comprise a pretreatment section designed to remove feedstock compounds that are harmful to the catalyst: sulfur, nitrogen and metals. This involves hydrodesulfurization, or hydrodenitration if need be, which takes place in the presence of catalysts based on cobalt and molybdenum or nickel and molybdenum on alumina support, at a temperature of about 320 to 380°C, and a hydrogen partial pressure of around 0.5 to $0.8 \cdot 10^6$ Pa, with LHSV of 5 to 12 h⁻¹ and hydrogen recycle ratios from 50 to 75 by volume.

The installation flow sheet (Fig. 2.22 d) comprises the following in succession:

- (a) Preheating of the feedstock and hydrogen, first by heat exchange with the hydrodesulfurization reactor effluent, and then by passage through a furnace.
- (b) The reactor itself.
- (c) Effluent flash under high pressure after cooling and partial condensation, to separate unconverted hydrogen, NH₃, H₂S etc. Part is recycled, and the rest is removed.
- (d) Supplementary liquid phase stripping to remove residual light compounds and to adjust the product to the specifications required for reforming.

Among the main processes marketed are those developed by BP (*British Petroleum*), Engelhard, Esso, IFP, Shell, Standard Oil, UOP, etc., which reduce the sulfur content of 70-180°C naphtha from 200 to 1000 ppm to between 1 and 0.5 ppm.

2.2.2.7 Average reforming performance

The feedstock composition, and particularly its naphthenes and aromatics content, are important parameters. To measure the ability of a gasoline to yield aromatics, use was first made of the characterization factor K_{UOP} ⁽¹⁾. It is now more popular to use the sum $N + 2.4$, where N is the percentage by weight of naphthenes, and A that of aromatics.

Theoretically, the possible aromatics yield is much higher if the feed contains a larger amount of direct precursors ($N + 2.4$ normally varies from 30 to 80). With present-day catalysts, however, a high yield can be achieved, even for gasolines with a low $N + 2.4$ index. The factor K_{UOP} is related to $N + 2.4$ by the following empirical equation:

$$K_{UOP} = 12.6 - \frac{(N + 2.4)}{100}$$

With conventional processes, the specific production of aromatics is facilitated by the treatment of narrow cuts : 60-140°C for all BTX, 65-85°C for benzene, 85-110°C for toluene, and 110-145°C for xylenes.

(1) Equal to 10 for pure aromatics, 11 for pure naphthenes or slightly substituted aromatics, 12 for mixed hydrocarbons, and 13 for pure paraffinic products.

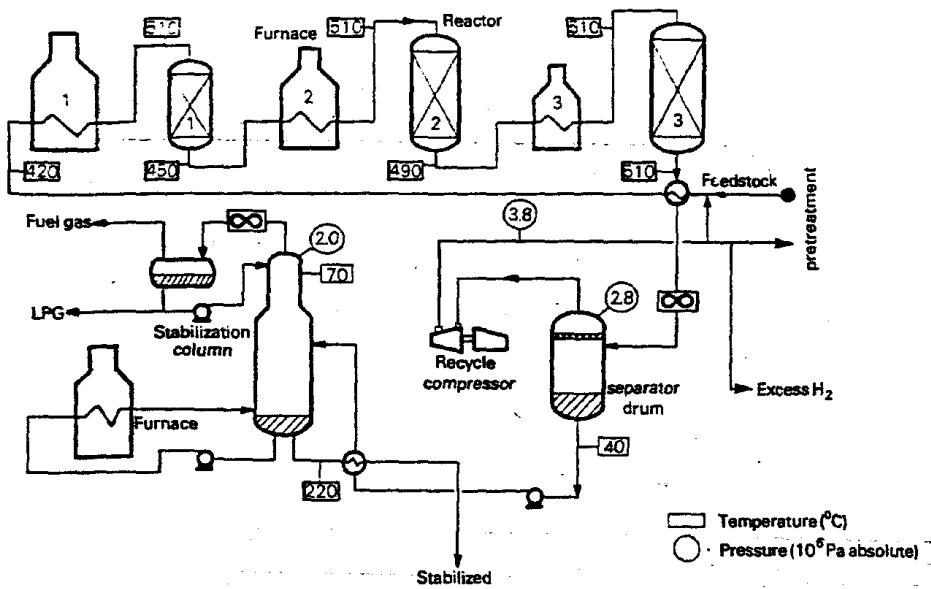


Fig. 2.22 a. Classic semi-regenerative catalytic reforming.

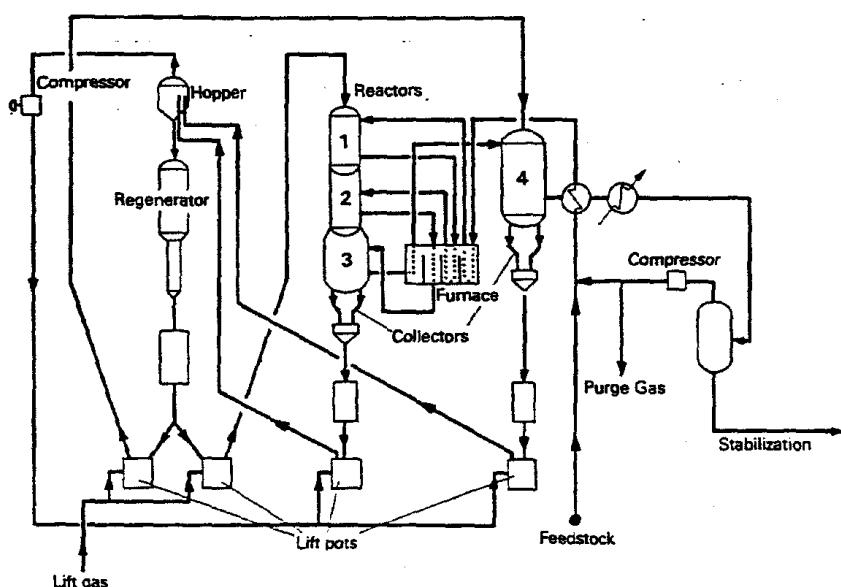


Fig. 2.22 b. Regenerative reforming. UOP process (continuous platforming).

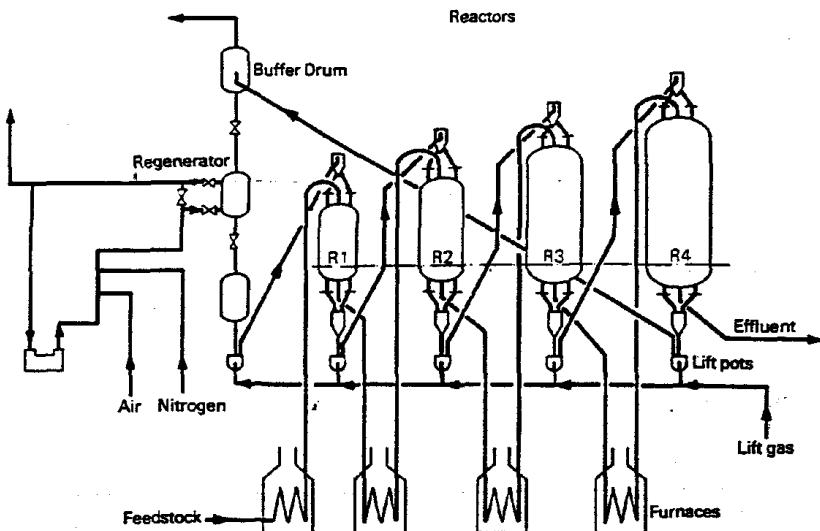


Fig. 2.22 c. Regenerative reforming, IFP process.

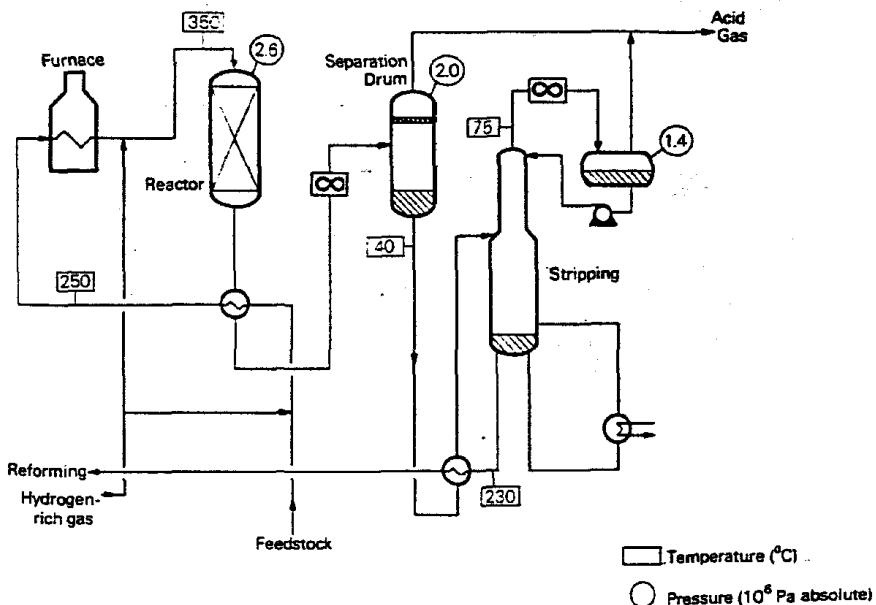


Fig. 2.22 d. Catalytic reforming, Pretreatment.

TABLE 2.24
CATALYTIC REFORMING, KUWAIT CRUDE, TYPICAL MATERIAL BALANCES

Type of reforming.....	Conventional NO 95 ⁽¹⁾		Regenerative NO 95 ⁽²⁾		Aromizing				
	75-140	107-160	75-140	107-160	60-85	60-107	60-160	107-160	90-160
Distillation range (°C)	75-140	107-160	75-140	107-160	60-85	60-107	60-160	107-160	90-160
% Weight based on crude.....	8.5	7.1	8.5	7.1	2.4	5.1	12.6	7.1	8.5
Feedstock composition (% Wt)									
Paraffins	63.6	62.2	63.6	62.2	79.8	79.3	69.6	62.2	64.2
Naphthenes	22.9	21.2	22.9	21.2	18.2	17.4	19.5	21.2	22.2
Aromatics	13.5	16.6	13.5	16.6	2.0	3.3	10.9	16.6	13.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Product composition (% Wt)									
Hydrogen	1.9	2.2	2.2	2.4	2.1	2.7	2.7	3.0	3.0
C ₁ + C ₂	5.8	3.2	4.6	2.9	9.6	9.2	8.8	5.1	6.9
LPG	11.2	9.6	9.2	7.7	24.5	19.9	14.3	9.8	11.6
C ₃ + gasoline	81.1	85.0	84.0	87.0	63.8	68.2	74.2	82.1	78.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Benzene	2.1	1.7	2.0	1.7	31.9	19.5	9.3	1.6	5.2
Toluene	12.7	13.2	13.0	13.7	3.7	25.4	21.7	19.0	25.1
C ₈ aromatics	21.8	21.2	22.3	21.7	1.1	2.9	20.8	34.3	26.2
C ₉ + aromatics	16.3	19.2	17.2	19.5	0.3	0.3	8.8	15.2	11.2
Total	52.9	55.3	54.5	56.6	37.0	48.1	60.6	70.1	67.7
Hydrogen purity (% vol.)	81	86	84	88	67	73	74	85	80

(1) Pressure 1.5 · 10⁶ Pa.(2) Pressure 1 · 10⁶ Pa.

With regenerative reforming, and more specifically with techniques such as Aromizing, the aromatics yields are even higher. Table 2.24 lists and compares the figures obtained for these two types of process.

2.2.3 Economic data

Tables 2.25 and 2.26 give economic data concerning the two main types of catalytic reforming and the auxiliary units: hydrodesulfurization and C₅ separation.

TABLE 2.25
CATALYTIC REFORMING. ECONOMIC DATA
(France conditions, mid-1986)
TREATMENT CAPACITY 800,000 t/year

Type of reforming	Reforming		Aromizing		
	Conventional	Regenerative			
Distillation range (°C)	75-140		60-107	107-160	60-160
Battery limits investments (10 ⁶ US\$)	16	20	25	22	26
Initial catalyst loads					
Support (10 ⁶ US\$)....	0.7	0.6	1.1	1.1	1.3
Precious metals content (% Wt).....	0.35	0.35	0.6	0.6	0.6
Material balance	see Table 2.24		see Table 2.24		
Consumption per ton of feed- stock					
Utilities					
Fuel (10 ⁶ kJ).....	2.5	2.5	1.9	1.8	3.3
Steam (t)					
HP consumed....	0.12	0.12	—	—	0.5
HP produced	(—) 0.11	(—) 0.11	—	—	(—) 0.3
MP produced	(—) 0.17	(—) 0.16	—	—	(—) 0.5
Electricity (kWh) ...	15	25	45	30	5
Cooling water (m ³) ..	—	—	10	10	1
Nitrogen (m ³)	0	0.6	0.7	0.7	0.7
Catalyst (US\$) ⁽²⁾	0.35	0.30	0.45	0.45	0.45
Chemicals (US\$)	0.20	0.20	0.20	0.20	0.20
Labor (Operators per shift)	3	3	3	3	3

(1) In mid-1986 precious metals cost about 430 \$/oz.

(2) Including make-up of precious metals.

TABLE 2.26
CATALYTIC REFORMING. AUXILIARY TREATMENT. ECONOMIC DATA
(France conditions, mid-1986)

Treatment	Pretreatment	Depentanizer	
Capacity (t/year)	Feedstock: 800,000	Distillate: 60,000	
Battery limits investments (10^6 US\$)	5.4	0.9	
Initial catalyst load (10^6 US\$)	0.2	—	
Material balance	See ⁽¹⁾	See ⁽²⁾	
Consumption per ton			
Utilities			
Fuel (10^6 LJ)	1.3	—	
MP steam (t)	0.15	2.3	
Electricity (kWh)	10	20	
Cooling water (m ³)	0.5	—	
Catalyst (US\$)	0.20	—	
Chemicals (US\$)	0.15	—	
Labor (Operators per shift)	1	—	
(1) Feedstock (t)	1.0	(2) Feedstock (t)	11.5
Make-up hydrogen (kg)	12.5	Light ends (t)	1.0
Purge hydrogen (kg)	0.1	Heavy ends (t)	10.5
Fuel gas (kg)	9.8		
Desulfurized gasoline (t)	1.003		

2.3 OTHER SOURCES OF OLEFINIC HYDROCARBONS

2.3.1 Catalytic cracking

This process, more closely oriented towards refining than catalytic reforming, cannot be covered by a specific study here. However, some of its by-products represent significant effective or potential sources of olefins. Unit treatment capacities today reach an average of 1,000,000 t/year. Moreover, as shown by the typical analysis in Table 2.27, the yields of light cuts obtained on a fluid bed catalytic cracking installation, for instance, optimized for the maximum production of middle distillates, constitutes a large fraction of the feedstock (15 to 20 per cent weight).

Finally, as shown by Table 2.28, these light cuts themselves contain significant concentrations of olefinic hydrocarbons. Moreover, they are the only effluents of catalytic cracking that the refiner may agree to make available for petrochemicals.

On the whole, process performance, namely the product distribution, varies according to the operating conditions (space velocity, pressure, temperature, catalyst circulation

TABLE 2.27
FLUIDIZED BED CATALYTIC CRACKING ADJUSTED
FOR MAXIMUM PRODUCTION OF MIDDLE DISTILLATES, TYPICAL YIELDS

Products	% Weight of feedstock
C ₂ - cut	4.4
C ₃ cut	2.7
C ₄ cut	4.9
C ₅ cut	5.0
Gasoline	27.5
Light gas oil	43.0
Residue (heavy fuel oil No. 2)	8.5
Coke (burned in the unit)	4.0
Total	100.0

TABLE 2.28
TYPICAL ANALYSES OF LIGHT CUTS FROM CATALYTIC CRACKING

C ₂ - cut		C ₃ cut		C ₄ cut		C ₅ cut	
Hydrocarbon	% Wt	Hydrocarbon	% Wt	Hydrocarbon	% Wt	Hydrocarbon	% Wt
Hydrogen	1.3	C ₂ -	0.4	C ₃ -	0.5	C ₄ -	2.0
Methane	29.5	Propane	26.9	n-butane	11.0	Isopentane	31.5
Ethane	25.4	Propylene	72.0	Isobutane	33.0	n-pentane	5.5
Ethylene	20.9	C ₄ -	0.7	1-butene	12.0	1-pentene	2.5
Propane	3.5			Cis 2-butene	11.0	Cis 2-pentene	8.0
Propylene	11.8			Trans 2-butene	14.0	Trans 2-pentene	12.0
Inerts	7.6			Isobutene	18.0	2-methyl 1-butene	12.5
				Butadiene	ε	3-methyl 1-butene	3.5
				Acetylenics	ε	2-methyl 2-butenes	21.5
				C ₅ -	0.5	C ₆ -	1.0
Total	100.0	Total	100.0	Total	100.0	Total	100.0

rate), the feedstock and catalyst, and the inherent design of the unit (moving or fluidized beds, reactor and regenerator design). Hence the values given in Tables 2.27 and 2.28 provide only one illustration.

2.3.2 Thermal cracking of paraffin waxes

The thermal cracking of high molecular weight normal paraffins produces linear olefins with an essentially terminal double bond, that find markets in the field of plasticizers and detergents.

The cracking feedstocks must normally contain the least possible isoparaffins and cycloparaffins in order to produce fairly pure olefins. The paraffins (waxes) normally used for the purpose are those contained in heavy petroleum distillates and separated by extraction during the manufacture of lubricating oils. For example, use can be made of purified paraffin waxes with a melting point between 50 and 60°C and an oil content less than 0.5 per cent weight. These waxes consist of normal paraffins with 17 to 34 carbon atoms (90.5 mole per cent), isoparaffins (8.2 per cent) and cycloparaffins (1.2 per cent). After cracking, about 60 per cent weight of olefins are obtained, containing up to 90 per cent weight of α -olefins. Straight-run distillation gas oils from high paraffin crudes can also be used, but, in this case, the purity of the olefins is necessarily lower. This is because they are soiled by aromatic, diolefinic and saturated hydrocarbons.

A thermal cracking unit for waxes consists of a furnace, a primary separation column, a stabilization column and a distillation section. The feedstock is vaporized, mixed with steam to 40 per cent weight, and enters a tubular furnace in which the residence time is a few seconds (2 to 10 s) at 500 to 600°C. Once-through conversion is relatively low (15 to 30 per cent) to avoid side reactions. Operation is at atmospheric pressure or slightly above. Direct quench, or quench with a heat transfer fluid, generates steam. Primary fractionation allows the recycling of the unconverted part of the feedstock.

Olefins lower than C_5 or C_6 are removed by means of a stabilization column. The other two columns are then used to separate the C_6-C_9 , $C_{10}-C_{13}$ cuts at the top and $C_{14}-C_{18}$ cut at the bottom. The olefins produced are not as pure as those resulting from the oligomerization of ethylene. They contain small amounts of dienes and cyclic compounds.

2.3.3 Oligomerization of light olefins

The polyaddition of light olefins (ethylene, propylene, butenes), gives rise to oligomeric olefins with a molecular weight that is a multiple of the starting olefin. The following can be distinguished.

- Oligomerization of ethylene by means of organometallic complexes.
- Dimerization and codimerization of olefins with two, three or four carbon atoms.

2.3.3.1 Ethylene oligomers

Linear α -olefins with an even number of carbon atoms are produced from ethylene by means of catalysts discovered by K. Ziegler and consisting of coordination complexes

of aluminum and titanium. This method was marketed originally by *Conoco (Continental Oil Company)* (Alfene process).

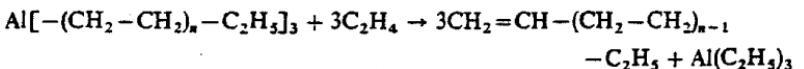
A. Processes

The reaction takes place in two steps:

- (a) Polymerization or growth reaction, during which the ethylene molecules are progressively inserted into the carbon-metal bond of triethylaluminum, leading to trialkylaluminum molecules with a long alkyl chain. This reaction takes place between 100 and 120°C. at a pressure of about $10 \cdot 10^6$ Pa:



- (b) Displacement, during which the alkyl chain leaves the aluminum in the form of an olefin with a terminal double bond, while the ethylene reforms the ethyl chain of triethylaluminum:



This second conversion takes place between 200 and 300°C, at lower pressure ($5 \cdot 10^6$ Pa). The triethylaluminum is recovered and recycled.

Industrially, the process is usually conducted in two steps, growth followed by displacement, but it can be carried out in a single step around 200°C, at $25 \cdot 10^6$ Pa pressure, in the presence of much smaller amounts of triethylaluminum (0.5 per cent weight). In this case, it is unnecessary to recover the alkylaluminum, and it can be hydrolysed with the formation of alumina. *Ethyl Corporation* in the United States uses the two-step process, while *Gulf Oil* in the United States and *Mitsubishi Chemical* in Japan use the one-step process.

Variants of this ethylene oligomerization technique have been developed by *Esso* and *Mitsui Petrochemical*, which use titanium base catalysts, and *Shell*, which uses a complex of nickel with phosphines.

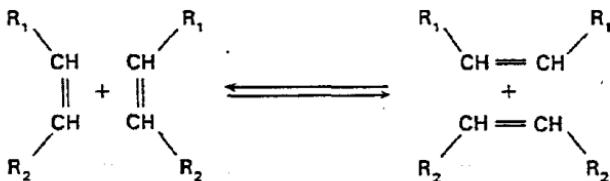
B. Performance

The α -olefins obtained have a purity of more than 95 molar per cent of terminal olefins and are devoid of branched structures or diolefinic or cyclic impurities. These α -olefins, which all have an even number of carbon atoms, are produced with yields that vary according to a statistical distribution, with a maximum of $\text{C}_{10}-\text{C}_{12}-\text{C}_{14}$, for example, if the final product is intended for the manufacture of linear alkylbenzene. Due to the low yield of a given cut, it is understandable that the upgrading of all the other fractions is economically necessary. Since the upgrading of the light and heavy fractions is often a problem, *Shell* in the United States has developed the SHOP (Shell Higher Olefin Process), in which these effluents are converted to a cut for detergents by isomerization and metathesis.

C. Metathesis of olefins

The metathesis or transalkylidenation reaction is catalyzed by complexes of tungsten, molybdenum or rhenium, in a heterogeneous or homogeneous phase, and consists in the scission of the double bond with the formation of two new olefins.

This takes place by the following reaction:



The latest industrial application of metathesis was developed by Phillips, who started up a plant in late 1985 at Channelview, Texas, on the Lyondell Petrochemical Complex, with a production capacity of 135,000 t/year of propylene from ethylene. This facility carries out the disproportionation of ethylene and 2-butenes, in the vapor phase, around 300 to 350°C, at about $0.5 \cdot 10^6$ Pa absolute, with a VHSV of 50 to 100 and a once-through conversion of about 15 per cent. 2-butenes are themselves obtained by the dimerization of ethylene in a homogeneous phase, which may be followed by a hydroisomerization step to convert the 1-butene formed (see Sections 2.3.3.2. A and B). IFP is also developing a liquid phase process in this area.

TABLE 2.29

PRODUCTION OF PROPYLENE AND C₁₁-C₂₀ OLEFINS BY METATHESIS. ECONOMIC DATA
(France conditions, mid-1986)

Product	Propylene	C ₁₁ -C ₂₀ olefins
Typical process	Phillips	SHOP (Shell)
Production capacity (t/year)	100,000	250,000 ⁽¹⁾
Battery limits investments (10 ⁶ US\$)	13 ⁽²⁾	95
Consumption per ton of product		
Raw material, ethylene (t)	1.18	1.03
By-products, gasoline (t)	(-) 0.18	-
Catalyst and chemicals (US\$)	5	15
Utilities		
Steam (t)	0.75	3.5
Electricity (kWh)	110	180
Fuel (10 ⁶ kJ)	0.75	1.05
Refrigeration to 0°C (10 ⁶ kJ)	0.3	-
Cooling water (m ³)	55	170
Labor (Operators per shift)	2	8

(1) Including 75,000 t/year of C₁₂-C₂₀ α -olefins and 150,000 t/year of internal C₁₁-C₁₄ olefins.

(2) Estimated.

TABLE 2.30
ALPHA OLEFINS PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Surfactants	61	4	55
Plastics ⁽¹⁾	3	36	11
Plasticizers	23	25	32
Lubricants and additives	7	15	
Alkyldimethylamines		6	
Miscellaneous ⁽²⁾	6	14	2
Total	100	100	100
Sources (% product)			
Ethylene oligomerization	40	93	100
Paraffin wax cracking	60	7	—
Total	100	100	100
Production (10^3 t/year)	290	410	25
Capacity ⁽³⁾ (10^3 t/year)	430	600	30
Consumption (10^3 t/year)	225	270	50

(1) HDPE, LLDPE, polybutene-1.

(2) Alkenylsuccinic anhydrides, amines and derivatives, epoxides, linear mercaptans, lube oil additives, synthetic lubricants...

(3) The worldwide producers of alpha-olefins are the following:

(a) In Western Europe: *Shell Chimie* (Berre, France = $90 \cdot 10^3$ t/year), *Shell Nederland* (Pernis, The Netherlands = $170 \cdot 10^3$ t/year), *Shell Chemicals* (Stanlow, England = $170 \cdot 10^3$ t/year).

(b) In the United States: *Chevron* (Richmond, Ca. = $40 \cdot 10^3$ t/year), *Gulf Oil* (Cedar Bayou, Tx. = $90 \cdot 10^3$ t/year), *Ethyl Corporation* (Pasadena, Tx. = $365 \cdot 10^3$ t/year), *Shell Chemical* (Geismar, La. = $105 \cdot 10^3$ t/year).

(c) In Japan: *Mitsubishi Chemicals* (Mizushima = $30 \cdot 10^3$ t/year),

Shell Chemicals UK is raising Stanlow capacity to $220 \cdot 10^3$ t/year in 1987, *Chevron Chemical* its Cedar Bayou capacity to $115 \cdot 10^3$ t/year at the end of 1986. *Iidemitsu Petrochemical* built a $50 \cdot 10^3$ t/year plant in 1987.

D. Economic data

Table 2.29 provides some economic data on the Phillips and Shell SHOP processes.

Alpha-olefins data related to production, capacities and consumption in Western Europe, the United States and Japan in 1984 are given in Table 2.30.

2.3.3.2 Dimers and codimers of olefins

Olefins with four to eight carbon atoms can be obtained by dimerization and codimerization of ethylene, propylene and butenes.

A. Dimerization of ethylene to butenes

Although it can be carried out with Ziegler type catalysts, and is hence widely investigated in the laboratory, this conversion only reached the industrial stage in 1985.

since naphtha steam cracking was the most economic source of butenes. Recent achievements and developments under way are stimulated by the increase in ethylene availabilities, especially the cheap ethylene obtained from ethane in the oil- and associated gas-producing countries. Another impetus was provided by the need for C₃ and C₄-olefins, which are nonexistent in practice in the effluents from ethane pyrolysis.

The dimerization of ethylene, according to whether the final product is pure 1-butene or a mixture of *n*-butenes, exists in two industrial versions:

- (a) The first, commercialized by *IFP* as the Alphabutol process, is designed to produce 1-butene, a comonomer intended for the production of low-density linear polyethylene. The reaction takes place around 50 to 60°C, under sufficient pressure to maintain the medium in the liquid phase, in the presence of a homogeneous titanium-based catalyst, which avoids the isomerization of 1-butene to 2-butenes, and to limit the production of C₆₊ oligomers. The latter are partly used to place the catalyst system in solution. The molar yield of the operation exceeds 93 per cent. At present, several industrial plants are in operation or under construction around the world (Saudi Arabia, Thailand,...) with production capacities ranging from 3,000 to 50,000 t/year.
- (b) The second, industrialized by *Phillips* at Channelview, Texas (see Section 2.3.3.1.C), and by *IFP* as the Dimersol E process in Taiwan and in Africa, also operates in the liquid phase at about 50°C, using a Ziegler type catalyst. This may be a nickel derivative, activated by an organometallic reducing agent. Its special feature is to cause both dimerization and isomerization, so as to produce a mixture of butenes and oligomers, of which the proportions depend on the type of feed and catalyst, and the desired conversion rate. Thus, for polymerization grade ethylene, the Dimersol E technique yields 30 to 70 per cent of *n*-butenes for a once-through conversion of 100 to 90 per cent. The remainder consists of C₆₊ gasoline, making the process preferable for this type of production (see Section 2.3.3.2.D), especially if the feed also contains propylene. The 2-butenes/1-butene ratio is approximately 50/50.

B. Dimerization of propylene

In the presence of triethylaluminum, the Goodyear-Scientific Design process produces 2-methyl 1-pentene with a selectivity of 99 molar per cent. The reaction takes place around 200°C at 20 . 10⁶ Pa. 2-methyl 1-pentene is the starting material for the synthesis of isoprene, in which it is first isomerized to 2-methyl 2-pentenes, and then cracked to produce isoprene.

In the presence of potassium or organopotassium compounds, 4-methyl 1-pentene is formed with a molar selectivity greater than 95 per cent. Operations are conducted around 150 to 200°C in the presence of K/K₂CO₃, in the liquid phase. This process, developed by *BP* in the United Kingdom, is currently industrialized by *Mitsui Petrochemical* in Japan, which uses the product as a monomer of poly 4-methyl 1-pentene (TPX), a transparent plastic with a high melting point.

In the presence of acid catalysts (for example, phosphoric acid on support), propylene yields a mixture of the trimer and the tetramer. The UOP process is conducted in a

fixed bed on H_3PO_4/H_2SO_4 around $200^\circ C$ and at $5 \cdot 10^6$ Pa. The tetramer (dodecene) has been used as a base for detergents which, being insufficiently biodegradable, are currently prohibited by legislation.

C. Dimerization of isobutene

This is carried out industrially on acid catalysts (H_2SO_4 , ion exchange resins) and leads to isoctenes, a mixture of 2,2,4-trimethyl 1-pentene and 2,2,4-trimethyl 2-pentenes.

The Bayer process operates in the liquid phase at $100^\circ C$, in the presence of an ion exchange resin. With a very high conversion ratio (99 per cent), 75 mole per cent of dimers and 25 per cent of trimers are formed. A 90,000 t/year unit operates on this process in Dormagen (*Erdölchemie*). The main market for isoctenes is nonyl alcohol, which is used to synthesize plasticizers.

D. Dimerization of propylene and butenes separately or combined

This is a refining process, whose initial purpose was to improve gasoline octane numbers. The interest shown by plastics manufacturers in octanols and nonanols led to the development of variants designed to produce olefins for oxo synthesis. For heptenes in particular, it is essential to produce C_7 cuts which do not contain compounds such as 2,2-dimethyl 2-pentenes, whose oxonation rate is low due to the steric hindrance of the double bond. The dimerization reaction, which is exothermic ($\Delta H_{298}^0 = -94.2$ kJ/mol of octenes for example) takes place in the liquid phase. It can be catalyzed in a heterogeneous phase (phosphoric acid deposited on kieselguhr or silica) or in a homogeneous phase, using a system formed by the action of an alkylaluminum compound on the derivative of a transition metal.

A number of license holders, including *UOP*, have proposed the industrial use of phosphoric acid deposited on a support. Operations in this case are conducted around $250^\circ C$, at a pressure of $8 \cdot 10^6$ Pa. The water content of the reaction medium must be kept at an optimum value, since any excess leads to entrainment of the acid, and a deficiency to the deactivation of the catalyst by the formation of pyrophosphoric acid.

An increase in the isobutene content of the feedstock C_4 cut raises the heptenes yield. In optimal conditions, 75 per cent by weight of the products are C_6 , C_7 and C_8 , with heptenes accounting for 40 to 45 per cent of all the oligomers. Yet 80 per cent weight only of the heptenes are oxonable.

The reactor consists of a vertical tower with superimposed catalyst beds. The feedstock is mixed with the recycle of unconverted C_3 - C_4 and with heavy products. The light saturated compounds serve as diluents and avoid excess conversions that would cause a drop in selectivity. On the other hand, the recycling of heavy components exerts the opposite effect.

The high exothermicity of the reaction entails a liquid quench by heavy products and the C_3 - C_4 cut at the catalyst beds. At the reactor exit, a fractionation train allows the necessary recycles and separations.

The Octol process, developed jointly at Marl by *Hüls* and *UOP* for the specific production of octenes from *n*-butenes, is a more recent version of the technique employing phosphoric acid, the so-called "Catalytic Condensation Process" or "Poly Process". The silica/alumina catalyst always appears to be used in a fixed bed in this case, but

the quality of the octenes produced is significantly improved, especially their degree of linearity, associated with their aptitude to produce better plasticizers.

Another variant called the Hexall process, is also commercialized by UOP. It is designed to produce hexenes for fuel purposes.

The IFP (Dimersol) process (Fig. 2.23) uses an organometallic catalyst formed by the action of an alkylaluminum on a nickel salt. It is adapted to the production of gasolines by the dimerization of propylene to isohexenes (Dimersol G) or by the oligomerization of ethylene and propylene from catalytic cracking gases (Dimersol E), or to the production of heptenes and octenes from propylene and butenes (Dimersol X) for the synthesis of plasticizers. The feedstock and a very small amount of liquid catalyst are introduced into the reactor or at a suitable point of a circulation loop allowing the removal of the heat liberated by the reaction. Conversion to dimers (or oligomers) depends on the retention time and the catalyst concentration. The effluent at the reactor exit passes through a catalyst neutralization and elimination section, and is then washed with water and fractionated.

Conversion can be improved by using several reactors in series. The heptenes and octenes obtained by this process are distinguished by an oxonation rate that is higher than that of the "phosphoric heptenes" of the previous process.

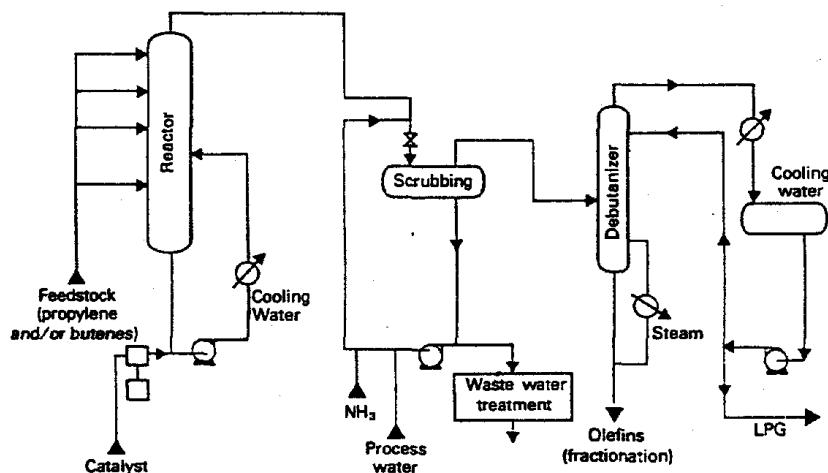


Fig. 2.23. Dimersol process (IFP).

E. Economic data

Table 2.31 gives some economic data concerning the production of i-butene, heptenes and octenes, by the IFP and UOP processes.

TABLE 2.31
PRODUCTION OF DIMERS AND CODIMERS OF LIGHT OLEFINS. ECONOMIC DATA
(France conditions, mid-1986)

Product	1-butene	Heptenes	Octenes	
			Alphabutol (IFP)	H ₃ PO ₄ (UOP)
Typical process				
Production capacity (t/year)	30,000	50,000	25,000	25,000
Battery limits investments (10 ⁶ US\$)	4.6	6.5	3.0 ⁽¹⁾	4.0 ⁽²⁾
Initial catalyst load (10 ⁶ US\$)	—	0.2	0.3	—
Consumption per ton of product				
Raw materials				
Ethylene (99.9%) (t)	1.08	—	—	—
C ₃ cut (93% propylene) (t)	—	0.97	—	—
C ₄ cut (47% Wt n-butenes, 43.5% Wt isobutene) (t)	—	2.04	—	—
C ₄ cut (75% Wt n-butenes) (t)	—	—	1.96	1.94
By-products				
LPG (t)	—	0.35	0.77	0.77
Light naphtha (t)	0.08	0.26	—	—
Heavy naphtha (t)	—	1.29	0.19	0.12
Fuel oil (t)	—	0.11	—	0.05
Catalysts and chemicals (US\$)	7.0	10.0	12.0	25.0
Utilities				
Steam (t)	0.7	4.6	1.13	0.78
Electricity (kWh)	15	95	40	35
Cooling water (m ³)	90	10	30	65
Labor (Operators per shift)	1	2	2	2

(1) Estimated without pretreatment.

(2) Including pretreatment and catalyst storage.

2.3.4 Paraffin dehydrogenation

2.3.4.1 General characteristics

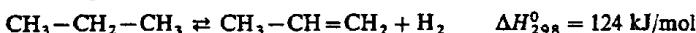
Although the use of the process is declining and it is only slightly used for the production of diolefins, such as butadiene and isoprene (see Sections 6.1.1.2 and 6.3.1.1), the dehydrogenation to olefins of certain light paraffins, such as propane, n-butane and isobutane, appears to be attracting revived interest. This trend is confirmed in particular in the ethane and LPG producing countries, whose requirements of propylene, isobutene and possibly n-butenes are growing. This section will only provide details on the production of propylene by this method, since the production of the related n- and isobutenes is discussed elsewhere (see Sections 3.1.3.2, D, 6.1.1.2 and 6.3).

By contrast, the most direct method for obtaining C_{10} - C_{13} olefins consists in dehydrogenating the corresponding *n*-paraffins, which may be obtained by extraction on molecular sieves. This technique was researched by many companies and industrialized by UOP under the name "Pacol". Dehydrogenation produces a mixture of olefins and unconverted paraffins which can be subjected directly to the alkylation of benzene to yield a linear alkylbenzene which, by sulfonation, yields a biodegradable detergent (LABS). The paraffins are easily separated from the alkylate and recycled.

To obtain olefins in the pure state, intended for other uses than alkylation (oxo synthesis, alkyl sulfates), they can be separated by selective and reversible adsorption on solids. UOP employs a technique designated "Olex", which is similar in principle to that of its Molex and Parex processes.

2.3.4.2 Dehydrogenation of propane to propylene

The following reaction is involved:



The reaction is highly endothermic and exentropic, and is favored at high temperature ($> 700^\circ\text{C}$) and low pressure (< 100 kPa absolute). A number of cracking, hydrocracking and dehydrogenation side reactions occur, especially with rising temperature, and lead to the formation of methane, ethylene, ethane, coke, methylacetylene, allene, etc. To operate at a more accessible thermal level (550 to 650°C), while maintaining an acceptable conversion rate, catalysts must be employed. Coke deposits are rapidly formed, however, so catalyst activity can only be maintained by frequent regenerations, either cyclic or continuous. At the industrial stage, these two possibilities have led to two types of process, also employing catalysts of different types. The former is associated with the Air Products (*Houdry*) Catofin and Phillips Star technologies, and the latter with the UOP Oleflex technique.

Air Products employs a chromium oxide/alumina system (20/80 per cent weight), doped with potassium or sodium oxides, operating between 550 and 650°C , at 15 to 100 kPa absolute, with LHSV of 0.2 to 4, once-through conversions of 50 to 80 per cent weight, and propylene selectivities of 75 to 85 per cent. The catalyst is placed in fixed beds 1 to 3 m thick, in large-diameter adiabatic reactors, which are grouped in combinations of three (minimum), five, six, seven or eight units to guarantee continuous operation, depending on the production capacity. In succession, the installation flow sheet comprises preheating of the fresh and recycle feed by heat exchange with the reactor effluent and passage through a furnace, the actual reaction section, cooling of the products with the by-production of steam and their compression to 1 to $2 \cdot 10^6$ Pa absolute, recovery by absorption or cryogenics of the condensable hydrocarbons stripped in the residual gaseous fraction, stabilization of the liquid obtained (de-ethanizer), and its selective hydrogenation to remove the acetylenics it contains. Most of the hydrogen in the incondensables can be isolated by adsorption on molecular sieves (PSA process, for example). Catalyst regeneration, which is also accompanied by the production of steam, takes place periodically by controlled combustion in air, following steam purges. Run length is 15 to 25 minutes.

The Phillips process is also based on the principle of the operation of two reactors in parallel, one in the reaction phase, and the second in the regeneration phase. It operates

the presence of a multimetallic catalyst, which has a life of one to two years, together with steam, which is intended to reduce the partial pressure of the hydrocarbons, provide the heat required to maintain the thermal level, and slow down the formation of coke. Added in a molar ratio of 2 to 3 in relation to the feed, it is produced in a separate boiler. The actual conversion takes place in furnaces similar to steam-cracking furnaces, which are pseudo-isothermal and are equipped with two rows of tubes heated by radiation means of sidewall gas burners. Recycling of unconverted hydrocarbons is not provided for, and run length is 8 hours.

The UOP technology is totally different in principle. It is very compact, and comparable to that of regenerative reforming (see Section 2.2.5). It features a series of three stacked reactors, through which the catalyst flows by gravity. Heat is provided by the passage of the feed, recycles of unconverted hydrocarbons and hydrogen gas, and also of intermediate effluents, in the different compartments of the same furnace. At the bottom of the lower reaction stage, the catalyst system is picked up by a nitrogen lift and introduced into the regeneration section, from which it is continuously re-injected to the top of the first reactor. Similar to that used in the Pacol process for the dehydrogenation of long-chain linear paraffins, but having been subjected to specific adjustments, this catalyst is based on precious metals deposited on alumina and operates in the presence of hydrogen gas (90 molar per cent). With propane, the process offers molar selectivities up to 85 per cent of propylene.

In the foregoing three technologies, *n*-butane treatment takes place in substantially identical conditions to those adopted for propane conversion. However, the *n*-butenes selectivities are slightly lower, around 80 molar per cent.

2.3.4.3 UOP Pacol/Olex process

The Pacol/Olex technique comprises two sections, dehydrogenation and extraction (Fig. 2.24).

A. Dehydrogenation

Dehydrogenation takes place in a fixed bed reactor in the gas phase, at a temperature of about 400 to 500°C, and low pressure (0.2 to 0.3 · 10⁶ Pa) and in the presence of hydrogen (H_2 /feedstock molar ratio = 5/10).

Conversion is limited to about 10 per cent. Selectivity exceeds 90 mole per cent in linear mono-olefins, whose internal double bond is statistically distributed along the chain, with less than 10 per cent in the alpha position. The catalyst is platinum on alumina promoted by lithium and arsenic. The main co-products are diolefins (2 to 3 per cent), aromatics (3 to 4 per cent), light hydrocarbons and hydrogen, which is more than 96 per cent volume pure.

B. Extraction

This is carried out by selective adsorption of olefins in the liquid phase on a solid. The distribution of the circuits is designed to simulate a countercurrent exchange between the liquid and solid phases, without any effective movement of the adsorbent.

Desorption is carried out by a hydrocarbon compound, whose boiling point is lower than that of the feedstock, and which is recycled continuously to the extraction section after the separation of olefins.

The preheated feedstock and desorbent are introduced at the same temperature into the adsorption column divided into several superimposed sections, while the olefinic extract and paraffinic raffinate are drawn off simultaneously. These four circuits pass through a distribution valve which switches the connections of these lines at preset intervals, and places them in contact successively with each of the sections of the adsorbent bed. Figure 2.24 shows only one of the different possible fluid stream circulations.

The extract and raffinate both contain desorbent, which is separated at the top in two distinct columns and recycled to the preheater. The paraffins drawn off are sent to dehydrogenation.

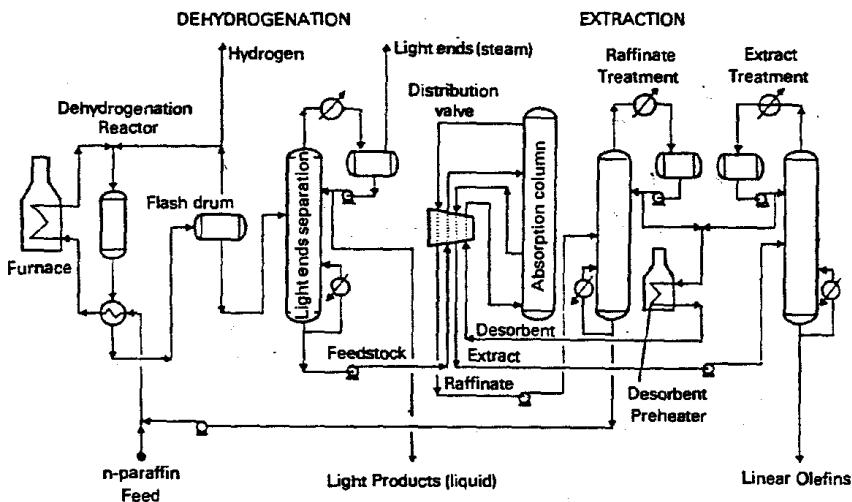


Fig. 2.24. UOP Pacol/Olex process.

2.3.4.4 Economic data

Table 2.32 provides economic data concerning the production of propylene and *n*-butenes by the Catofin and Oleflex processes, and the production of long-chain olefins by the Pacol-Olex technique.

2.3.5 Other routes

Some olefins can be manufactured industrially by various chemical processes usually employing removal reactions on functional saturated compounds. These specifically involve the dehydration of alcohols and the dehydrochlorination of chlorinated derivatives.

TABLE 2.32
PRODUCTION OF OLEFINS BY *n*-PARAFFIN DEHYDROGENATION. ECONOMIC DATA
(France conditions, mid-1986)

Typical process	Catofin ⁽⁷⁾ (Houdry)	Olefplex - (UOP)	Pacol-Olex (UOP)
Products	Propylene ⁽²⁾	Propylene ⁽³⁾	<i>n</i> -butenes ⁽⁴⁾
Production capacity (t/year)	200,000	200,000	300,000
Battery limits investments (10 ⁶ US\$) ⁽⁵⁾	56	53	55
Consumption per ton of product ⁽¹⁾			
Raw materials			
Propane (t)	1.22 ⁽²⁾	1.24 ⁽³⁾	—
Butane (t)	—	—	1.34 ⁽⁴⁾
<i>n</i> -paraffins C ₁₂ -C ₁₅ (t)	—	—	1.07
Chemicals and catalysts (US\$)	15	7	10
Desorbent (kg)	—	—	1.02
Utilities			
HP steam (t)	—	(-)2.9	(-)2.7
LP steam (t)	—	0.7	0.4
Electricity (kWh)	80	(-)15	(-)25
Fuel (10 ⁶ kJ)	0.4	2.1	1.7
Cooling water (m ³)	220	5	3
Boiler feedwater (m ³)	1	3	3
Labor (Operators per shift)	5	5	5
			4

(1) Expressed as 100 per cent pure products.

(2) Composition (% Wt)

Feed,	C ₂ - 1.0	C ₃ 95	C ₄₊ 4.0
Product,	C ₂ - —	C ₃ 0.5	C ₄₊ 99.5

(3) Composition (% Wt)

Feed,	C ₃ 100		
Product,	C ₃ 0.5	C ₄₊ 99.5	

(4) Composition (% Wt)

Feed,	<i>n</i> C ₄ 98	iC ₄ 2.0	
Product,	iC ₄ - 2.1	<i>n</i> C ₄₊ 34.6	<i>n</i> C ₄₊ 58.1
	other C ₄ and C ₄₊ 5.2		

(5) Product composition (molar per cent): linear olefins 94 including mono-olefins 96.

(6) Including initial loads.

(7) New process.

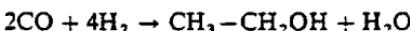
2.3.5.1 Dehydration of alcohols

The synthesis of ethylene by the dehydration of fermentation ethanol was formerly practised in the industrial countries before the development of steam cracking. This

process may be economically viable in some industrializing countries with a high production of saccharigenous plants (Brazil, India, Africa etc.) and for low unit production capacities.

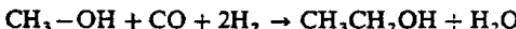
In countries which already possess a petrochemical industry, the reverse reaction is practised to produce the bulk of the ethanol consumed : this is the hydration of ethylene.

New processes currently being developed could rehabilitate the dehydration of ethanol by making use of non-petroleum raw materials. These include the direct production of ethanol from synthesis gas or its indirect manufacture from the same gas, passing through methanol. The former process was developed by *Union Carbide* on a rhodium catalyst:



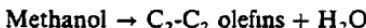
Its ethanol selectivity is low (33.6 mole per cent of carbon employed) because many co-products are formed, including methane (49.6 per cent), acetaldehyde (2.6 per cent) and acetic acid (6.5 per cent).

The Shell process uses a cobalt/phosphine catalyst for the homologation of methanol:



Ethylene or higher olefins can also be produced directly from synthesis gas or methanol. Several methods are proposed for this purpose:

- (a) The Ruhrchemie process, which is a variant of the Fischer-Tropsch technique, and which uses a complex iron base catalyst, produces a mixture of olefins and low molecular weight (C_1 to C_5) alkanes.
- (b) The Mobil process starts with methanol and employs a zeolite ZSM-5 promoted with trimethylphosphite:



- (c) The MTO (Methanol To Olefins), process developed by *Union Carbide* operates with a fluid bed of a small pore silicoaluminophosphate (SAPO-34) to produce $\text{C}_2\text{-C}_5$ olefins with a 90 percent weight selectivity and a methanol once-through conversion of 100 percent.

Ethylene and propylene account for 50 mole per cent of the hydrocarbons formed.

2.3.5.2 Dehydrochlorination of chlorinated paraffins

This offers an indirect means of dehydrogenating paraffins. In the first step the paraffin is chlorinated, and in the second the monochlorinated derivative form is dechlorinated. This yields linear olefins with an internal double bond. This process was developed by *Chemische Werke Hüls*.

Chlorination is carried out in the liquid phase at 120°C with a conversion rate of 40 per cent to limit the formation of polychlorinated compounds. Chlorination takes place mainly at the middle of the chain. The mixture of mono-, di- and polychlorinated derivatives and unconverted paraffin is sent to the dehydrochlorination reactor, which operates between 300 and 350°C in the presence of silico-alumina. The monochlorinated derivatives are converted with a conversion yield of more than 99 per cent to mono-olefins with an internal double bond. The dehydrochlorination of di- and polychlorinated paraffins yields diolefins and polyolefins.

2.4 OTHER SOURCES OF AROMATIC HYDROCARBONS

While olefins can be obtained industrially by synthesis from shorter molecules, or from functional molecules, aromatic hydrocarbons are not yet produced individually by these two methods. They are produced in a mixture by dehydrocyclization as part of naphtha catalytic reforming, and are likely to be produced shortly by the aromatization of short-chain alkanes.

BP, KTI, Mobil, UOP, Shell etc. are currently trying to produce them by the conversion of ethane or propane. With ethane, the operation takes place around 620 to 630°C, in the presence of gallium deposited on zeolite or silica/alumina, with once-through conversions of 30 to 50 per cent, and BTX molar selectivities of 20 to 60 per cent. With propane, the reaction takes place around 500 to 525°C, in the presence of gallium or aluminum deposited on zeolite or silicates, promoted by zinc, with once-through conversions of 60 to 85 per cent, and BTX molar selectivities of 25 to 60 per cent. *BP/UOP* are developing the Cyclar process, which uses the UOP regenerative reforming operating principle, and is capable of synthesizing aromatics starting with propane, butane or pentanes, with a weight yield close to 65 per cent. *KTI* proposes a two-step technology, one thermal and the second catalytic, the Pyroform process. *Mobil* is investigating variants of the technique, industrialized in New Zealand for the production of gasoline from methanol on ZSM 5 zeolite, which can be adapted by the impregnation of 0.5 per cent weight of gallium for the preferential production of aromatics (M2 Forming technology, for example, to upgrade various olefinic or paraffinic light hydrocarbon streams). *IFP* is developing equivalent technologies (Shapeforming and Aroforming processes).

Moreover, aromatics may be of non-petroleum origin. In fact, about 10 per cent of the aromatics consumed today worldwide are obtained from coal.

During the conversion of coal to coke required for the production of pig iron, crude gases or coke oven gases are formed, together with benzols and tars (coal tars). The carbonization balance depends on the volatile matter index of the coal feedstock. On the average, one ton of dry coal yields:

Gas at 20,000 to 23,000 kJ m ³	300 to 350 m ³
Benzols	10 kg
Tar	25 to 40 kg
Coke	750 to 800 kg

Benzols are essentially produced by the purification of crude gas, with a small part produced by tar distillation. Coke oven gas has the following average composition:

	% vol.
Hydrogen	55 to 65
Methane	25 to 30
Carbon monoxide	5 to 10
N ₂ , CO ₂ and miscellaneous hydrocarbons	< 1

It is no longer employed as a city gas, but is used as a fuel in a number of steel complexes, or as a raw material for ammonia synthesis.

The benzols are treated with sulfuric acid or by catalytic hydrorefining to remove compounds containing sulfur (thiophene, mercaptans), oxygen (phenols) and nitrogen (pyridine, cyanides). The refined product is then distilled to yield crude benzene containing the following hydrocarbons:

	% Wt
Light (cyclopentane)	2
Benzene	65
Toluene	18
Xylenes	5
Ethylbenzene	2
C ₈ -	7

from which the components can then be extracted by the standard processes.

As for tar, 90 per cent of its production is used for road coatings, oils and miscellaneous slurries, pitch etc. The remainder is treated to obtain pure chemical compounds. Vacuum distillation in the presence of superheated steam yields the following cuts by decreasing order of volatility:

- Benzols between 80 and 160°C, making up 0.5 to 2 per cent weight of the tar, and yielding cyclopentane, benzene, toluene and xylenes by distillation.
- Phenolic oils from 160 to 195°C (3 to 6 per cent weight of the tar) leading to phenols, and also to pyridine bases.
- Medium oils (or naphthalenic oils) between 195 and 235°C (8 to 16 per cent weight), from which naphthalene, the major component, is extracted by crystallization, and the residual denaphthalened oil is used to recover anthracene from anthracenic oils.
- Acenaphthene or debenzolization oils, between 235 and 290°C, accounting for 5 to 8 per cent weight of the tar, and employed, without secondary treatment, to extract the benzols from coke oven gases, and also as a fluxing oil for road binders. Monomethylnaphthalene can also be recovered from this cut.
- Anthracenic oils, distilling between 290 and 360°C, account for 10 to 15 per cent weight of the tar. They essentially contain phenanthrene, carbazole and anthracene. Only the latter is extracted from the denaphthalened oil.

Finally, chrysene oils distilled between 360 and 400°C (6 to 12 per cent weight of the tar) and are used to flux pitches, for the manufacture of road binders, or simply as a fuel.

Above 400°C, pitch, which accounts for 50 to 55 per cent weight of the tar, finds applications in the aggregation of coal fines into briquettes, in the manufacture of electrodes, in anticorrosion protection, etc.

Chapter 3

THE TREATMENT OF OLEFINIC C₄ AND C₅ CUTS

The tremendous growth in demand for ethylene and propylene, satisfied by the building of steam-cracking plants, and the equally vital expansion of catalytic cracking, have given rise to the immediate and growing availability of olefinic by-products, such as C₄ and even C₅ cuts. Research conducted in recent years for energy conservation has led to the emergence of new processes and schemes for the upgrading and conversion of these cuts, which were heretofore little or inappropriately used in petrochemicals manufacture.

3.1 UPGRADING OF C₄ CUTS

3.1.1 Main processing schemes

As shown by Table 3.1, the components of C₄ cuts from steam cracking and catalytic cracking, and particularly olefins, offer many potential applications, either separately or blended. Butadiene has enjoyed its own market in the field of elastomers for several decades. Each of these uses requires, for the raw material, precise specifications, which, depending on the case, concern the crude or debutadienized C₄ cut, the mixture of n-butenes and butanes, or extremely pure isolated products. To meet these different possibilities, the extensive processing of C₄ cuts appears necessary, with due consideration of the different possible hydrocarbon separation and conversion schemes. This procedure seems especially appropriate since the physical properties of the C₄ components, particularly the boiling points, are very close, as shown by Table 3.2. Thus, simple distillation is inadequate in practice to separate certain hydrocarbons, such as 1-butene and isobutene, or even butadiene, given the very slight differences between the relative volatilities. Superfractionation, which is difficult to conduct in the presence of diolefins, may be performed, but is often costly. This also applies to crystallization which, in view of the closeness of the crystallization points of the different compounds, must be carried out at very low temperatures without any guarantee of effectiveness. Manufacturers are

TABLE 3.1
UPGRADING OF BUTYLENES CONTAINED INTO STEAM CRACKING AND CATALYTIC CRACKING C₄ CUTS

1-butene	Polymerization	→ Poly 1-butene	→ Plastics	(n-butlenes, butanes mixture)
	Copolymerization	→ HDPE	→ Plastics	(pure 1-butene)
	Copolymerization	→ LDPE	→ Plastics	(pure 1-butene)
	Oxidation	→ 1,2-butylene oxide	→ Stabilizers - Polyols	(pure 1-butene)
1-or 2-butenes	Dehydrogenation	→ Butadiene	→ Elastomers - Resins	(n-butlenes, butanes mixture)
	Codimerization	→ Heptenes, octenes	→ Plasticizers - Additives	(debutadienized C ₄ cut)
	Hydration	→ Butanols, MEK	→ Solvent	(n-butlenes, butanes mixture)
	Oxonation	→ Amylic alcohol	→ Solvent - Additives	(n-butlenes, butanes mixture)
	Oxidation	→ Maleic anhydride	→ Polyesters - Additives	(n-butlenes, butanes mixture)
	Oxidation	→ Acetic acid	→ Solvents	(n-butlenes, butanes mixture)
Isobutylene	Polymerization	→ Polyisobutylene	→ Additives - Adhesives - Sulfonates	(pure isobutylene)
	Copolymerization	→ Butyl rubber	→ Elastomers	(pure isobutylene)
	Dimerization	→ Diisobutylene	→ Plasticizers	(debutadienized C ₄ cut)
	Etherification	→ MTBE	→ Gasoline additive	(debutadienized C ₄ cut)
	Hydration	→ t-butyl alcohol	→ Solvent - Methacrolein	(debutadienized C ₄ cut)
	Oxidation - Esterification	→ Methyl methacrylate	→ Organic glass	(85-90% isobutylene)
	Alkylation	→ p-t-butylphenol	→ Resins	(debutadienized C ₄ cut)
	Alkylation	→ di-t-butyl p-cresol (BHBT)	→ Antioxidant - UV inhibitor	(debutadienized C ₄ cut)
	Amination	→ t-butyl amine	→ Rubber accelerator, herbicides, lubricating oil additives, pharmaceuticals	(pure isobutylene)
	Carbonylation	→ Neopentanoic acid	→ Resins - Paints	(pure isobutylene)
	Prins reaction	→ Isoprene	→ Elastomers	(debutadienized C ₄ cut)

TABLE 3.2
MAIN PHYSICAL PROPERTIES OF C₄ CUT COMPONENTS
FROM STEAM CRACKING AND CATALYTIC CRACKING

Components	Boiling point (°C) at 1.013.10 ⁶ Pa	Relative volatility at 40°C	Crystallization temperature (°C)	$d_4^{20(1)}$
Propylene	-47.7	3.15	-185.3	0.514
Propane	-42.1	2.65	-187.7	0.501
Propadiene	-34.5	2.95	-136.0	-
Propyne	-23.2	2.00	-102.7	-
Isobutane	-11.7	1.20	-159.6	0.557
Isobutene	-6.9	1.02	-140.4	0.594
1-butene	-6.3	1.00	-185.4	0.595
1,3-butadiene	-4.4	0.99	-108.9	0.621
n-butane	-0.5	0.87	-138.4	0.579
Trans 2-butene	+0.9	0.85	-105.6	0.604
Cis 2-butene	+3.7	0.79	-138.9	0.621
Vinylacetylene	+5.6	0.82	-	-
1-butyne	+8.1	0.70	-125.7	0.650
1,2-butadiene	+10.9	0.60	-136.2	0.652
2-butyne	+27.0	0.35	-32.3	0.691

(1) Specific gravity, 68.0/39.2.

therefore forced to resort to more complex procedures, such as adsorption and extractive distillation, or to circumvent these problems by exploiting the differences in chemical reactivities. This complexity is further accentuated by the presence of residual acetylenic and diolefins which initiate polymerization reactions, contribute to the formation of gums, inhibit the active sites of potential catalysts, and, due to their polarity, influence the performance of the solvents employed. These compounds must therefore first be removed.

Figure 3.1 indicates the main schemes that this evaluation gives rise to, in accordance with the products desired and the separation methods adopted. On the whole, indeed, the markets for these products primarily guide the technological decisions.

Thus, butadiene is first recovered from steam-cracked C₄ cuts by solvent extraction, an operation that is sometimes facilitated by preliminary selective hydrogenation of the acetylenic compounds. In a number of applications, the raffinate itself must undergo similar treatment to rid it of residual diolefins. The initial cut, after being debutadienized by hydrogenation, can also serve the same purpose. This also applies to catalytic cracker effluents that are very often directly upgradable, but whose albeit low butadiene content may justify hydrogenation pretreatment for certain uses.

Once the diolefins are removed, the problem of subsequent processing of the C₄ cuts resides essentially in the separation of 1-butene or isobutene. Two principal methods are available, depending on whether the goal is to produce one or the other of these two components to meet the relevant specifications. The remaining product, which is necessarily impure, then requires supplementary treatment to be upgradable.

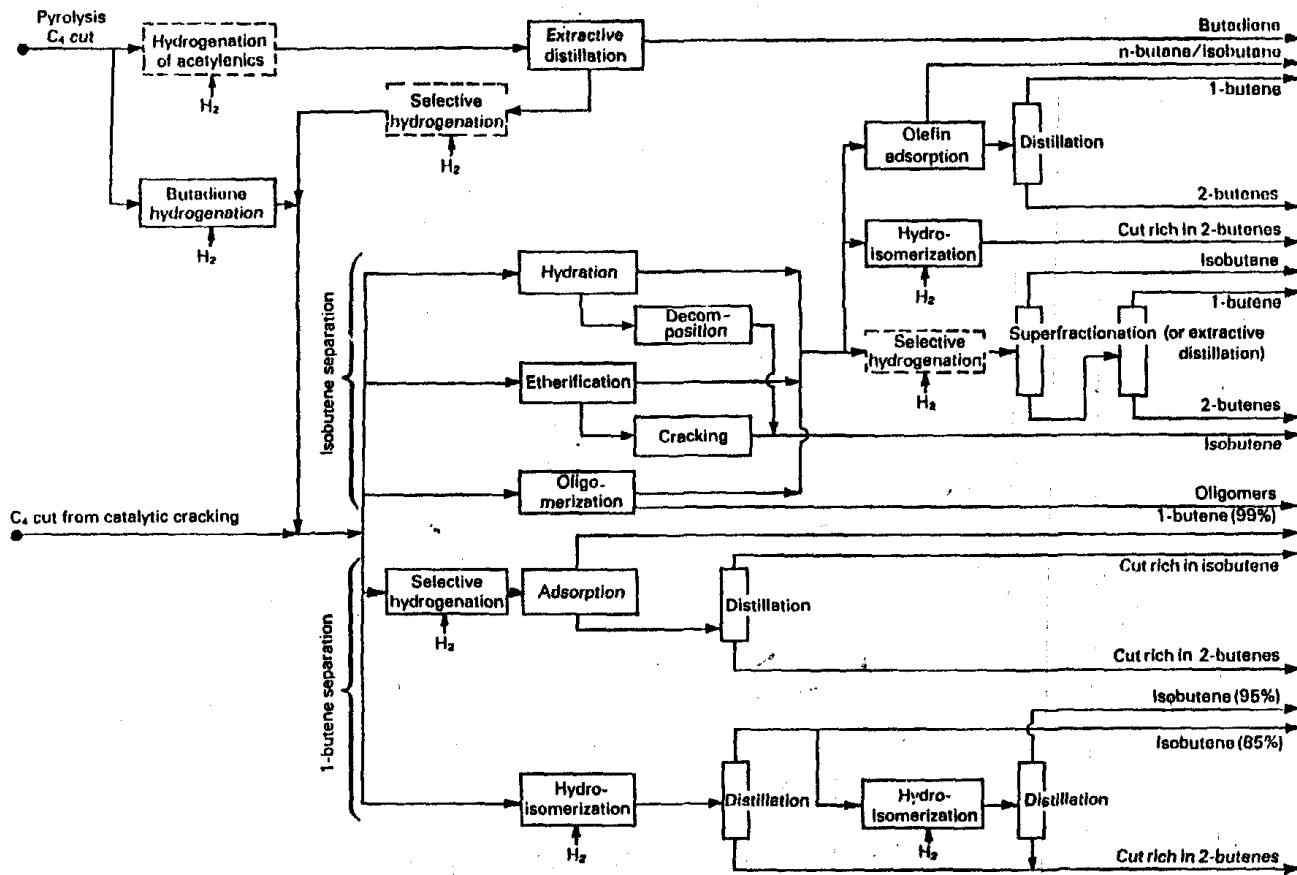


Fig. 3.1. Petrochemical processing of C₄ cuts from steam cracking and catalytic cracking.

A. Isobutene separation

Given the markets available, an attempt is first made to recover the pure isobutene. Two competitive routes are currently available for the purpose :

- Extraction in acidic medium. This method, which is older, has many variants. Separation is conducted in two steps : the first consists in hydrating the isobutene in the cut to t-butanol in the presence of H⁺ ions, and in the second, the alcohol thus formed is dehydrated.
- Etherification. This technology, of more recent date, follows a procedure similar to the above. The isobutene is first removed from the initial cut by etherification to methyl-t-butyl ether by means of methanol, and is then regenerated by cracking of the compound obtained, which is previously isolated.

In both cases, the alcohol or ether may themselves constitute the desired intermediates. In these conditions, however, the objective is the removal or preferably the direct upgrading of isobutene, rather than its recovery. For this purpose, a third method is available, selective oligomerization, whose reaction product finds a valuable application in gasoline, due to its high octane number.

In so far as nearly all the initial isobutene is converted, the subsequent operations may include intense fractionation in two columns to separate isobutane at the top of the first, with 1-butene separated at the top of the second, and 2-butenes and residual n-butane at the bottom, or a simple fractionation followed by extractive distillation on each of the cuts obtained.

B. 1-butene separation

Subsequent efforts were devoted to the extraction or elimination of 1-butene:

- Recovery. Recovery is achieved by adsorption on molecular sieves, using a number of technological variants.
- Conversion. In this process, the 1-butene is isomerized or preferably hydroisomerized to 2-butenes.

In both cases, subsequent operations include simple distillation to separate the cuts rich in isobutene and in 2-butenes at the top and bottom respectively. A second hydroisomerization on the fraction containing isobutene enhances the purity. This technique can also be applied to residual C₄ cuts from acid extraction or etherification, in order to obtain an effluent rich in 2-butenes.

3.1.2 Butadiene extraction from steam-cracked C₄ cuts

The differences that still exist between butadiene supply sources, in different geographic areas, are now tending to disappear gradually for economic reasons. Current world availabilities of butadiene essentially originate in the treatment of C₄ cuts produced by the steam cracking of naphtha or gas oil. The only exception is the United States, where the dehydrogenation of n-butane and n-butenes is still in practice, although

gradually declining. In 1980 it accounted for nearly half of national output, compared with 80 per cent in 1970, and its is expected to represent less than 5 per cent in 1990.

This specific situation of the North American continent can be explained by the original use of privileged precursors for the manufacture of ethylene, namely ethane, propane and, to a lesser degree and more recently, *n*-butane. The consequences of this technological option are the co-production of butadiene that is insufficient to meet requirements, and the need to resort to other manufacturing processes. Subsequently, as the national availability of liquefied gases tended to decrease, it proved impossible to satisfy the rise in ethylene demand using these raw materials, despite greater imports. This resulted in the use of naphtha and gas oil, which are steam-cracked to supply about 4 per cent by weight of butadiene based on the feedstock. In this way, the recovery of butadiene as a co-product from the C₄ cuts thus obtained is much less expensive than its specific production by the dehydrogenation of *n*-butane or *n*-butenes.

3.1.2.1 Physico-chemical characteristics of butadiene separation from steam-cracked C₄ cuts

As shown by Table 3.3, commercial specifications for polymerization grade butadiene are extremely severe, especially concerning acetylene derivatives, which are present at the rate of 0.5 to 0.7 per cent weight in the initial cut.

TABLE 3.3
TYPICAL COMMERCIAL SPECIFICATIONS OF POLYMERIZATION GRADE BUTADIENE

Characteristics	Values
1,3-butadiene (%) min.	99.6
Butenes (ppm) max.	4,000
Methylacetylene (ppm) max.	25
Vinylacetylene (ppm) max.	200
C ₄ and dimers (ppm) max.	2,000
Carbonyl compounds (as aldehydes) (ppm) max.	50
Inhibitor (<i>p</i> -tertiobutylcatechol) (ppm) max.	100 to 200
Non-volatile residue (ppm) max.	2,000

Highly elaborate separation methods must be used to reach this level of purity. At the industrial level, these include:

- (a) Extraction by cuprous ammonium salts.
- (b) Extractive distillation.

Extraction exploits the ability of cuprous ammonium acetate to form a complex selectively with butadiene, which is retained preferentially in the cuprous salt solution. The absorption of butenes is 10 to 50 times less. On the other hand, acetylenic compounds are complexed first, and the process is not easily reversible. The effectiveness of the method thus depends heavily on their concentration in the feedstock, which must not exceed 500 ppm in practice. However, steam-cracked C₄ cuts do not directly meet this specification, and prior selective hydrogenation is therefore indispensable. This require-

ment explains why, at the outset, when hydrogenation techniques were not sufficiently effective, this butadiene recovery procedure was only developed in association with facilities for the dehydrogenation of *n*-butane and *n*-butenes (see Section 6.1.1).

The solvents employed in extractive distillation must combine a number of properties fairly similar to those required for the separation of aromatic hydrocarbons (Section 4.2). They must therefore exhibit all or part of the following properties:

- (a) Specific selectivity to diolefins, as opposed to that existing towards acetylenic compounds and olefins: in other words, a good ability to increase the differences in relative volatility between the different components of the cut to be treated.
- (b) High solvent power: this capacity decreases in most extraction agents, for hydrocarbons containing the same number of carbon atoms, when going from acetylenic derivatives to dienes, and then to olefins.
- (c) Relative ease of implementation: low viscosity, sufficient boiling point differential with that of butadiene, absence of the formation of azeotropes or chemical reaction with the components of the mixture.
- (d) Good stability in the conditions of use: the solvents must display thermal resistance, low corrosiveness, low flammability, and must be totally miscible with water etc.
- (e) Sufficient availability at an accessible price.

The choice of an industrial solvent results from a compromise between these different properties and an economic optimization of the technology used for the process.

Table 3.4 lists a number of physical properties of the principal butadiene extractants employed industrially.

3.1.2.2 Industrial separation of butadiene from steam-cracked C₄ cuts

A. Selective hydrogenation of feedstock acetylenic compounds

This operation is essential for the extraction of butadiene contained in a steam-cracked C₄ cut by means of cuprous ammonium. It is not absolutely necessary in the case of extractive distillation. In this case, however, hydrogenation pretreatment significantly improves the operating conditions of the separation step, and helps to raise the recovery rate of polymerization grade butadiene. Indeed, this leads to a reduction of its losses as a diluent for acetylenic compounds in the effluent rich in these compounds and separated by extraction. Energy costs are reduced simultaneously.

The process flow sheet first comprises the elimination of uncombined water from the C₄ cut in a coalescer, and the addition of a hydrogen-rich gas. The combination is sent to a reactor, operating in the liquid phase, under pressure (0.5 to 1 . 10⁶ Pa), between 10 and 60°C, and with downflow or upflow as required. This unit has several palladium-based catalyst beds. The heat of reaction is removed by partial vaporization of the reaction medium or the use of a tube bundle with cooling by propylene refrigeration cycle. After cooling, the effluent is flashed, which serves to recycle part of the unconverted hydrogen, after it is recompressed to the reactor pressure.

If this pretreatment applies to both the fresh C₄ cut and the recycle of the effluent rich in acetylenic hydrocarbons produced by the subsequent separation stage, the buta-

TABLE 3.4
PHYSICAL PROPERTIES OF THE MAIN INDUSTRIAL SOLVENTS USED TO SEPARATE BUTADIENE
FROM STEAMED-CRACKED C₄ CUTS

Company	Solvent		Physical properties				Relative volatility 1-butene/ butadiene	Solvent ratio (weight based on feedstock)
	Name	Formula	mp (°C)	bp _{1,013} (°C)	d ₄ ²⁵⁽¹⁾	Viscosity (ml ² /g · s)		
Shell	Acetonitrile	CH ₃ -C≡N	-45.7	81.8	0.776	0.38 (20°C)	1.78	—
Phillips	Furfural		-36.5	161.8	1.155	1.71 (20°C)	1.67	—
Nippon Zeon	Dimethylformamide		-61.0	153.0	0.944	0.80 (25°C)	1.78	6
BASF	N-methylpyrrolidone		-24.4	204.0	1.027	1.65 (25°C)	2.04	10
Union Carbide	Dimethylacetamide		-20.0	166.1	0.937	0.92 (25°C)	1.46	8.5

(1) Specific gravity, 77.0/39.2.

diene recovery rate based on the initial feedstock exceeds 99 per cent. The leading license holders are *BASF (Badische Anilin und Soda Fabrik)*, *Bayer*, *Dow*, *Engelhard* and *IFP (Institut Français du Pétrole)*. The Dow process stands out from the rest by its operating conditions (vapor phase, 200°C, palladium/copper-based catalyst), very short 24-hour cycles, and a high butadiene yield.

B. Extraction by cuprous ammonium salts

This technique, developed in the United States during the Second World War, has been employed mainly by *Esso Research and Engineering*, chiefly for the production of butadiene by dehydrogenation of *n*-butenes and/or *n*-butane. Its industrial implementation involves the following steps:

- (a) Preliminary absorption of acetylenic compounds by a 20 per cent weight solution of cuprous ammonium acetate, and the desorption by heating at 65°C of the butadiene entrained, which is then recycled, followed by the desorption of the acetylenic compounds by raising the temperature to 90°C.
- (b) The use of a series of mixer/settlers, operating in countercurrent flow, between -20 and +5°C, at 0.3 to $0.4 \cdot 10^6$ Pa, to absorb the butadiene and to achieve the progressive enrichment of the ammonium solution by liquid/liquid contact.
- (c) Butadiene desorption by heating around 80°C at $0.12 \cdot 10^6$ Pa.
- (d) Recovery of the ammonia entrained by water washing of the butadiene and its purification before recycling by distillation of the solution obtained.
- (e) Purification by distillation in the presence of a butadiene inhibitor (*t*-butylpyrocatechol).

C. Extractive distillation

As a rule, industrial processes involving this method for separating butadiene are all based on the same scheme, which comprises the following main steps:

- (a) Extractive distillation in one or two steps, in which all the acetylenic compounds and butadiene are extracted: if this is carried out in two steps, the butenes are separated in the first, while the acetylenic compounds are removed in the second.
- (b) Recovery of the solvent used in each of these operations by vaporization.
- (c) Superfractionation of the extract, to eliminate acetylenic impurities and butenes, so as to meet the requisite specifications.
- (d) Water scrubbing of the butadiene-depleted cut to recover the stripped solvent.

The foremost license holders are the following :

a. Shell

Shell first used acetone as a solvent, and then replaced it by acetonitrile (1956). In this case, the process involves only a single extractive distillation, but includes intensive fractionation of the extract.

b. Phillips

Phillips was the first to practise extractive distillation on the industrial scale around 1940, using furfural as the solvent. A number of improvements were made in the 1960s. The process has a single extraction regeneration step and a purification step.

c. Nippon Zeon

The *Nippon Zeon* butadiene separation technique, which uses dimethylformamide as the solvent, led to the first industrial unit in 1965 and has since witnessed a brilliant commercial career.

On the whole, the process flow sheet (Fig. 3.2) comprises two extraction/regeneration steps in series, with intermediate recompression of the gaseous effluents. In greater detail, the C₄ cut is first preheated and vaporized at about 50°C by heat exchange with the hot solvent recycle stream. It then goes to the first extractive distillation column, operating with about 200 trays, between 45 and 115°C at $0.5 \text{ to } 0.7 \cdot 10^6 \text{ Pa}$, in which a countercurrent solvent stream flows, introduced at the top. The distillate, which mainly consists of C₃-, butanes and butenes, is sent to the limit of the unit. The butadiene-rich extract is sent to the first regeneration column operating with about 15 trays, between 45 and 160°C, at $0.11 \text{ to } 0.14 \cdot 10^6 \text{ Pa}$. The distillate is partly condensed. The vapor phase, consisting mainly of butadiene, is recompressed to $0.5 \cdot 10^6 \text{ Pa}$ and sent to the second extractive distillation column, which has about 60 trays and operates between 45 and 180°C. The acetylenic compounds are extracted preferentially by the solvent, which is then regenerated in conditions similar to those prevailing in the previous treatment. The butadiene recovered at the top still contains methylacetylene and heavier impurities. It is purified by simple distillation in two columns, one a light ends column (30 trays) and the second a heavy ends column (90 trays), in the presence of *t*-butyipyrocatechol (100 ppm) as oxidation inhibitor. The dimethylformamide removed at the bottom on the two regenerators is cooled and recycled. It is partly purified to distill off the water and butadiene polymers which it ultimately accumulates with time.

d. BASF/Lurgi

The BASF Lurgi process, industrialized since 1968 and employing N-methylpyrrolidone as solvent, is also one of the most widespread technologies today. It is similar in principle to the other techniques, but is different in its practical implementation, as shown by Fig. 3.3. The process takes place as if the first extraction/regeneration step was actually divided into three parts:

- An absorption zone in which the acetylenic compounds, butadiene and a certain quantity of butenes are extracted from the feedstock in countercurrent gas/liquid treatment with N-methylpyrrolidone, containing about 8 per cent weight water. This operation takes place in a column with about 80 trays operating between 45 and 55°C, at $0.4 \text{ to } 0.6 \cdot 10^6 \text{ Pa}$, on a feedstock previously vaporized by heat exchange with the hot solvent recycle and introduced at the bottom. The N-methylpyrrolidone is introduced at the top, where the unabsorbed gases, chiefly butanes and butenes, leave the column.
- A rectification zone in which the dissolved butenes fraction is displaced from the solvent in countercurrent flow with butadiene vapor, which is obtained by controlled reboiling of the extract. These butenes, which contain butadiene, are returned to the absorption zone. A sidestream is drawn off at a level where the olefin content is practically nil, the acetylene content low, and the 1,3-butadiene content a maximum. Separation takes place in a column with about 45 trays operating at the bottom around 75°C at $0.7 \cdot 10^6 \text{ Pa}$.

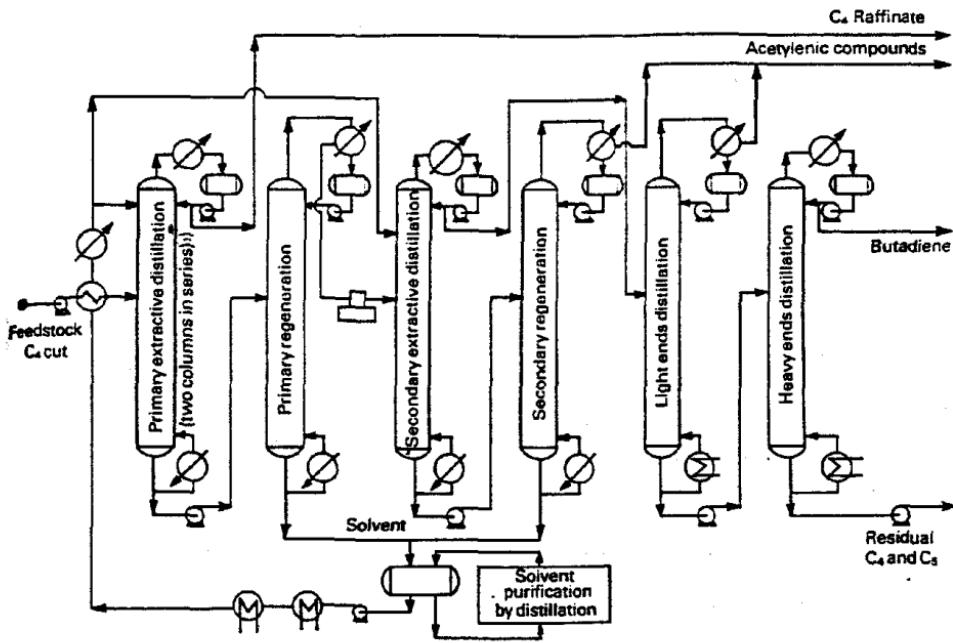


Fig. 3.2. Separation of butadiene from steam-cracked C_4 cuts. Nippon Zeon dimethylformamide process.

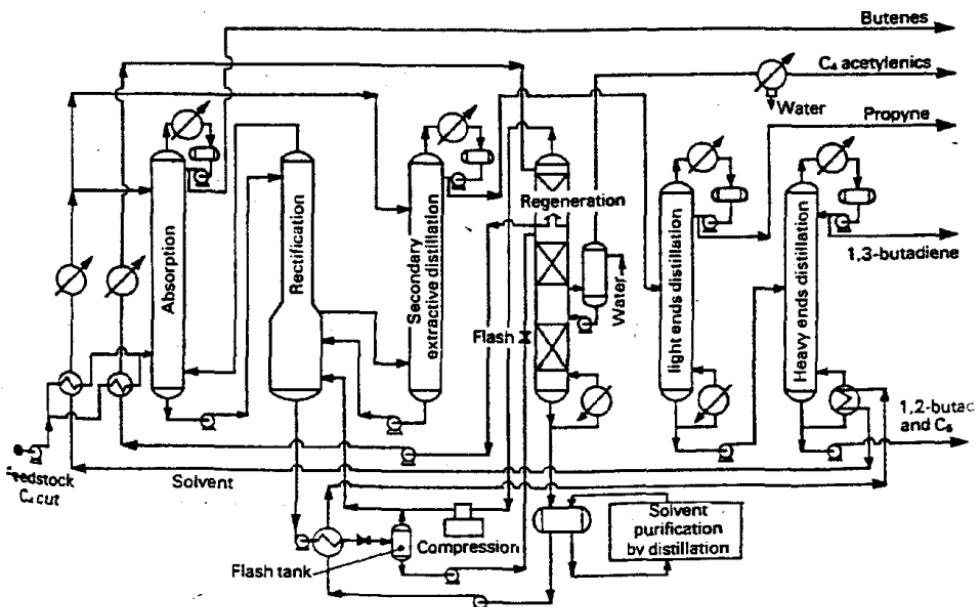


Fig. 3.3. Separation of butadiene from steam-cracked C_4 cuts. BASF N-methylpyrrolidone process.

• A regeneration zone in which a liquid extract is introduced from the rectification stage, previously rid of residual butenes by heating, pressurization and flash. The following are separated in succession during this operation:

- (a) At the bottom, the solvent, which is recycled to the absorption step, possibly after partial purification.
- (b) As a sidestream, an effluent rich in acetylenic compounds, 1,2-butadiene and C₅ hydrocarbons.
- (c) At the top, 1,3-butadiene in gaseous form, which is returned to the rectification step after recompression.

The treatment is materialized by three beds of packings in a column operating around 45°C at the top, 150°C at the bottom, and under low pressure ($\approx 0.2 \cdot 10^6$ Pa). This procedure helps to avoid the formation of polymers by an excessive temperature rise, but requires recompression of the recycled gaseous effluents.

At the side draw-off points, the process comprises the following supplementary operations:

- (a) A second absorption/purification for the effluent leaving the rectification zone. This first involves preferentially dissolving the acetylenic compounds contained. A second extractive distillation, in the presence of N-methylpyrrolidone, is carried out to achieve this in a column with about 70 trays, operating at 45°C and 0.5 . 10⁶ Pa. The liquid extract recovered at the bottom is returned to the rectification stage, while the unabsorbed butadiene is obtained at the top. This distillate is then rid of the impurities it still contains, consisting of methylacetylene, 1,2-butadiene and heavy hydrocarbons, by simple distillation in two light (≈ 70 trays) and heavy end (≈ 80 trays) columns.
- (b) Solvent recovery from the effluent rich in acetylenic compounds leaving the regeneration zone. The treatment consists in a water scrubbing of the gases in a packed tower and the recycling of the N-methylpyrrolidone solution obtained.

e. Union Carbide

The first industrial facility dates from 1965. Others have followed suit, but they are essentially built at locations belonging to *Union Carbide*. The process employs dimethylacetamide, containing 10 per cent weight water, as solvent. In its latest version, it comprises a single absorption/regeneration step.

The feed C₄ cut is first treated in countercurrent flow by the solvent in an extractive distillation column with about 90 trays, operating between 45 and 70°C, at 0.5 to 0.6 . 10⁶ Pa. Butenes and unabsorbed butanes leave at the top.

The extract is then flashed to liberate the dissolved olefins and, after recompression, to return them to the extractive distillation step. The liquid fraction rich in butadiene and acetylenic compounds is preheated and sent to a regeneration column with 20 trays operating at about 0.2 . 10⁶ Pa, at 90°C at the top and 150°C at the bottom. The solvent drawn off is recycled, possibly after purification if required. The distillate is partly condensed. The liquid fraction serves as a reflux, and that in the gas phase is recompressed and partly returned to the absorption step. The crude butadiene remaining is rid of methylacetylene and heavier compounds in two simple distillation columns, with about 40 and 110 trays respectively, in the presence of *t*-butylpyrocatechol.

TABLE 3.5
SELECTIVE HYDROGENATION OF C₄ CUTS AND BUTADIENE EXTRACTION. ECONOMIC DATA
(France conditions, mid-1986)

Process	Selective hydrogenation of acetylenics	Butadiene extraction				
		Shell	BASF/Lurgi	Phillips (improved)	Union Carbide	Nippon Zeon
Solvent		Acetonitrile	N-methyl-pyrrolidone	Furfural	Dimethyl-acetamide	Dimethyl-formamide
Production capacity (t/year)	100,000	50,000	50,000	50,000	50,000	50,000
Battery limits investments (10 ⁶ US\$)	0.5	12.5 (1)	11.4 (1)	11.6 (1)	15.5 (1)	12.4 (1)
Initial loads (10 ⁶ US\$)	0.05					
Consumption per ton of feed or of butadiene						
Steam (t)	0.1	2.5	5.4	2.5	1.7	2.2
Electricity (kWh)	—	250	35	120	280	260
Cooling water (m ³)	1	235	240	255	220	150
Solvent (kg)	—	0.2	0.25	0.25	0.20	0.20
Unit price (US\$)	—	1,200	1,700	1,400	2,800	1,700
Chemicals (US\$)	0.5	0.9	0.9	0.9	0.9	0.9
Labor (Operators per shift)	—	2	2	2	2	2
Butadiene recovery (%)	—	97.5	97	98	98	97

(1) Initial solvent load included in battery limits investments.

3.1.2.3 Economic data

Table 3.5 indicates the economic performance of the main selective hydrogenation techniques for acetylenic compounds contained in the feed C₄ cut, and for the separation of butadiene.

3.1.3 Separation of olefins from C₄ cuts produced by steam cracking and catalytic cracking

The extraction and conversion of isobutene and 1-butene are justified by the markets offered by the products themselves, which demand increasingly higher levels of purity, and also from the purely technical standpoint, in order to facilitate the subsequent separation of other constituents.

3.1.3.1 Feedstock preparation

C₄ cuts from catalytic cracking contain little butadiene and acetylenic compounds. Hence they can be used directly for isobutene separation processes, but require prior hydrogenation to obtain 1-butene. By contrast, steam-cracked effluents must systematically undergo hydrogenation pretreatment. This is necessary to eliminate the compounds liable to cause highly exothermic side-polymerizations, and to form gums that disturb the operation of the catalyst systems, solvents and adsorbents used in steps designed to produce the different C₄ olefins.

Two types of hydrotreating can be distinguished at this level, according to whether the steam-cracked effluents have been debutadienized or not:

- (a) For debutadienized effluents, selective hydrogenation is preferably carried out on a cut that is also free of most of the isobutene, but is sometimes justified before such an operation. The temperature and pressure at which the conversion takes place also favor the isomerization of 1-butene to 2-butenes. However, if the α -olefin constitutes one of the end products, it is indispensable to limit this side reaction. This is achieved by regulating the operating parameters and by altering the design of the unit. In practice, the flow sheet comprises the elimination of uncombined water from the feed by passage through a coalescer, in order to avoid separation during its mixture with hydrogen. The mixture is then preheated and introduced in downflow streams (or upflow streams for small capacities) in the reactor which operates in mixed phase, around 40 to 60°C, and 0.5 to 1 . 10⁶ Pa, in the presence of a fixed bed of palladium-based catalyst. After cooling, the residual gases are separated by flash. The main license suppliers are *Bayer*, *Engelhard* and *IFP*. If the main end product is 1-butene, special modified palladium-based catalysts, or those of other metals, must be used to limit its isomerization to 2-butenes. This is because this conversion is actually very rapid with conventional palladium systems. The process holders in this case are *Hüls* (whose technique is licensed by *UOP : Universal Oil Products*) and *IFP*.
- (b) In the second case, which is more theoretical, in which butadiene is present in substantial amounts, the operation can be conducted in a mixed phase and

dilute medium by product recycle, around 60 to 80°C, at 0.5 to 1 . 10⁶ Pa, in the presence of a fixed bed of noble metal (palladium) catalyst. If required, a finishing reactor can be used to eliminate the final traces of butadiene and acetylenic compounds.

To provide an illustration, Table 3.6 indicates the performance levels obtained with hydrogenation pretreatment.

TABLE 3.6
SELECTIVE HYDROGENATION OF BUTADIENE IN STEAM-CRACKED C₄ CUTS (% vol.)

Components	Feedstock	Product	Feedstock	Product ⁽¹⁾
Vinylacetylene	—	—	0.7	<0.01
Ethylacetylene	—	—	0.2	<0.01
1,2-butadiene	—	—	0.3	<0.01
1,3-butadiene	0.8	10 ppm	49.1	1.0
1-butene	41.0	40.6	14.0	41.8
2-butenes (cis and trans)	31.1	31.8	7.6	26.2
Isobutene	18.9	18.9	22.5	22.2
n-butane	5.8	6.3	3.0	5.9
Isobutane	2.4	2.4	2.6	2.9
Total	100.0	100.0	100.0	100.0

(1) Without finishing reactor.

3.1.3.2 Isobutene separation

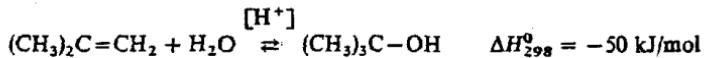
In order first to extract or convert the isobutene contained in the feedstock C₄ cut, two industrial methods are available:

- (a) Hydration.
- (b) Etherification.

Other separation methods have also led to developments, without necessarily culminating in plant construction. Thus, Hoechst has proposed esterification, or, more precisely, passage through *t*-butylacetate, and Union Carbide has proposed adsorption on molecular sieves. Butenes isomerization, isobutane dehydrogenation, and *t*-butyl alcohol dehydration (ARCO Chemical) offer complementary methods for synthesizing isobutene.

A. Hydration

Processes employing *t*-butanol carry out the hydration of isobutene in acidic medium, according to the following exothermic reaction:



followed by catalytic dehydration of the alcohol formed, previously isolated and purified.

They are based on the greater stability of tertiary carbonium ions in comparison with secondary and primary ions, allowing the selective conversion of isobutene in a

mixture in a C₄ cut. This selectivity depends heavily on the acid concentration and the temperature, and decreases with more severe operating conditions. Side polymerization reactions take place in particular, with the formation of the dimer, among other products. In some cases, this side-production is exploited or even favored for solvent and gasoline applications. As a rule, however, the dimer is kept at a level less than 5 per cent by weight. Moreover, the kinetics of isobutene conversion depends on its solubility in the aqueous phase, and the solubility of the olefin varies proportionally with the *t*-butanol content. Nevertheless, given the reverse decomposition reaction, a compromise must be found which limits the maximum alcohol concentration. To avoid polymerization side reactions, the acetylenic compounds and butadiene in the feedstock must not exceed 1 per cent weight. At the industrial level, two main methods are distinguished in accordance with the type of acid employed, in other words according to whether the hydration processes take place in sulfuric or hydrochloric acid medium. Only the former have led to commercial implementation, especially by *BASF*, *CFR* (*Compagnie Française de Raffinage*), *Esso* and *Petrotex*. The latter, developed in particular jointly by *Nippon Oil* and *Nippon Petrochemicals*, have been tested in pilot plants.

In the earliest hydration techniques in sulfuric medium, the operation is conducted in the presence of concentrated sulfuric acid. This leads to high losses of isobutene as well as acid, by the formation of sulfates and polymers. Subsequently, the concentration was reduced to about 60 to 65 per cent weight (*Esso*, *Petrotex* etc.), but the yield remained low and product purity did not exceed 96 per cent weight.

Processes have also been developed using 40 to 45 per cent weight solutions and operating at low temperature (*CFR*, *BASF* etc.), with yields between 90 and 95 per cent and purities above 99 per cent. In fact, it has been shown that, at 30°C. and with a 45 per cent weight sulfuric acid solution, the hydration of isobutene is 1500 times faster than that of *n*-butenes, and 300 times faster than that of 1,3-butadiene.

An example can be provided by a closer examination of the operating principle of the *CFR* process (Fig. 3.4). This technique, industrialized at Grangemouth (United Kingdom) in 1963, comprises three steps:

- (a) Absorption: this is carried out in a series of three absorbers/settlers, of lead-lined carbon steel. The feed flows in a countercurrent stream with a 50 per cent weight sulfuric acid solution, at a temperature of about 50°C., and 0.4 to 0.5 . 10⁶ Pa. External circulation of the reaction medium allows for the necessary agitation and cooling. The hydrocarbon phase (raffinate) is scrubbed with caustic diluted with water, and then sent to the battery limits.
- (b) Regeneration: the aqueous phase (extract) is first flashed under vacuum in several stages to remove the hydrocarbons. This phase is in the form of a sulfate partly hydrolysed to *t*-butyl alcohol. It is sent to a regeneration column of lead-lined carbon steel, which performs three functions, acid dilution, isobutene regeneration, and acid concentration, and which operates around 120°C.
- (c) Purification: the gaseous effluent from the regenerator contains the isobutene formed, unconverted alcohol, polymers and water. It is scrubbed with caustic to condense the polymers and part of the *t*-butanol. The remaining alcohol and isobutene are recovered by cooling, and then separated by distillation. The polymer-free *t*-butyl alcohol is distilled in the form of an azeotrope with water and recycled to regeneration. In this way, 87 to 93 per cent of the feed isobutene is

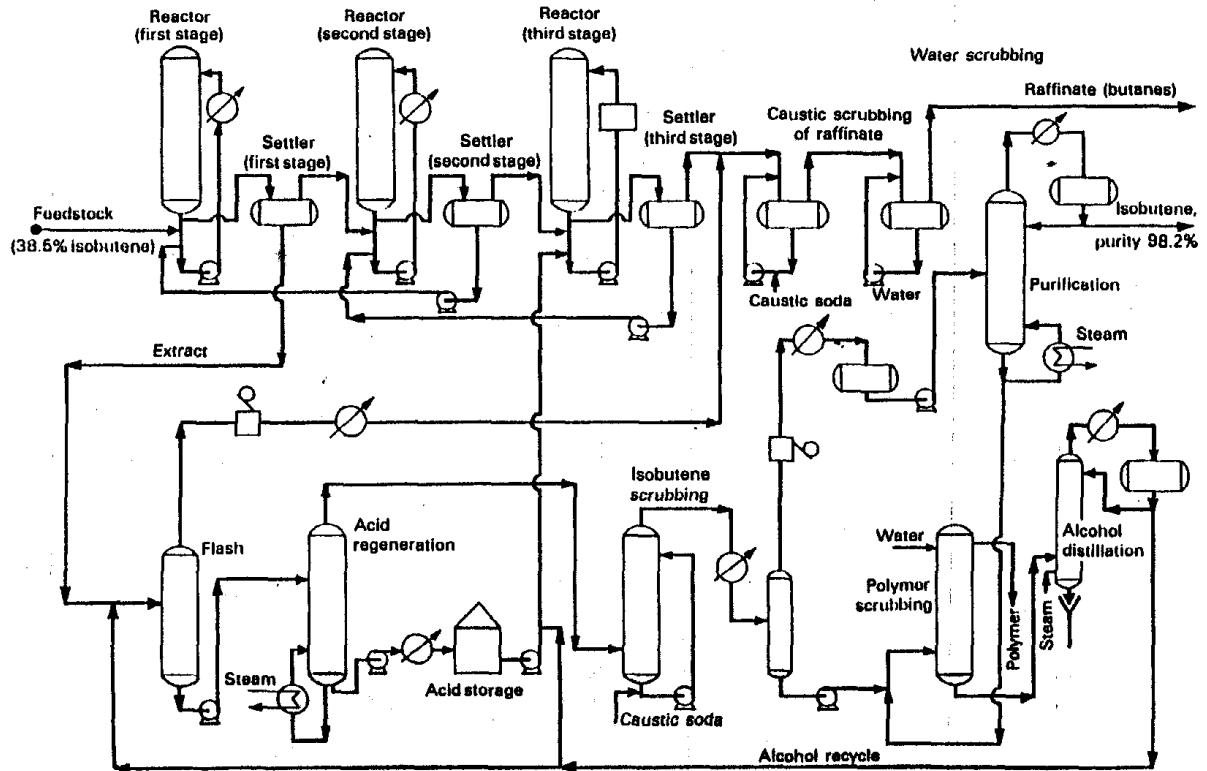


Fig. 3.4. Separation of isobutene by hydration. CFR process.

recovered in a purity of 99 to 99.8 per cent, and 5 per cent of polymerized by-products usable in gasolines.

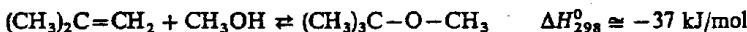
B. Etherification

Methyl Ter Butyl Ether (MTBE), which is obtained by the action of methanol on isobutene in a C₄ cut, is a compound of vital interest to refiners because of its antiknock properties, which allow it to improve the quality of commercial gasolines, and the possibility of introducing methanol indirectly into them. It is also a valuable intermediate for petrochemicals, in so far as its decomposition leads to the regeneration of the starting olefin in a high degree of purity, and because, by ensuring the virtually complete conversion of the isobutene, etherification facilitates subsequent separation operations on the residual C₄ cut. Hence two steps must be considered from this standpoint:

- (a) MTBE synthesis and purification.
- (b) MTBE cracking and purification of the isobutene formed.

a. MTBE production

The etherification of isobutene in a blend in a C₄ cut is carried out according to the following equilibrium reaction:



This exothermic reaction takes place in the liquid phase between 50 and 85°C at 0.7 to $1.5 \cdot 10^6$ Pa, depending on the specific process. It is catalyzed by cation exchange resins of the Dowex 50 W, Amberlite IR 1 or IR 100, Nalcite MX type etc., or heteropolyacids promoted by a metal. At the reactor inlet, the methanol to isobutene mole ratio is about 1.15 to 1.10/1, and the WHSV (Weight Hourly Space Velocity) is around 10 to 15. The main by-products formed are diisobutylene and *t*-butyl alcohol. Their production is limited by controlling the temperature level for the first, and the water content of the reaction medium for the second. Catalyst life is usually one year.

Feedstocks for MTBE production plants include C₄ effluents from catalytic cracking, steam-cracking, or mixtures. Once-through isobutene conversion is high, but nevertheless depends on the composition of the raw material employed. Hence, in the case of C₄ cuts from catalytic cracking, whose isobutene content does not exceed 17 to 18 per cent weight, conversion is as high as 93-94 per cent. For steam-cracked effluents, in which the isobutene concentration after debutadienization is 43 to 45 per cent weight, conversion is at least 96 per cent, and even 98 per cent. If one of the goals is to produce butene-1, the isobutene is nearly completely eliminated by raising its conversion to 99.9 per cent using a second etherification step.

The main license holders for MTBE manufacture are: ANIC (*Azienda Nazionale Idrogenazione Combustibili*) (SNAM Progetti), ARCO (*Atlantic Richfield Co*), Davy, Erdölchemie, Gulf Canada, Hüls (UOP), IFP, Shell, Sohio (*Standard Oil of Ohio*), Suntech (*Houdry*), Texaco etc. In terms of operating principle, the schemes are substantially the same for these different licensors. They comprise three steps: ether synthesis, its separation, and the treatment of the residual C₄ cut (raffinate). They differ essentially in the design of the reaction section:

- (a) MTBE synthesis: the C₄ cut feed and make-up and recycle methanol are introduced

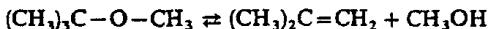
simultaneously into the reaction zone. This mixture may be preheated, by heat exchange with the effluent produced by etherification. Depending on the process, this requires one or more reactors in series, in which the catalyst is either distributed in multitube systems (*ARCO, Hüls*), employed in the form of fixed beds (*ANIC, Suntech*) or expanded (*IFP*). In the first case, external circulation of a heat transfer fluid in the shell removes the heat liberated by the reaction and produces steam. In the second, the reaction medium itself passes into an external circuit, where it is cooled and then sent to the reactor. Most of the processes operate with a downflow stream, but the use of expanded beds requires an upflow stream. However, this procedure offers several advantages, first from the heat transfer standpoint through the uniform elimination of heat without the risk of hot points in the catalyst, and by exploiting the vaporization of a fraction of the medium, and from the mechanical standpoint, by preventing the progressive fouling of catalytic beds by residues and fines. The combination of several reactors in series, required for the final conversion of isobutene, can be achieved by means of different systems, including multitube and single fixed bed reactors (*Hüls*), expanded and fixed bed reactors (*IFP*) etc.

- (b) MTBE separation: in practice, this section has only one distillation column, operating under pressure so as to use a water-cooled condenser. It separates MTBE at the bottom, and methanol and unconverted C₄ at the top. This is because the azeotropes formed by these hydrocarbons with alcohol have boiling points lower than that of the azeotrope formed by methanol and ether. The latter has a boiling point of 51.6°C at 0.1 · 10⁶ Pa. Its weight composition for each of its components is 14 and 86 per cent (30 to 70 at 0.8 · 10⁶ Pa).
- (c) Raffinate treatment: this section comprises two-step water scrubbing of the raffinate to remove the methanol, followed by fractionation of the water/methanol mixture. The alcohol recovered is recycled to the reactor.

Figure 3.5 illustrates the flow sheet of an installation using the IFP process.

b. MTBE cracking

Industrial plants designed for this operation have not yet been built. However, much development work already undertaken in the area serves to highlight the main characteristics of a technology based on the following cracking reaction:



This is an endothermic conversion, which takes place in the gas phase between 150 and 300°C (preferably at about 275°C), at a pressure as low as possible, but sufficient to recover the isobutene in the liquid phase by cooling with water, namely about 0.6 · 10⁶ Pa absolute. To avoid dehydration side reactions, operations are conducted in the presence of steam, with a typical H₂O/MTBE mole ratio at the reactor inlet of 5/1. As in the steam cracking of hydrocarbons, this procedure serves to reduce the partial pressure of the components and to facilitate the production of isobutene and methanol.

The reaction takes place in the presence of an acid catalyst. The materials proposed for this include Dow 50X 12 resins, polyphosphoric acids, both solid or deposited on kieselguhr, metallic oxides or alumina with a specific surface area of 200 m²/g. These systems operate with a VHSV approaching 1; once-through conversions are as high as

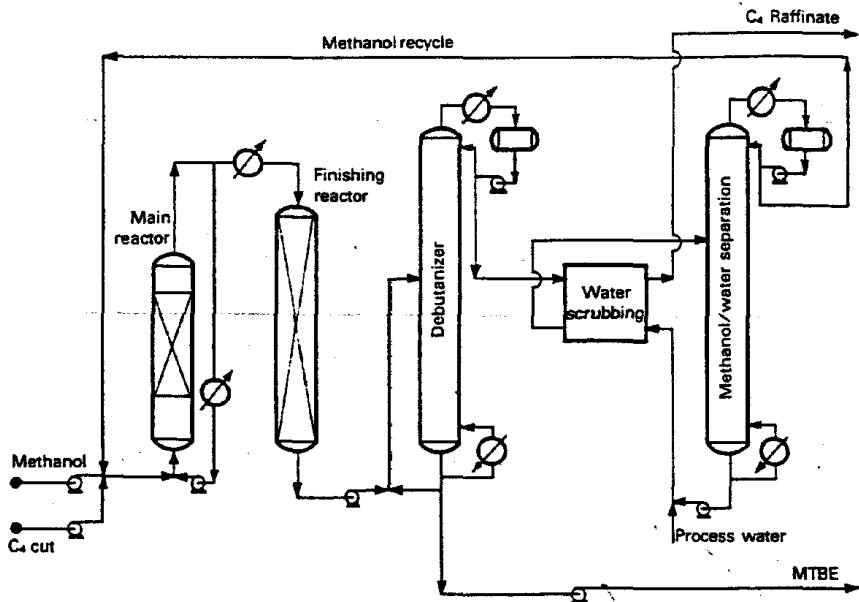


Fig. 3.5. Etherification of isobutene to MTBE. IFP process.

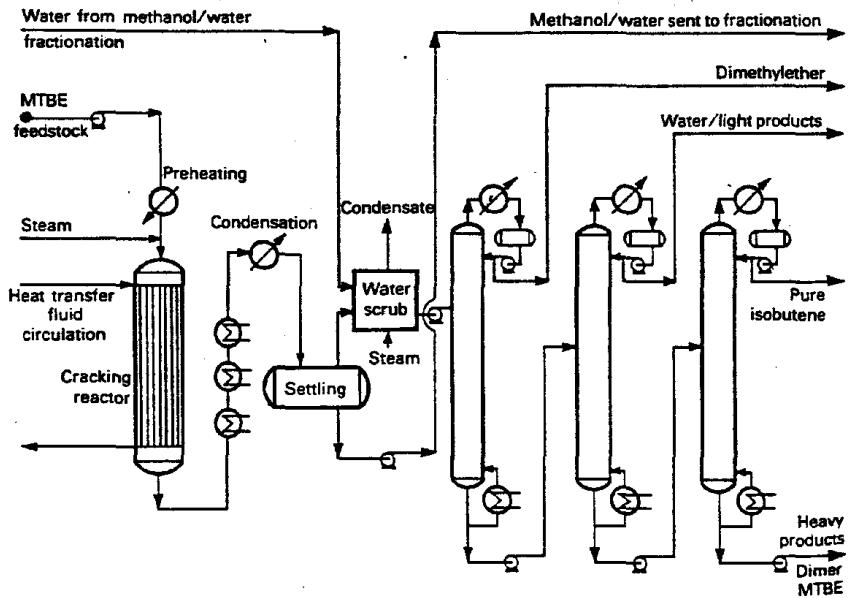


Fig. 3.6. Cracking of MTBE to isobutene. IFP process.

95 to 98 per cent, and selectivities are even better, over 99.9 molar per cent in relation to the isobutene and 94 per cent in relation to the methanol. Such performance tends to eliminate the need for MTBE recycling, which produces azeotropes of comparable boiling points (51.6 and 52.6°C respectively at $0.1 \cdot 10^6$ Pa absolute) with methanol and water. In certain cases, however, where conversion does not exceed 65 per cent, this operation becomes necessary. In this case, the temperature is also lower ($\geq 150^\circ\text{C}$).

The main by-products of MTBE cracking are dimethyl ether obtained by methanol dehydration, the dimer and trimer of isobutene, and *t*-butyl alcohol resulting from the polymerization and hydration of the olefin.

The flow sheet (Fig. 3.6) of an industrial MTBE cracking facility comprises three main sections:

- (a) Conversion, carried out in a tubular reactor of the heat exchanger type, in which a heat transfer fluid flows at the shell side, while the feedstock, and possibly a recycle stream, and the process steam enter the tubes after being preheated. After cooling, the effluent is condensed and separated into two liquid phases.
- (b) Isobutene purification, achieved by washing the hydrocarbon phase with water to eliminate soluble components such as methanol and *t*-butyl alcohol, followed by distillation in a series of three columns, where dimethyl ether, water, and heavy products such as the dimer of isobutene and MTBE are removed in succession.
- (c) Recovery of the methanol present in the aqueous phase and the wash waters by reconcentration in a distillation column.

Among the main license holders in this area are *IFP* and *UOP*.

C. Oligomerization

A wide range of processes is available in the area of oligomerization applicable to C₄ olefins. However, a distinction must be drawn between those intended for the effective manufacture of the higher olefinic hydrocarbons, which operate either in a homogeneous phase (*Bayer*, *IFP Dimersol*), or in a heterogeneous phase (*IFP Polynaphta*, *Petrotex*, *UOP*), which were discussed in Section 2.3.3.2, and those that are only intended to facilitate subsequent treatment.

Two methods are available for the selective oligomerization of isobutene. They are practised by *UOP* and *IFP* in particular, and apply to the following situations:

- (a) Conversion of large amounts of isobutene such as those contained in C₄ cuts from catalytic cracking or debutadienized steam cracking (e.g. *IFP's Selectopol process*).
- (b) Elimination of residual contents of isobutene such as those in effluents produced by hydration or etherification (e.g. *IFP's Polyfining process*).

These techniques operate in accordance with similar principles (Fig. 3.7). The pre-heated feed, normally heated by heat exchange with the reactor effluent, is introduced in the reactor in a downflow stream. Conversion takes place in the presence of acid catalysts such as phosphoric acid deposited on silica or silico-aluminates, placed in several fixed beds. This arrangement allows effective control of the temperature rise due to the exothermic nature of the reaction, by the injection between the beds of a quench liquid consisting of unconverted C₄. The operating conditions are moderate (temperatures: average 120°C, limits 50 to 200°C, pressure 1 to $4 \cdot 10^6$ Pa absolute). The reactor effluent

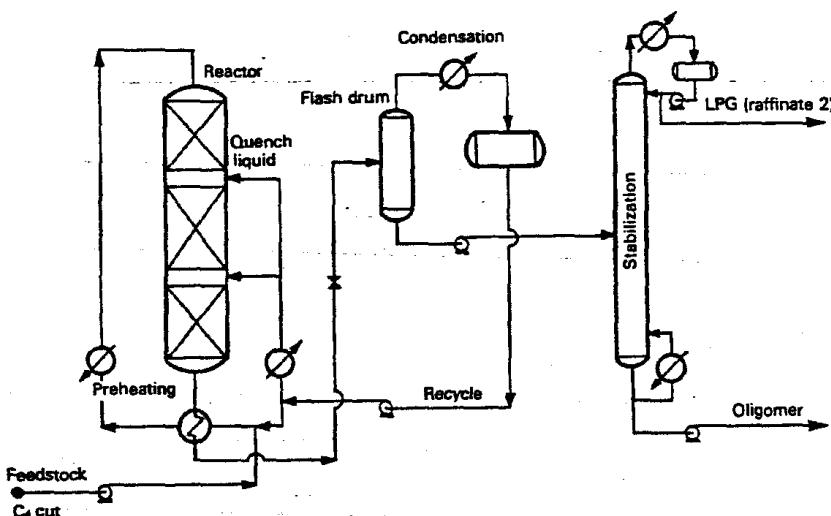


Fig. 3.7. Isobutene oligomerization. IFP process (Selectopol).

is first cooled and flashed to allow recycling of the quench liquid, and then distilled to separate a butene-rich cut at the top and the oligomers formed at the bottom.

D. Other methods for separating and obtaining isobutene from C₄ cuts from various sources

Union Carbide has proposed adsorption on molecular sieves to separate isobutene, particularly from steam-cracked C₄ cuts. This is the Olefin-Siv process, which simultaneously produces 1-butene, and is discussed in greater detail in Section 3.1.3.A.

In connection with the treatment of C₄ cuts, it is important to mention the possibility of producing additional amounts of isobutene by the isomerization of n-butenes present in these effluents. This rearrangement of the molecule's skeleton appears to be a thermodynamically limited conversion, slightly exothermic ($\Delta H_{298}^0 \approx -6$ kJ/mol) in the direction of the formation of the isoolefin, and very slow at moderate temperature. Hence it is normally conducted in the vapor phase around 500°C at low pressure (0.1 to 0.2 · 10⁶ Pa absolute). To minimize side reactions at elevated temperature, particularly the oligomerization of isobutene, the reaction medium is diluted with steam, which offers the additional advantage of facilitating heat input and temperature control. This procedure also helps to minimize cracking and coke deposits on the catalyst. The process takes place in the presence of fixed silica-alumina beds, with which once-through conversion is as high as 30 per cent, and molar selectivity is 75 to 80 per cent, for a WHSV of about 2.5.

The basic principle of the process, which is licensed by *IFP, SNAM (Societa Nazionale Metanodotti)* etc., comprises preheating of the hydrocarbon feedstock and boiler feed-

water, by heat exchange with the reactor effluent and passage through a furnace. The mixture is then introduced in a downflow stream into the reaction zone containing the catalyst. At the outlet, the product is cooled in several stages. The recovered condensates are recycled. As for the gaseous fraction, it is first compressed to about $0.6 \cdot 10^6$ Pa absolute, and then again cooled to liquefy most of the hydrocarbons. Residual gases are purged and the liquid phase is pressurized by pumping at about $1.8 \cdot 10^6$ Pa absolute, to remove the light (C₃) and heavy (C₅-C₈) constituents, by distillation in two columns in series. The C₄ cut produced, which is rich in isobutene, is then sent to the extraction step.

Among the different methods for manufacturing olefins discussed in Section 2, the dehydrogenation of paraffins and the dehydration of alcohols find a specific application in the manufacture of isobutene. The following is one of the schemes proposed:

- (a) Dehydrogenation of isobutane, whose availability can be enhanced by the isomerization of *n*-butane. The manufacture of the olefin is examined in greater detail in Section 6. As for the isomerization step, this takes place industrially around 150 to 200°C at 1.5 to $2.5 \cdot 10^6$ Pa absolute, namely in the vapor phase, in the presence of hydrogen and a catalyst based on alumina and platinum (BP, IFP processes, UOP's Butamer etc.).
- (b) Dehydration of *t*-butyl alcohol, a by-product of the manufacture of propylene oxide by the ARCO Chemical technique involving the co-oxidation of isobutane and propylene. This conversion is discussed in greater detail in Section 6.2.4.

3.1.3.3 1-butene separation

Two main methods are currently marketed to primarily extract or convert 1-butene. They involve the following operations:

- (a) Adsorption on molecular sieves.
- (b) Hydroisomerization of α -olefins to internal olefins.

A. Adsorption

The molecular sieves employed for this operation are synthetic silico-aluminas which carry metallic ions, with uniform pore diameters between 3 and 10 Å, and whose structure is comparable to that of natural zeolites. They are capable of separating linear carbon chains, which are specifically adsorbed, from those that are branched. Many technologies have been developed, particularly by Exxon, BP (British Petroleum), Texaco, UQP and Union Carbide, which exploit their capacity for selective adsorption to isolate *n*-paraffins from their branched isomers as well as linear olefins from their branched homologues.

In the specific area of C₄ cut treatment, two techniques have culminated in industrial plants, Union Carbide's Olefin-Siv process and UOP's Sorbutene process.

a. Union Carbide Olefin-Siv process

This process operates in short cycles, with three main phases, in a series of adsorbers laid out in parallel, containing the molecular sieves in fixed beds, and capable of being switched in their operation by a set of automatically controlled valves.

The first phase selectively separates the *n*-butenes from a feedstock previously vaporized around 100°C, at $0.2 \cdot 10^6$ Pa absolute, by circulation in an upflow stream through the adsorbent. The isobutene-rich fraction of the residual C₄ cut also contains a heavier hydrocarbon such as hexane, an eluant used in subsequent operations, which is displaced from the pores it initially occupied. This effluent is cooled to 40°C and partly condensed. The liquid and gaseous fractions are separated, and then pumped and compressed respectively at $0.6 \cdot 10^6$ Pa absolute, to allow the production, by simple distillation, of isobutene at the top and the eluant at the bottom.

The second phase consists in a co-current purge, namely in an upflow stream, of the adsorbent bed loaded with *n*-butenes, with a quantity of eluant that is just sufficient to displace only the unretained C₄ compounds from the interstitial voids which they occupy. The effluent collected is added to the previous one.

The final phase involves the co-current washing of the adsorbent bed, namely in a downflow stream, using the effluent to displace the retained *n*-butenes. As above, the effluent recovered is cooled and partly condensed. The liquid and gaseous fractions are separated, and then pumped and compressed respectively at $0.5 \cdot 10^6$ Pa absolute, to allow the production, by simple distillation, of *n*-butenes at the top around 40°C, and of the eluant at the bottom.

To guarantee continuous operation, a minimum of three adsorbers in parallel is therefore necessary. In fact, additional regeneration equipment must also be provided. This is because side reactions take place during the treatment, including the isomerization of 1-butene to 2-butenes, the dimerization of isobutene, and, above all, polymerization and the formation of coke deposits on the adsorbent. Consequently, controlled combustion must be carried out periodically, every three to four days, at 400°C, using air depleted of oxygen (1 per cent volume). For safety reasons, this reaction is preceded and followed by nitrogen purges.

The eluant itself, which gradually accumulates heavy compounds, must be purified by distillation before recycling.

Table 3.7 gives the typical composition of the main effluents.

TABLE 3.7
TYPICAL PERFORMANCE OF UNION CARBIDE'S OLEFIN-SIV PROCESS (% Wt)

Components	Feedstock	Extract (butenes)	Raffinate (isobutene)
Isobutene	50.7	0.5	99.1
1-butene	32.7	56.1	0.1
Trans 2-butene	11.4	32.3	0.2
Cis 2-butene	5.2	11.1	0.6
Total	100.0	100.0	100.0

b. UOP's Sorbutene process

This process, applied to the treatment of C₄ cuts and more specifically to the manufacture of 1-butene, is one of the many variants of adsorption technology on molecular sieves called Sorbex and developed by UOP, to separate paraffins (Molex), olefins (Olex)

and *p*-xylene (Parex). The production of 1-butene requires prior selective hydrogenation of the butadiene and acetylenic compounds in the feed.

This technique (Fig. 3.8), which is examined in greater detail in connection with the upgrading of aromatic C₈ cuts, is based on the use of a pseudo-countercurrent between the liquid feedstock and the adsorbent bed. The displacement of the solid is in fact simulated by means of a rotary valve with multiple inlets and outlets, which causes a gradual change in the injection and collection points of the liquid streams in the molecular sieve placed in a multi-stage column.

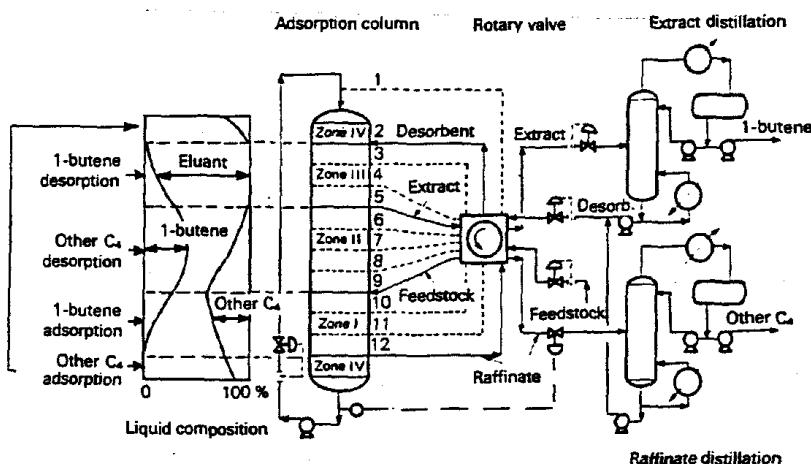


Fig. 3.8. Separation of 1-butene from C₄ cuts. UOP process (Sorbitene).

As in the case of xylenes, at any given moment and in steady state conditions, a concentration gradient is established across the adsorbent, between the different feedstock components and the eluant employed to displace them. This C₄ distribution profile in the molecular sieve bed results from different adsorption selectivities: in relation to 1-butene, these are roughly 2.26 for isobutene, 3.10 for trans 2-butene, and 2.98 for cis 2-butene. Hence a specific zone appears in which, at the time concerned, only 1-butene and the desorbent are present. A suitable draw-off at this level, followed by simple distillation, serves to produce the olefin in the requisite degree of purity (99.2 per cent). An optimal region also exists for recovering the other compounds in a mixture with the eluant. As above, their separation by distillation allows the recycling of the desorbent liquid, normally a hydrocarbon with a molecular weight higher than that of the C₄ compounds and with a clearly distinct boiling point.

As the process continues, the concentration profile shifts in connection with those of the feedstock and eluant injections, required to simulate the countercurrent flow, and consequently that of the draw-off levels.

To achieve good stability in the distribution conditions of the different compounds on the adsorbent, the operation must be conducted at a perfectly controlled temperature ($< 100^{\circ}\text{C}$) and under pressure ($< 2 \cdot 10^6 \text{ Pa absolute}$) in order to keep all the hydrocarbons in the liquid state. A pump picks up the mixture leaving the bottom of the adsorption column, recycles it to the top, to ensure continuous countercurrent flow.

The Sorbutene process achieves a 1-butene recovery rate of 92 per cent. Table 3.8 indicates the composition of the main effluents.

TABLE 3.8
TYPICAL PERFORMANCES OF UOP SORBUTENE PROCESS (% Wt)

Components	Feedstock	Extract	Raffinate
1-butene	30.4	99.2	3.3
Isobutene	50.5	0.7	70.1
2-butenes	10.0	0.1	13.9
n-butane, isobutane	9.1	—	12.7
Total	100.0	100.0	100.0

B. Hydroisomerization

The isomerization of 1-butene to 2-butenes is valuable for two reasons:

- (a) For petrochemicals, it serves to simplify the schemes for subsequent separations of the components of C₄ cuts.
- (b) In refining, the alkylates produced with isobutane lead to higher octane numbers than those resulting from the direct alkylation of the initial hydrocarbon feedstock.

As shown by the graph in Fig. 3.9, which indicates the variation of the composition at thermodynamic equilibrium as a function of temperature at $0.1 \cdot 10^6 \text{ Pa absolute}$:

- (a) of the mixture of n-butenes only.
- (b) of the combination of n-butenes and isobutene.

this virtually athermic operation is favored at low temperature. On the contrary, the rearrangement of the skeleton, in the direction of the formation of linear olefins from their branched homologue, takes place at high temperature.

Furthermore, since the C₄ cuts employed exhibit a 1-butene percentage of about 10 to 15 per cent weight, this graph also shows that, to achieve effective conversion, it is necessary to operate at less than 150°C . In practice, the operation is conducted at about 100°C , which maintains a residual 1-butene content of about 5 per cent weight in the effluent. In these conditions, however, the reaction rate becomes slow. Catalysts are used to accelerate it, usually based on precious metals deposited on inert alumina (palladium, rhodium etc.), whose operation is considerably improved in a hydrogen atmosphere. This also permits the selective hydrogenation of the residual butadiene, and explains why this conversion is called hydroisomerization.

In principle, the flow sheet of an industrial facility is similar to those of the different hydrotreatings already discussed. The feedstock C₄ cut is first rid of water in a coalescer. It is then pressurized to about 1.5 to $2 \cdot 10^6 \text{ Pa absolute}$ by pumping injected with a

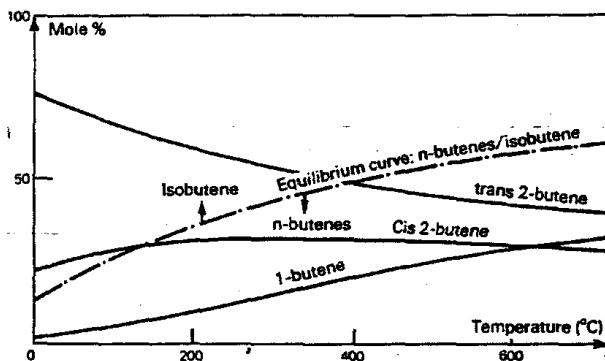


Fig. 3.9. Composition of mixtures of butenes at thermodynamic equilibrium.

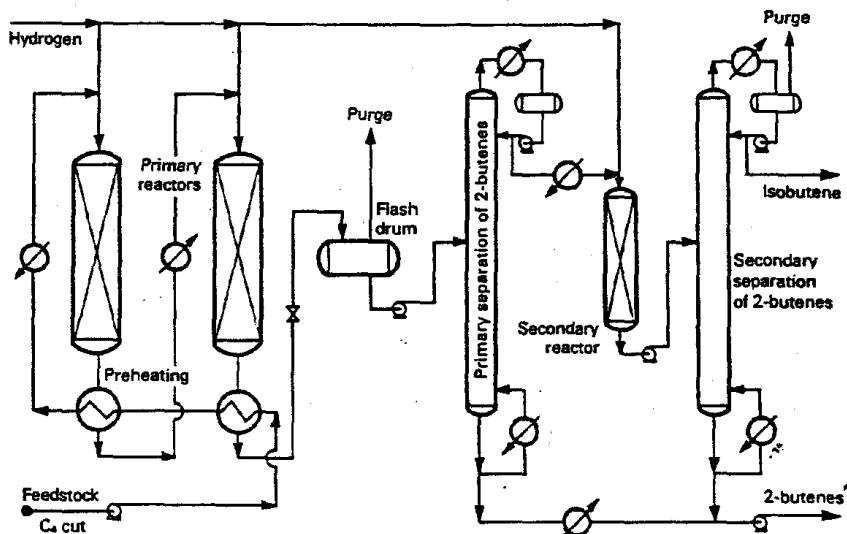


Fig. 3.10. Hydroisomerization of 1-butene to 2-butenes.

hydrogen-rich gas, and then preheated by heat exchange with the reaction effluent and by steam. In a downflow or upflow stream, it then enters the reactor, which operates in a mixed phase with one or more catalyst beds. After cooling, the isomerization products are flashed to remove excess hydrogen gas.

To produce a cut rich in isobutene (90 to 95 per cent), two hydroisomerization steps are necessary in series, with intermediate separation of most of the 2-butenes, in order to enhance the effectiveness of the second conversion stage (Fig. 3.10). Table 3.9 provides an idea of the composition of the effluents obtained.

The main license holders are *Engelhard*, *IFP*, *UOP* etc. and *Phillips*, which also carries out reverse isomerization in a two-step process, with the second operating around 500°C.

TABLE 3.9
TYPICAL COMPOSITIONS OF HYDROISOMERIZATION EFFLUENTS (% Wt)

Components	Feedstock	Isobutylene cut	2-butenes cut
Isobutylene	35	31.9	2.8
1-butene	38	0.4	0.5
2-butenes	20	0.5	54.0
n-butane	5	0.1	8.4
Isobutane	1	1.4	—
Butadiene	1	—	—
Total	100	34.3	65.7
n-butylenes content	—	2.6	83.0
Isobutylene content	—	93.0	4.3

3.1.3.4 Treatment of the residual C₄ cut

Depending on the method used to separate isobutene or butene-1, and in accordance with the desired application for the remaining components of the C₄ cuts initially available, supplementary treatments may exhibit a range of complexity. Hence it may or may not be possible, both for technical and economic reasons, to incorporate them in the extraction facilities that serve as a basis for the upgrading schemes selected. In certain cases, in fact, one of the primary separation processes already examined can be used as an auxiliary for another technology, that is also designed as an initial step.

As shown by Fig. 3.1, the main situations encountered involve the following connected treatments:

- (a) Separation of cuts or products by superfractionation. This includes distillations combined with adsorption or hydroisomerization, whose economic data take into account those associated with the complementary operations.
- (b) The juxtaposition of basic technologies. This is the case of adsorption combined with hydration of isobutene, and hydroisomerization, which is widely employed as a complement for itself or of hydration and etherification. The reader is invited to refer to the foregoing sections dealing with these processes, and to adapt the data given therein accordingly.

(c) Development of a complex purification scheme involving superfractionation or extractive distillation.

The first alternative is currently the most widespread. It consists in setting up a series of four distillation columns grouped in pairs. The first, with 65 trays each, separates isobutane at the top with a reflux ratio of 140/1. They operate at 0.8 to $0.9 \cdot 10^6$ Pa absolute, around 60°C, in series, to minimize the total pressure drop and hence the reboiling temperature. To do this, they comprise direct vapor phase injection of the top effluent from the first distillation column at the bottom of the second, and the use of a pump to draw off the liquid from this column to reintroduce it at the top of the first. The second pair of columns operates under the same arrangements at 0.7 to $0.8 \cdot 10^6$ Pa absolute, around 60°C, with 70 trays for each column and a reflux ratio of 16/1. They serve to obtain 1-butene at the top at about 99.5 per cent purity, and a 2-butenes-rich cut at the bottom, in which the main impurity is *n*-butane.

The second alternative first involves simple distillation for the separation of two cuts:

- (a) At the top: isobutane, 1-butene, possibly with residual isobutene.
- (b) At the bottom: *n*-butane, 2-butenes.

In a second step, the olefins are isolated from each of these effluents by extractive distillation, for example using furfural, acetone, acetonitrile, or other solvents. Extractive distillation can also be carried out on the entire cut rid of isobutene, to separate the butanes from the butenes.

This technique is offered in particular by *Nippon Zeon* to manufacture polymerization-grade 1-butene with the GDP III process, which uses dimethylformamide as solvent. In its principle, the installation flow sheet comprises the following main steps:

TABLE 3.10
PREPARATION OF C₄ CUTS BY SELECTIVE HYDROGENATION. ECONOMIC DATA
(France conditions, mid-1986)

C ₄ cut butadiene content	Low ⁽¹⁾	High
Production capacity (t/year)	50,000	150,000
Battery limits investments (10^6 US\$)	0.35	0.9
Initial catalyst load (10^9 US\$)	0.05	0.09
Consumption per ton of feed		
Net hydrogen (kg)	0.4	⁽²⁾
Steam (t)	0.02	—
Electricity (kWh)	1	3
Cooling water (m ³)	0.5	40
Catalyst (US\$)	0.3	0.4
Labor (Operators per shift)	1	1

(1) Butadiene content 0.4%.

(2) To be determined according to feed composition.

TABLE 3.11
PROCESSES FOR ISOBUTYLENE SEPARATION AND PRODUCTION, ECONOMIC DATA
(France conditions, mid-1986)

Production or separation method	H_2SO_4 hydration	Etherification			Dehydration	Oligomerization		Adsorption	Isomerization ⁽⁴⁾		
		MTBE Synthesis		MTBE synthesis and cracking		Oxirane	IFP				
		CFR	From steam cracking				High isobutylene content ⁽¹⁾	Low isobutylene content ⁽²⁾			
Processes			From steam cracking	From catalytic cracking	From steam cracking	Oxirane		Union Carbide	IFP		
Product	Isobutylene (k _t /MM)	MTBE (k _t /MM)	MTBE 100,000	Isobutylene (k _t /MM)	Isobutylene 60,000	Oligomers 45,000	C ₄ cut 60,000	Isobutylene (k _t /MM)	C ₄ cut 120,000		
Capacity (t/year)											
Battery limits investments (10 ⁶ US\$)	13.0	2.6	4.4	7.5	7.5	1.8	0.55	7.3 ⁽⁵⁾	6.1		
Initial catalyst load (10 ⁶ US\$)	—	0.04	0.05	0.05	—	0.07	0.05	—	0.2		
Consumption per ton of product											
Raw material											
C ₄ cut (t)	2.23	1.47	4.56	2.64	—	2.22	—	1.63	1.02		
Methanol (t)	—	0.37	0.37	0.02	—	—	—	—	—		
t-butanol (t)	—	—	—	—	1.4	—	—	—	—		
By-products											
C ₄ cut	1.14	0.84	3.93	1.53	—	1.22	—	0.60	—		
Heavy compounds (t)	0.09	—	—	0.13	—	—	—	0.03	0.02		
Utilities											
Steam (t)	3.0	0.5	1.6	7.0	2.1	0.5	0.1	3.3	0.5		
Electricity (kWh)	150	7	15	95	15	25	2	55	50		
Fuel (10 ⁶ kJ)	—	—	—	—	—	—	—	0.3	0.4		
Cooling water (m ³)	160	20	90	275	150	50	5	145	40		
Process water (m ³)	1	—	—	—	—	—	—	—	—		
Catalysts and miscellaneous (US\$)	—	0.4	0.4	1.8	1.8	0.4	0.5	2.6	0.5		
Chemicals											
Sulfuric acid (kg)	4.4	—	—	—	—	—	—	—	—		
Caustic soda (kg)	3.9	—	—	—	—	—	—	—	—		
Labor (Operators per shift)	2	1.5	1.5	3	2	1	1	2	1		

(1) Selectopol (2) Polyfining (3) Including adsorbent charge (4) Composition (% weight):
 Feed C₂ = 0.3; nC₃ = 7.2; nC₄ = 20.7; nC₄⁺¹ = 2.2; nC₄⁻¹ = 58.4; IC₄ = 1.2; C₅ = 5;
 Product C₂ = 2.0; IC₂ = 6.1; nC₃ = 20.4; nC₄⁺¹ = 15.1; nC₄⁻¹ = 33.8; IC₄ = 20.9; C₅ = 2.0.

TABLE 3.12
PROCESSES FOR THE SEPARATION AND PRODUCTION OF *n*-BUTYLENES, ECONOMIC DATA
(France conditions, mid-1986)

Treatment	Adsorption			Hydroisomerization		Superfractionation	Extractive distillation
	UOP		Union Carbide	IFP	Phillips		
Processes	Sorbutene from steam cracking	Sorbutene from catalytic cracking	Olefin-Siv from steam cracking	Direct in two steps	Direct and reverse		Dimethylformamide
Product	1-butene	1-butene	1-butene	2-butene rich cut	1-butene rich cut	1-butene ⁽¹⁾	1-butene
Capacity (t/year)	50,000	50,000	50,000	50,000	50,000	50,000	50,000
Battery limits investments (10 ⁶ US\$)	15 (1-2)	22.5 (1-2)	18 (1-2)	5.3 0.09	20.1 (1-2)	10.5	11.4
Initial catalyst load (10 ⁶ US \$)	—	—	—	—	—	—	—
Consumption per ton of product							
Raw material							
C ₄ cut (t)	3.89	7.91	3.84	1.80	2.33	2.29	2.32
Hydrogen (kg)	—	—	—	1.0	2.1	—	—
By-products							
Isobutane (t)	—	—	0.06	—	—	0.11	—
Isobutene (t)	—	—	1.65	0.80	1.28	—	—
2-butylene (t)	—	—	—	—	—	1.16	—
C ₄ cut (t)	2.89	6.91	1.03	—	—	—	1.32
Heavy compounds (t)	—	—	0.10	—	—	—	—
Utilities							
Steam (t)	2.2	3.7	8.4	2.5	5.1	5.9	3.5
Electricity (kWh)	50	80	130	10	35	20	70
Fuel (10 ⁶ kJ)	—	—	0.75	—	2.1	—	—
Cooling water (m ³)	70	115	225	135	280	250	300
Catalysts and chemicals (US\$)	2.6	5.3	3.5	1.8	2.6	—	0.9
Labor (Operators per shift)	2	2	3	2	3	0.5	2

(1) Initial adsorbent or catalyst loads included.

(2) Distillations included.

(3) Purity ~ 99.5%.

- (a) A first extractive distillation to separate butane and isobutane at the top.
- (b) Stripping of the *n*-butenes contained in the extract, with solvent regeneration at the bottom and its recycle.
- (c) Distillation under pressure to obtain the 2-butenes at the bottom, and the 1-butene and acetylenic and dienic compounds at the top.
- (d) A second extractive distillation, whose raffinate consists of pure 1-butene (99.5 per cent) and whose extract contains dienes, acetylenic compounds and some 1-butene.
- (e) A second stripping to regenerate and recycle the solvent.

3.1.3.5 Economic data

Tables 3.10, 3.11 and 3.12 provide economic data on techniques for the selective hydrogenation of butadiene contained in a C₄ cut, on the processes for the separation and manufacture of isobutene, and on those relative to the production of *n*-butenes.

3.1.3.6 Uses and producers

Tables 3.13 and 3.14 indicate the uses, production and consumption of butylenes, *n*-butenes and isobutene in Western Europe, the United States and Japan in 1984 and some capacity data for 1986 for these three areas.

TABLE 3.13
PRODUCTION AND CONSUMPTION OF BUTYLENES IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% products)			
Chemical uses	20	6	29
<i>n</i> -butenes	10	3	12
Isobutene	10	3	17
Fuel uses	80	94	71
Alkylation	22	86	4
LPG, polygas	50	3	
MTBE	8	5	67 ⁽¹⁾
Total	100	100	100
Sources (% product)			
Refinery			
Catalytic cracking	57	82	47
Thermal cracking	2	9	—
Steam cracking	39	7	53
Miscellaneous	2	2	—
Total	100	100	100
Supply (10 ⁶ t/year)	4.6	13.7	1.5
Demand (10 ⁶ t/year)	4.5	13.6	1.5

(1) MTBE is produced as an intermediate for methyl methacrylate.

TABLE 3.14
n-BUTYLENES AND ISOBUTYLENE: DEMANDS FOR CHEMICALS IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% products)			
<i>n</i> -butylenes			
Butadiene	—	4	—
sec-butanol (MEK)	54	46	62
1-butene ⁽¹⁾	6	28	14
Heptenes, octenes	36	22	11
Maleic anhydride	—	—	13
Miscellaneous ⁽²⁾	4	—	—
Total	100	100	100
Isobutene			
Butyl rubber	37	30	29
Diisobutylene-triisobutylene	22	—	16
Methyl methacrylate	—	—	26
Polybutenes, polyisobutylene	32	57	15
Miscellaneous ⁽³⁾	9	13	14
Total	100	100	100
Demand (10 ³ t/year)			
<i>n</i> -butylenes	435	440	175
Isobutylene	440	450	245

(1) 1-butene is used as polyethylene comonomer (HDPE, LLDPE) and solvent and to produce 1,2-butylene oxide, *n*-butyl mercaptan, *o*-sec-butylphenol, dinitro-sec-butylphenol, polybutene-1 resin, valeraldehyde. In 1986 production capacities of 1-butene were the following:

(a) In Western Europe: *Hüls* (West Germany, Mari, 70.10³ t/year), *Neste Oy* (Finland, 20.10³ t/year) and *Shell* (Netherlands, Pernis, 20.10³ t/year).

(b) In the United States: *Chevron* (Cedar Bayou, Tx., 14.10³ t/year), *Ethyl* (Pasadena, Tx., 36.10³ t/year), *Exxon* (Baytown, Tx., 82.10³ t/year), *Shell* (Geismar, Tx., 14.10³ t/year), and *Texas Olefins* (Houston, Tx., 91.10³ t/year).

(c) In Japan: *Mitsubishi Chemical* (Mizushima, 4.10³ t/year), *Mitsui Petrochemicals* (Ichihara, 22.10³ t/year), *Nippon Petrochemicals* (Kawasaki, 5.10³ t/year), *Suntomo Chemical* (Ichihara, 10.10³ t/year) and *Tonen Sekiyu* (Kawasaki, 10.10³ t/year).

(2) *n*-valeraldehyde and isovaleraldehyde.

(3) *t*-butyl alcohol (TBA), *t*-butylamine, *t*-butylcatechol, 2-*t*-butyl-*p*-cresol, *t*-butyl mercaptan, 2- and 3-*t*-butyl-4-methoxyphenol, *p*-*t*-butylphenol, 2-*t*-butyl-toluene, di-*t*-butyl-*p*-cresol (BHT), di-*t*-butylphenol, isobutyl aluminum compounds, methylallyl chloride, neopentanoic acid.

3.2 UPGRADING OF C₅ CUTS

The use of C₅ cuts from steam cracking and catalytic cracking could theoretically lead to upgrading schemes similar to those implemented for the C₄ cuts. They exhibit similar characteristics, such as the virtual absence of dienic compounds in the catalytic cracking effluents or, on the contrary, their presence in substantial amounts in steam-cracking effluents (Table 3.15). But these cuts also display high contents of olefins and

branched compounds which impart high octane numbers. Moreover, they are necessary to obtain a regular distillation curve for gasolines. Hence they are not generally separated but distilled with the aromatic hydrocarbons to be sent directly to the gasoline pool.

Although available in smaller amounts, C₅ effluents, like C₄ effluents, are mainly suitable for the utilization of diolefins, especially isoprene, and olefins.

TABLE 3.15
TYPICAL COMPOSITIONS OF C₅ CUTS (% Wt)

Hydrocarbons	Source	
	Steam cracking	Catalytic cracking
C ₄ -	1.0	2.0
n-pentane	26.0	5.5
Isopentane	24.0	31.5
n-pentenes	4.5	22.5
Methylbutenes	12.0	37.5
Cyclopentene	1.5	—
Isoprene	13.5	—
Pentadiene (piperylene)	9.0	—
Cyclopentadiene	7.5	—
2-butyne	ε	—
C ₆ -	1.0	1.0
Total	100.0	100.0

3.2.1 Extraction of diolefins (isoprene) from steam-cracked C₅ cuts

The commercial specifications required for polymerization-grade isoprene are, like those for butadiene, extremely severe (Table 3.16).

Hence, to extract the isoprene contained in a C₅ cut, highly elaborate separation methods must be employed, especially since, as shown by Table 3.17, the boiling points of some other hydrocarbons are very close to that of the desired product. Furthermore, only steam cracking can produce effluents with a significant isoprene content (Table 3.15). However, even at this level of 10 to 15 per cent weight in relation to the treated cut, the quantities that are potentially recoverable are low. In comparison with naphtha feedstock, these values are reduced to 0.5 to 0.75 per cent weight, which, for a steam cracker producing 300,000 t/year of ethylene, treating 1,000,000 t/year of naphtha, means a unit production of isoprene of 5000 to 7500 t/year. To guarantee economic manufacture, it is therefore necessary to combine the C₅ effluents from several large-scale installations.

Among the industrial alternatives proposed to produce isoprene, extractive distillation appears to be the best. As for butadiene, the main solvents employed are acetonitrile (*ARCO, Exxon, Japan Synthetic Rubber, Nippon Petrochemical, Shell*), N-methylpyrrolidone (*BASF*), and dimethylformamide (*Nippon Zeon*). Their physical properties were given partly in Table 3.4. By modifying the relative volatilities of the components, as

TABLE 3.16
COMMERCIAL SPECIFICATIONS OF POLYMERIZATION GRADE ISOPRENE

Characteristics		Values
Isoprene (% Wt) min.		99.0
Cyclopentadiene (ppm) max.		10
Acetylenics (ppm) max.		50
Piperylene (ppm) max.		1,000
Cyclopentene (ppm) max.		100
Carbonyl compounds (as aldehydes) (ppm) max.		10
Inhibitor (<i>p</i> -tertiobutylcatechol) (ppm) max.		50
Peroxides (as hydrogen peroxide) (ppm) max.		5
Dimers (ppm) max.		1,000

TABLE 3.17
RELATIVE VOLATILITIES OF HYDROCARBONS WITH
BOILING POINTS CLOSE TO THAT OF ISOPRENE (AT 40°C)

Hydrocarbon	bp _{1.013} (°C)	Relative volatility	
		Without solvent	In the presence of DMF ⁽¹⁾
1-pentene	30.0	1.16	2.35
2-methyl 1-butene	31.2	1.11	2.05
Isoprene	34.1	1.00	1.00
<i>n</i> -pentane	36.1	0.94	3.60
Trans 2-pentene	36.4	0.93	2.00
Cis 2-pentene	36.9	0.92	1.90
2-methyl 2-butenes	38.6	0.86	1.65
Cyclopentadiene	41.0	0.82	0.55
Trans piperylene	42.0	0.76	0.75

(1) At infinite dilution.

shown by Table 3.17, their use considerably facilitates separation, which could not be achieved by conventional distillation facilities.

Another type of problem may also arise from the formation of azeotropes, whose boiling points are close to that of isoprene. This is the case of cyclopentadiene, whose separation, like that of piperylene, should normally take place by simple distillation, but which produces azeotropes with *n*-pentane (35.3°C), 2-methyl 2-butenes (38°C) and cis 2-pentene (36.9°C).

Although, in this case, extractive distillation provides a solution in itself, it may be interesting to improve its effectiveness by avoiding complications of this type, especially since cyclopentadiene, and, to a lesser degree, piperylene, have many specific applications. The former is used for elastomers (EPDM, polynorbornene, transpolypentenamer etc.).

resins, insecticides (hexachlorocyclopentadiene etc.), flame retardants (chlorendic acid), polyesters, medicines and perfumes, petroleum additives etc., and the latter is used for resins (synthetic polyterpene), elastomers etc.

One of the methods proposed industrially consists in exploiting the tendency of cyclopentadiene to dimerization, which appears at ambient temperature, but is considerably accentuated around 95 to 125°C and by an increase in pressure ($0.5 \cdot 10^6$ Pa absolute). The dicyclopentadiene formed, which boils at 170°C at atmospheric pressure, is easily separated. Moreover, its depolymerization also occurs at this temperature. Simple distillation is interesting if pure products do not need to be produced, but merely cuts enriched in cyclopentadiene, piperylene and isoprene. However, superfractionation is resorted to in this case.

Extractive distillation processes are all based on the same operating principle, already examined in connection with the extraction of butadiene from a C₄ cut. The only notable differences are of a technological nature, related to the type of solvent employed. Hence commercial installations use solvent weight ratios of 5 to 6, in the presence of a polymerization inhibitor, and of 5 to 10 per cent water in the case of acetonitrile and N-methylpyrrolidone, enhancing the selectivity of the operation; and in anhydrous medium, in the presence of dimethylformamide, in view of its tendency to hydrolyse more easily to formic acid and dimethylamine. Moreover, N-methylpyrrolidone and dimethylformamide, unlike acetonitrile, do not lead to the formation of azeotropes with the hydrocarbons treated.

This can be illustrated by the BASF process (Fig. 3.11) which comprises the following steps:

- (a) 90 per cent dimerization of cyclopentadiene, a reaction during which about 4 per cent of the feedstock isoprene is polymerized.
- (b) Extraction of diolefins and acetylenic compounds by liquid/liquid contact, using N-methylpyrrolidone containing water. This countercurrent washing serves to remove, in the raffinate at the top, most of the pentanes and pentenes, as well as the dicyclopentadiene. The stripped solvent is recovered by washing this raffinate with water.
- (c) Distillation of the extract to separate a mixture of paraffins, residual olefins (especially 2-methyl 2-butenes) and a certain amount of isoprene at the top. The hydrocarbons rid of C₄ components and 1,4-pentadiene in a debutanizer are recycled to the extraction step. The heavy end of the column treating the extract is stripped, so that the solvent is recovered at the bottom and recycled to the extractor, and the hydrocarbons are obtained at the top (isoprene, piperylene, residual cyclopentadiene, cyclopentene and acetylenic derivatives) together with excess water.
- (d) Absorption at atmospheric pressure, in the presence of N-methylpyrrolidone, of a fraction of the above hydrocarbons, and not including isoprene, whose losses in the extract are kept to a minimum by controlled reboiling in a distillation column operating on this extract. The extract is then stripped to separate the solvent at the bottom, which is recycled to the absorption step, and excess water, piperylene and C₅ acetylenic compounds at the top.
- (e) Purification of the isoprene-rich raffinate produced by absorption, in two distillation columns, the first a light ends column which separates 2-butyne at the

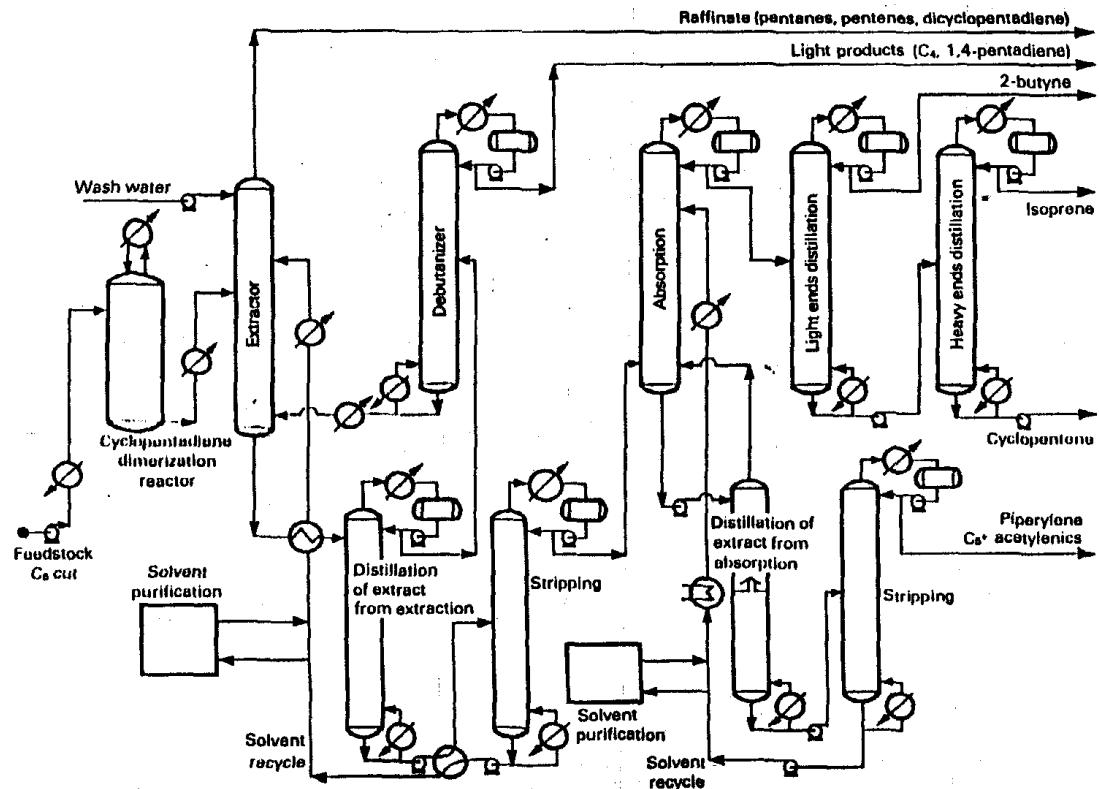


Fig. 3.11. Manufacture of isoprene from steam-cracked C₅ cuts. BASF N-methylpyrrolidone process.

top, and the second a heavy ends column, from which the bottom consists essentially of cyclopentene and traces of piperylene and cyclopentadiene. Polymerization grade isoprene is also obtained.

- (f) Periodic regeneration of the solvent by distillation with the removal of the dicyclopentadiene and cyclopentadiene contained, together with tars.

3.2.2 Upgrading of olefins of C₅ cuts

C₅ olefinic components find fewer applications than the C₄ compounds. The main applications concern isoamylanes with a tertiary carbon atom, i.e. essentially 2-methyl butenes, which produce isoprene by dehydrogenation and Ter Amyl Methyl Ether (TAME) by etherification. The first conversion is discussed in detail in Section 6. As for the second, its value, like that of MTBE, is associated with the antiknock properties of TAME which make it an excellent octane promoter for gasolines. By cracking, the ether can even reproduce isoamylanes. This operation offers one means of separating 2-methyl butenes and a method that is likely to be more economic than direct extraction to obtain isoprene.

To increase the amounts of TAME, i.e. an olefinic precursor, the presence of certain diolefins, such as isoprene, can be exploited. Prior selective hydrogenation, which is

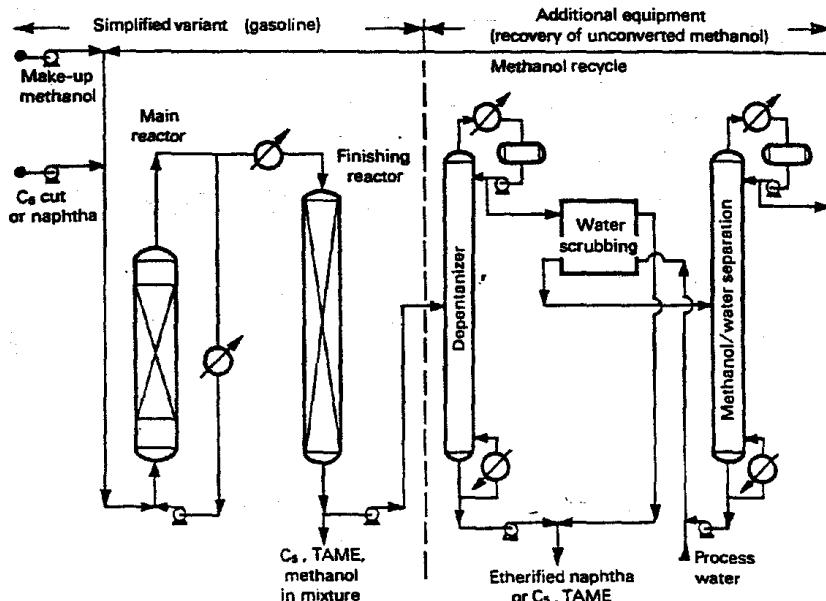


Fig. 3.12. Etherification of C₅ cuts. IFP process.

TABLE 3.18
TREATMENT OF STEAM-CRACKED C₅ CUT. ECONOMIC DATA
(France conditions, mid-1986)

Separation or transformation	Isoprene extraction with N-methylpyrrolidone	Selective hydrogenation	Etherification of a steam-cracked C ₅ cut	
			IFP	
Processes	BASF	—		
Product	Isoprene	Dedensitized C ₅ cut	Gasoline without methanol ⁽¹⁾	Gasoline with methanol ⁽²⁾
Capacity (t/year)	30,000	100,000	60,000	60,000
Battery limits investments (10 ⁶ US\$)	24	1.4	1.4	0.45
Initial catalyst loads (10 ⁶ US\$)	—	0.12	0.02	0.02
Consumption per ton of product				
Raw materials				
C ₅ cut (t)	5.88	—	0.915	0.851
Methanol (t)	—	—	0.085	0.149
Net hydrogen (kg)	—	10	—	—
Products				
Raffinate (t)	3.71	—	—	—
Light compounds (t)	0.31	—	—	—
Piperylene (t)	0.71	—	—	—
Cyclopentadiene (t)	0.12	—	—	—
2-butyne (t)	0.03	—	—	—
Utilities				
Steam (t)	9	—	0.2	—
Electricity (kWh)	190	25	4	3
Fuel (10 ⁶ kJ)	—	2	—	1
Cooling water (m ³)	440	9 ⁽³⁾	10	3
Solvent: N-methylpyrrolidone (kg)	2.5	—	—	—
Catalyst and miscellaneous (US\$)	1.8	0.4	0.4	0.4
Labor (Operators per shift)	4	8	1	0.5

(1) Etherified gasoline containing 27% Wt of TAME.

(2) Etherified gasoline containing 25% Wt of TAME and 7% Wt of methanol.

(3) Use of air coolers.

unnecessary for the effluents of catalytic cracking which are poor in these compounds, is necessary for the products of steam cracking.

This conversion is conducted at moderate temperature and pressure (100°C, $2.5 \cdot 10^6$ Pa absolute), and possibly in the presence of a hydrocarbon diluent, for better control of the temperature rise in the catalyst beds, due to the high exothermicity of the reaction, which is itself related to the high diolefinic content of the initial C₅ cut. As a rule, the feed is introduced in a downflow stream into the reactor, which contains several beds of a noble metal catalyst on alumina. Quench by recycling and diluent injection is carried out between the beds. The diluent is recovered, by distillation in a depentanizer, after flash to eliminate the inert compounds introduced with hydrogen gas at the same time as the feedstock. The leading licensors include IFP and Shell, etc.

Etherification itself is an exothermic conversion ($\Delta H_{298}^o \cong -37$ kJ/mol) which takes place in the liquid phase between 70 and 100°C, at 0.8 to $1.5 \cdot 10^6$ Pa absolute, in the presence of acid catalysts, particularly ion exchange resins, with a methanol to isoamylene molar ratio at the reactor inlet of about 1.1/1.5, and a LHSV of about 2 to 3. Once-through conversion exceeds 70 per cent and molar selectivity 95 per cent.

The TAME content of the etherified solution is about 28 per cent by weight. The main license holders are *Gulf Canada*, *IFP*, *Mobil*, *Standard Oil* and *Texaco*. Differences are mainly of a technological nature, particularly in the use of the catalyst: multitube reactor with downflow stream or catalyst bed expanded by an upflow stream, presence or absence of a finishing reactor, indispensable if the feed contains basic compounds.

To provide an illustration, the flow sheet of the IFP process shown in Fig. 3.12 comprises two possible variants. The simpler corresponds to the direct use of the etherified solution in the gasoline pool, without separating the excess methanol contained. Operations are conducted with two reactors in series: the first with an upflow stream and expanded bed with recycle of part of the previously cooled effluent for better control of the temperature rise, and the second with a downflow stream and a fixed bed. The more complex involves the recovery of excess methanol, first by azeotropic distillation in a depentanizer with part of the unconverted hydrocarbons, and then by water washing of this raffinate. The hydrocarbon phase is added to the bottom of the depentanizer. The water/methanol mixture is distilled to recover and recycle the alcohol to the etherification stage.

3.2.3 Economic data

Table 3.18 gives some economic data on the treatment of steam-cracked C₅ cuts to extract isoprene or for etherification.

Chapter 4

THE TREATMENT OF AROMATIC GASOLINES

A vast range of techniques are available for the treatment of reforming and pyrolysis gasolines, designed to isolate the aromatic hydrocarbons needed by the chemical industry. Since these operations produce the different constituents in proportions that do not match demand, supplementary conversions (of compounds whose petrochemical uses are limited to those of greater necessity) avoid the problematic upgradings of surpluses, ensure a better adjustment of production to requirements, and hence improve overall productivity.

4.1 MAIN PROCESSING SCHEMES

A conventional direct scheme (Fig. 4.1) displays the following sequence of operations:

- (a) Catalytic reforming or steam cracking to produce an aromatic gasoline.
- (b) Preliminary treatment of this cut: fractionation and/or selective hydrogenations (essentially pyrolysis gasoline).
- (c) Solvent extraction to eliminate non-aromatics.
- (d) Distillation to produce pure benzene and toluene, and, in the case of reformates, used alone or blended with a pyrolysis gasoline, the following additional treatment:
 - . Distillation of aromatic C₈ to yield, by superfractionation, ethylbenzene and o-xylene, after passage through a separation column in a light cut and a heavy cut ("splitter").
 - . Production of p-xylene at low temperature, with a mother liquor by-product rich in m-xylene.

Chronologically, the effort was initially directed towards a better petrochemical upgrading of toluene and m-xylene, which continue to be used as solvents and in the gasoline pool. Toluene is thus converted to benzene by hydrodealkylation. Through isomerization, m-xylene yields the ortho and para isomers in proportions corresponding to thermodynamic equilibrium in the reaction conditions, namely a mixture of C₈ from which the

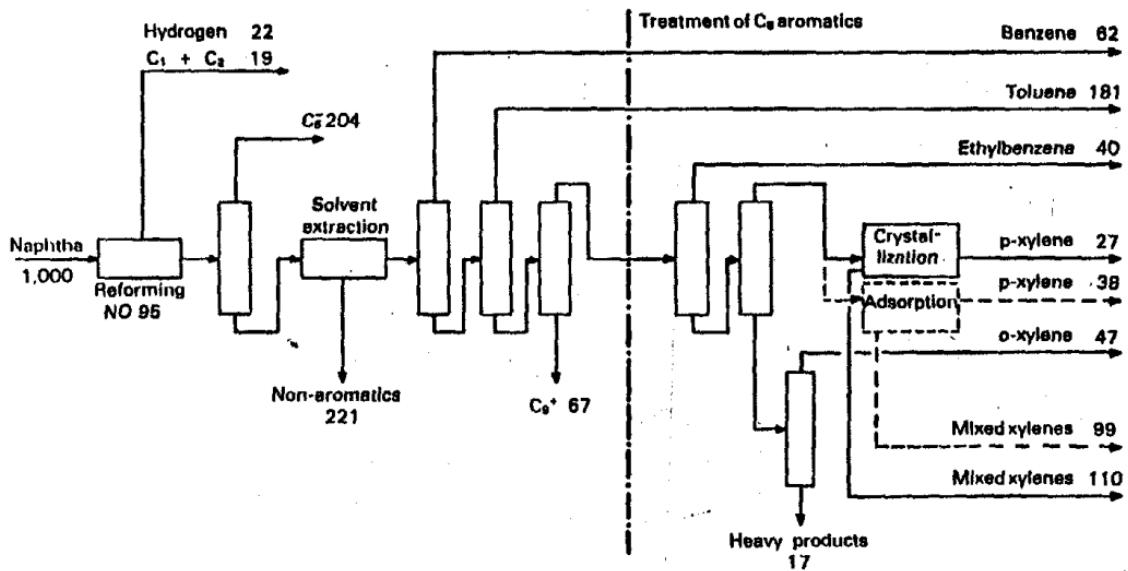


Fig. 4.1. Basic scheme (without aromatic loop).

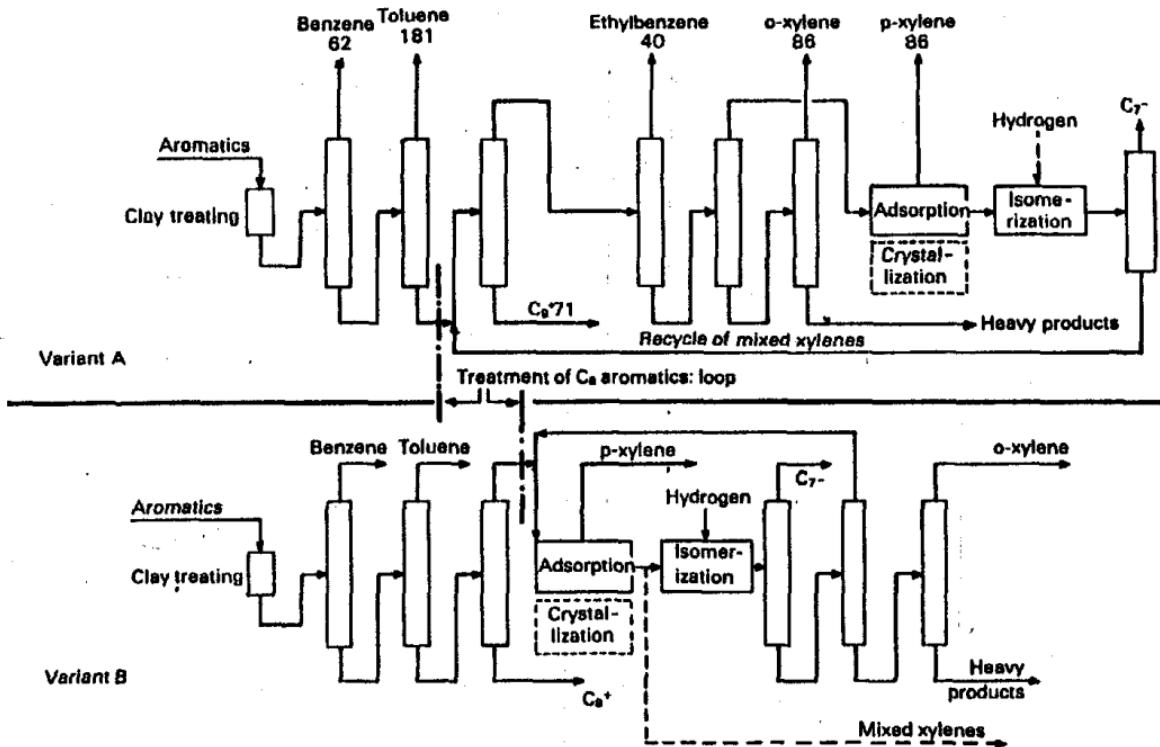


Fig. 4.2. Basic scheme (with aromatic loop).

desired products must again be separated. This serves to create a genuine "aromatic loop" which ultimately helps to exhaust all the *m*-xylene or, if applicable, to draw off C₈ compounds in a mixture for predetermined uses.

The basic scheme usually includes this loop (Fig. 4.2). Improvements were subsequently introduced either to increase the overall yield, to improve the economics, or to satisfy demand better. In particular, these techniques involved for the production or separation of aromatics are the following:

- (a) Aromizing or, more generally, regenerative reforming, with better yields, cyclization of paraffins and olefins and the possibility of separating and purifying the aromatics more easily.
- (b) Separation of *p*-xylene by sieve adsorption, which serves to raise the recovery rate considerably.
- (c) Preferential extraction of *m*-xylene, which leads to the easier recovery of *o*-xylene and *p*-xylene.

They sometimes provide access to certain processes which are known, but are simpler and hitherto difficult to apply, like extractive distillation instead of solvent extraction.

With respect to the mutual conversion of aromatics, improvements and new developments chiefly concerned:

- (a) Isomerization with a better upgrading of ethylbenzene, if it is not previously removed.
- (b) Dismutation and transalkylation which, starting with toluene and C₉-, serve to produce benzene and xylenes.

Market requirements encourage the combination of processes to treat aromatic gasolines in different ways, in order to obtain the minimum of non-upgraded by-products in satisfactory economic conditions. This results in many schemes which derive mostly from conventional cases, and using which it is possible, for example, to produce the maximum of aromatics in a mixture or individually (benzene, *o*-xylene, *p*-xylene) or to convert the toluene completely.

4.2 PHYSICAL METHODS FOR SEPARATING AROMATICS

Many techniques are available for extracting aromatic compounds at a high degree of purity from the gasolines produced by steam cracking or catalytic reforming. These treatments are mainly based on physicochemical processes and, at the economic level, are sometimes more specific to certain types of feedstock or certain operating conditions, although, in principle, they are suitable for the treatment of all types of aromatic gasoline. These techniques are distillation, crystallization, adsorption, azeotropic distillation, extractive distillation and solvent extraction.

4.2.1 Distillation

In recent years, simple fractionation has enjoyed very limited use and, in fact, has been used only for separating ethylbenzene and *o*-xylene (see Section 4.3.2). Even this is a case of superfractionation. This is because, owing to the small differences in boiling points, this treatment is unable to separate the different aromatics from the impurities which accompany them, in an economic manner and with the requisite purity. Hence it has been used mainly as preliminary or complementary to the other techniques.

The commercialization of certain processes for the production of aromatics, such as aromizing, serves to broaden the field of application of simple distillation, to the production of toluene and C₈ compounds to the required specifications. Thus, fractionation normally consists in treating an aromatic stream in three successive columns, separating the C₆, C₇ and C₈ distillates with high contents of benzene (mp = 5.55°C, bp_{1.013} = 80.1°C, d₄²⁰ = 0.879⁽¹⁾), toluene (bp_{1.013} = 110.6°C, d₄²⁰ = 0.867⁽¹⁾) and xylenes (see Table 4.7), and C₉₊ compounds as heavy ends. With equivalent distilled tonnages, the share of impurities with comparable boiling points that remain with these hydrocarbons has a very slight influence on the economic data (Table 4.1). Indeed it is only in complementary, preliminary or subsequent treatments that attempts are made to remove them.

TABLE 4.1
BTX SEPARATION. ECONOMIC DATA
(France conditions, mid-1986)

Distillation column	Benzene	Toluene	C ₈ aromatics
Capacity (t/year) (distillates)	100,000	100,000	200,000
Battery limits investments (10 ⁶ US\$)	1.1	0.9	1.6
Consumption per ton of distillate			
Utilities			
Steam (t)	0.6	0.75	1.2
Electricity (kWh) ⁽¹⁾	5	5	6
Labor (Operators per shift)	included with other units		

(1) Use of air-coolers.

4.2.2 Crystallization

This method applies to only two aromatics, benzene (mp = 5.55°C) and *p*-xylene (mp = 13.5°C). Crystallization is of undeniable economic value for the treatment of high benzene cuts (coal benzols and pyrolysis C₆ cut). However, this process, developed by Newton Chambers, has hitherto been used only for coal benzols.

(1) Specific gravity, 68.0 39.2.

The benzene crystals obtained by cooling are washed by the liquid resulting from their subsequent partial fusion, and are thus purified of the impurities which wet them. The composition of the non-aromatic compounds present in the feedstock determines the shape of the crystallization curve (eutectic temperature and composition) and, accordingly, the operating conditions.

On the other hand, crystallization was for many years the only method applied industrially to produce *p*-xylene economically at the required degree of commercial purity (see Section 4.3.3.1). This process now has a strong rival in adsorption, which achieves higher recovery.

4.2.3 Adsorption

Aromatics can be separated from non-aromatics preferentially by adsorption on certain solids. This type of process gives rise to cyclic operations which, schematically speaking, comprise a preliminary adsorption of the aromatics, followed by their desorption (by an eluant, heat or both). The eluant is then separated from the effluents by distillation, for example.

This technique, of the Arosorb type (*Sun Oil*), is uneconomic for the treatment of complex cuts from which the paraffins and naphthenes are to be eliminated. Hence it has not been generalized. However, to obtain special gasolines with very low aromatics contents, similar processes are sometimes employed. The main value of adsorption emerged through the possibility it offers of separating *p*-xylene from its isomers in aromatic C₈ cuts, with high yields (see Section 4.3.3.2).

Although not yet industrialized, the recovery of ethylbenzene contained in these cuts by selective adsorption is also planned, particularly by *Exxon* and *UOP* (*Universal Oil Products*). In Exxon's process, the desired hydrocarbon is preferentially adsorbed, while UOP's Ebex process is similar in principle to the Sorbex type of technique, in which the ethylbenzene remains in the raffinate. *Asahi* also has developments under way in this area.

4.2.4 Azeotropic distillation

Simple distillation cannot separate aromatics from non-aromatic, because the relative volatilities are very low, and many azeotropes are formed. Azeotropic distillation is based on the formation of an azeotrope between the non-aromatic hydrocarbons and a low boiling polar solvent. It is selected among the first terms of the series of alcohols, ketones, aldehydes and nitriles, and is employed pure or mixed with water. If the solvent forms a hetero-azeotrope, its recovery is accordingly facilitated. The yield is not limited in principle. The impurity content of the feedstock and the composition of the azeotrope determine the amount of solvent required. Cuts rich in aromatics can be treated in this way fairly economically. However, any variation in the type of impurity to be removed, and consequently in the composition of the azeotrope, may lead to less perfect purification. Furthermore, this method can be applied only to a narrow cut which contains

only one majority aromatic. Hence it requires an independent installation for each of them, possibly employing different solvents. In practice, it is used only to produce benzene and toluene.

4.2.5 Extractive distillation

The extractant used in this type of distillation displays very different characteristics from the solvent that can be employed in azeotropic distillation:

- (a) Its boiling point is higher than those of the feedstock components.
- (b) Its role is to retain the aromatics, and allow the non-aromatics to remain in the distillate.

Furthermore, in this operation, as opposed to solvent extraction, it must be non-polar to prevent the formation of two liquid phases, even if the impurity content is high. It is normally used in relatively large quantities, with feedstocks with high aromatics contents. It is regenerated by reboiling and recycled.

This method, like the previous one, applies only to the production of a single compound in a high degree of purity. Hence it implies that the feeds available are narrow cuts containing little or no competing aromatics, and that, if they are produced by the direct fractionation of a pyrolysis gasoline, they will have undergone prior selective hydrogenation. However, liquid/liquid extraction techniques for treating wide cuts exploit the fact that the solvents used are also good extractive distillation agents, to combine both separation methods (see Section 4.2.6).

The main extractants employed industrially were initially aniline, furfural, nitrobenzene, phenol (*Shell*), and more recently in extractive distillation alone or combined with extraction, sulfolane (*Shell*), N-methylpyrrolidone (*Lurgi*), N-formylmorpholine (*Koppers*, *SNAM*: *Societa Nazionale Metanodotti*), tetraethyleneglycol (*Union Carbide*), dimethylformamide (*IFP*) and dimethylacetamide (*Toray*: *Toyo Rayon*), of which certain physical properties and various characteristics of the processes employing them are given in Table 4.2. The extractive distillation flow sheet is substantially the same from one technique to another, with a few variants, like the possibility of treating feedstocks containing impurities without previous distillation, or the practice of secondary recovery of the solvent carried off in the raffinate.

- Thus, the Lurgi Distapex process (Fig. 4.3) can only be implemented directly to produce benzene and xylenes from narrow C₆ and C₈ cuts whose aromatics content is at least 70 per cent weight, or even better, 80 to 90 per cent. As a rule, the solvent is introduced a few trays below the top of the extractive distillation column, making it possible to achieve a benzene yield of 93 to 95 per cent, without significant stripping of extractant in the raffinate. If recovery is to reach 98 to 99 per cent, N-methylpyrrolidone is introduced at the top tray, but this entails the need to distill the raffinate to recover the entrained solvent and recycle it. Water scrubbing is preferably carried out in the case of xylenes.
- SNAM Progetti's Formex process and Koppers's Morphylane process can operate directly on feedstocks with non-aromatics contents up to 25 to 30 per cent weight.

TABLE 4.2
EXTRACTIVE DISTILLATION, PROCESSES, SOLVENT PROPERTIES AND PERFORMANCES

Company	Process	Solvent		Physical properties						Solvent ratio ⁽³⁾	Yield (%)	
		Name	Formula	mp (°C)	bp _{1,013} (°C)	d ₄ ¹⁰	t (°C)	μ (mPa.s.)	t (°C) ⁽²⁾		B	X
Lurgi	Distapex	N-methylpyrrolidone	$\begin{array}{c} \text{H}_2\text{C}—\text{CH}_3 \\ \\ \text{H}_2\text{C} \quad \text{N} \quad \text{CO} \\ \quad \backslash \\ \text{CH}_3 \end{array}$	-24.4	202	1.027 1.005	25 50	1.65 1.30	25 30	4 to 5	95 to 98	96
Koppers	Morphylane	N-formylmorpholine + 0 to 3% Wt of water	$\begin{array}{c} \text{H}_2\text{C}—\text{CH}_3 \\ \\ \text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\ \quad \backslash \\ \text{H} \quad \text{C=O} \end{array}$	20	244	1.150	15	8.13 2.45	20 70	4.5 to 6	95 to 99.5	99
SNAM Progetti	Formex	Id.	Id.	Id.	Id.	Id.	Id.	Id.	Id.	4.5	99	—
Union Carbide	Tetra	Tetraethylene glycol	$\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_4-\text{H}$	-6.2	328	1.130	20	60 1.8	20 150	5.5	99.9	99.2
IFP	—	Dimethylformamide	$\text{H}-\text{CO}-\text{N}\begin{pmatrix} \text{CH}_3 \\ \\ \text{CH}_3 \end{pmatrix}$	-61	153	0.945	25	0.80 0.38	25 100	3 to 5	95 to 99.5	—
Toray	Stex	Dimethylacetamide	$\text{CH}_3-\text{CO}-\text{N}\begin{pmatrix} \text{CH}_3 \\ \\ \text{CH}_3 \end{pmatrix}$	-20	161	0.945	15	0.92	25	—	—	87 ⁽⁴⁾

(1) Specific gravity t (°F)/39.2. (2) μ = viscosity mPa.s = CP. (3) By weight based on the feedstock. (4) Styrene.

Remark: Sulfolane is used only for extractive distillation combined with solvent extraction.

• IFP (*Institut Français du Pétrole*) has mainly attempted to obtain high purity benzene (50 to 200 ppm of impurities, crystallization point 5.52°C) from a C₆ cut derived from steam cracking or aromatizing. The process can handle feeds with an aromatics concentration ranging from 20 to 97 per cent, and prefractionation is only necessary below a content of 60 per cent. In addition to its solvent effect on benzene, dimethylformamide, like other conventional extractants, acts by forming azeotropes with the non-aromatics. For most of these compounds, the azeotropes can be broken by steam injection and others formed with water, making it possible to minimize solvent losses and avoid scrubbing the raffinate (50 ppm of dimethylformamide remaining in the raffinate for an injection of 7.3 per cent weight of steam based on the gas flow rate in the column). If the C₆ cut is produced by aromatizing, adsorption of the entrained solvent is more economic, and the desorption step uses the feed itself as eluent.

• Toray tried to recover the styrene present in pyrolysis gasolines, at a concentration level of 1 to 7 per cent weight, according to the severity of treatment and the type of feedstock, before the dedemetonization of these cuts. The closeness of the boiling points of o-xylene (144.4°C at 1 . 10⁶ Pa absolute) and styrene (145.2°C), as well as the latter's tendency to polymerize easily, prevent the use of simple distillation or superfractionation. Among the other alternatives, only extractive distillation in the presence of dimethylacetamide has led to industrial developments (Toray's Stex process). In principle, the flow sheet involves the preparation of a narrow cut, first by eliminating the light and heavy components of the pyrolysis gasoline by means of conventional distillations around 130 to 140°C, followed by selective hydrogenation at low temperature (40°C at 0.1 . 10⁶ Pa absolute) of the product, consisting of styrene (35 per cent weight), xylenes (42 per cent

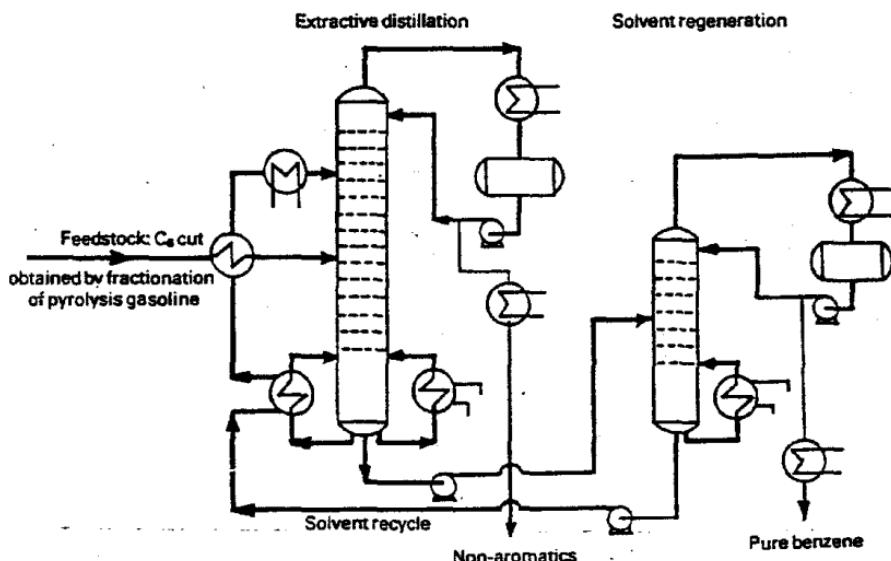


Fig. 4.3. Distapex process (Lurgi) with N-methylpyrrolidone.

weight) and ethylbenzene (9 per cent weight), in the presence of calcium carbonate containing 0.4 per cent weight of deactivated palladium, in order to saturate the dienic compounds and residual phenylacetylene without converting the styrene.

TABLE 4.3
EXTRACTIVE DISTILLATION. ECONOMIC DATA
(France conditions, mid-1986)

Process	IFP	Lurgi (Distapex)		Toray (Stex)	
Product		Benzene		Xylenes, Styrene	
Production capacity (t/year)	100,000	100,000	300,000	300,000	20,000
Product content in feedstock (%)	75 ⁽¹⁾	65 ⁽²⁾	90 ⁽³⁾	80 ⁽¹⁾	7
Battery limits investments (10^6 US\$)	1.6	2.6	3.0	3.5	13.0
Initial solvent load (10^6 US\$)	0.07	0.15	0.35	0.45	0.09
Yield (%)	99.5	97	98.5	96	88
Consumption per ton of product					
Feedstock (t)	1.340	1.585	1.130	1.300	1.010
Hydrogen (m ³)	—	—	—	—	8.0
Utilities					
Steam (t)	0.2	0.85	0.85	0.70	16.8
Electricity (kWh)	3.5	13.5	6.5	4.0	75
Cooling water (m ³)	3.5	8.5	—	21.5	680
Solvent (US\$)	0.15	0.07	0.15	0.15	0.17
Labor (Operators per shift)	1	1	1	1	1

(1) Prefractionation not required.

(2) Prefractionation required and included in investments.

The effluent thus obtained is introduced into the extractive distillation column operating between 80 and 130°C at $0.015 \cdot 10^6$ Pa absolute, in which the solvent enters at the top in a countercurrent stream. The mixture of dimethylacetamide and styrene, removed at the bottom, is separated by simple reboiling at about 120°C under partial vacuum. The solvent drawn off at the bottom is recycled after cooling. A fraction of this solvent must be purified in an evaporator to remove the polymers and heavy products formed, and to minimize solvent losses. The total yield of the operation is as high as 87 per cent weight.

Economic data on the techniques developed by IFP, Lurgi and Toray are given in Table 4.3.

4.2.6 Solvent extraction

Until very recently, solvent extraction was the only economic method available for producing a mixture of aromatics from wide cuts (C_6 to C_8). With the industrialization of processes designed to attain the degree of purity required for toluene and xylenes by simple distillation, extraction is liable to lose its value in view of the fact that extractive distillation suffices to treat the C_6 cut and to purify the benzene.

4.2.6.1 Operating principle

A. Properties of extraction solvents

Liquid/liquid extraction exploits the property of certain polar compounds to dissolve aromatics (which are themselves polarizable compounds) and to be relatively immiscible with paraffinic and naphthenic hydrocarbons.

The main properties of an industrial solvent are as follows:

- (a) High solvent capacity. This factor determines the amount of solvent to be employed and hence conditions the size of the unit.
- (b) High selectivity to obtain a very pure product.
- (c) The formation of a zone of immiscibility (range of concentrations in which two phases exist in equilibrium) with the feedstocks to be treated. Diagram a of Fig. 4.4 shows that this is not always the case. For an aromatics content in the feed higher than 70 per cent, for example, it is impossible to obtain two phases in equilibrium at 125°C, irrespective of the amount of diethyleneglycol (DEG) added. Moreover, to separate pure aromatics, this immiscibility zone must normally be bounded by a curve which intersects the axis of aromatics/solvent binary compositions (diagram b of Fig. 4.4, case of the DEG/water/benzene/n-heptane system at 125°C).
- (d) Density as different as possible from that of the feedstock and low viscosity. The production of the extractor increases with the difference in density between the phases, and decreases with rising viscosity. Diagram a of Fig. 4.4 shows that DEG could extract aromatics at 25°C, but, since its viscosity is too high, the operation must be conducted at 125°C.
- (e) Boiling point sufficiently different from that of the aromatics and good thermal stability. The solvent boiling point and throughput determine the amount of heat required for solvent regeneration. The optimum is generally 30 to 40°C above the boiling point of the aromatics to be recovered.
- (f) Low toxicity, without corrosive action, liquid in storage.
- (g) Low price.

Most of these properties can be examined in the effective conditions in which the solvent is used, particularly temperature, which affects the solvent power, selectivity, the immiscibility zone etc. (see diagram a of Fig. 4.4).

Since it is difficult to find an extractant which displays all these features, imperfections of the solvent have to be corrected. This can be done by adjusting the processing conditions, for example as follows:

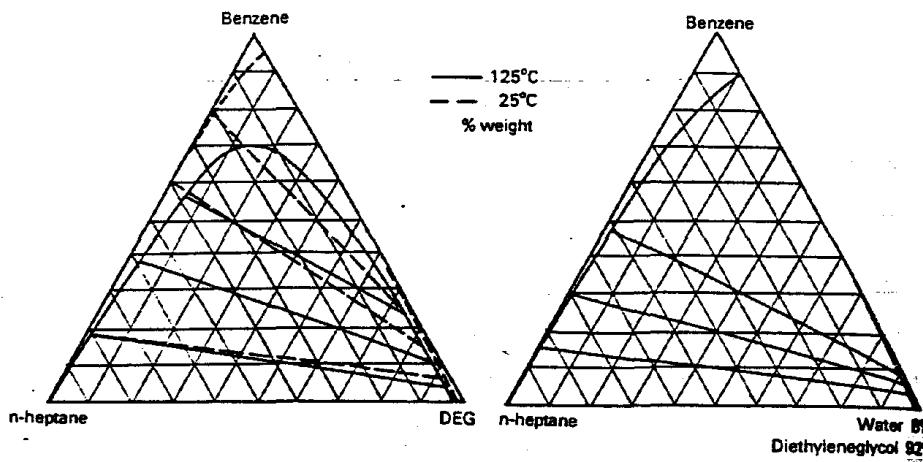


Fig. 4.4. Benzene/n-heptane/diethyleneglycol equilibrium diagrams.

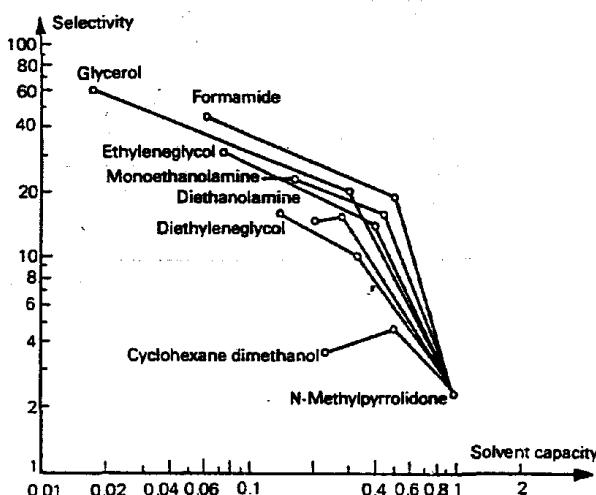


Fig. 4.5. Behavior of mixtures of solvents with N-methylpyrrolidone.

- (a) Recycling part of the extract, thus increasing the total aromatics content of the feedstock and hence the purity of the product, by salting out the paraffins (Udex process). However, it is difficult with this method to reach the commercial purity level currently required economically.
- (b) Backwash to reach the pure aromatics if the equilibrium diagram is not open. This operation consists in recycling an excess of paraffins to the extraction step, which are more volatile than those in the feedstock (dimethylsulfoxide, DMSO process), or the lightest of the feedstock provided that a distillation with extractive effect enables their separation and recycling (processes using sulfolane, N-methylpyrrolidone (NMP) etc.). Within the extract, they displace the small amounts of heavier paraffins dissolved, especially those whose boiling points are comparable to those of the aromatics. This produces a mixture that is easier to separate by distillation.

The solvents can also be mixed, which sometimes helps to alter the average properties of each taken individually. Water can also be added. Diagram b of Fig. 4.4 shows that the addition of 8 per cent water to diethyleneglycol helps to open the equilibrium diagram at 125°C.

Figure 4.5 also shows that, for a system involving a mixture of two solvents, benzene and *n*-heptane in the proportion of 70/20/10 by weight, in the same operating conditions, the low selectivity of N-methylpyrrolidone can be improved substantially at the cost of a slight decrease in solvent capacity, by the addition of formamide, ethyleneglycol, glycerol or monoethanolamine. Of these four compounds, ethyleneglycol is the most attractive, while formamide displays excessive thermal instability.

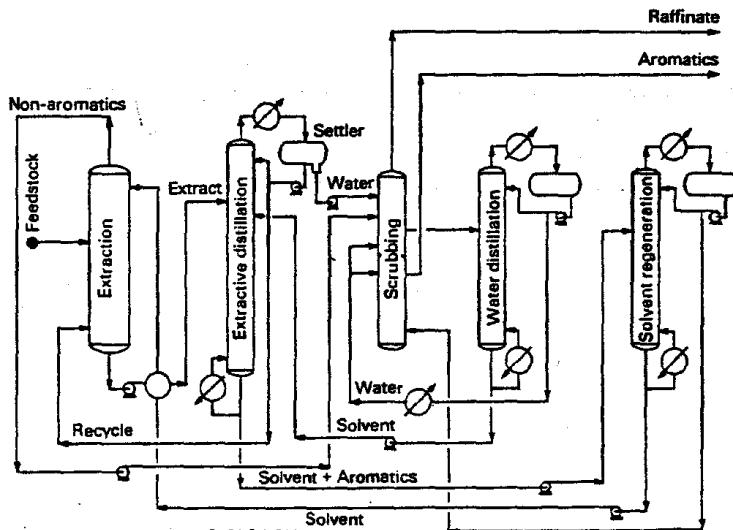


Fig. 4.6. Extraction of aromatics. Base scheme.

B. Liquid/liquid extraction procedure (Fig. 4.6)

The solvent, alone or in a mixture, with water added if necessary, is placed in countercurrent contact with the feed, and carries off the aromatics. The introduction of a reflux helps to remove nearly all the non-aromatics. The solvent is regenerated by distillation or reextraction. Distillation is normally carried out in two steps. The first exploits the extractive distillation property, thus increasing the purity of the aromatics, by using the paraffins leaving at the top (light paraffins and entrained benzene) as a backwash reflux. In the second, the solvent is separated by simple distillation and liberates the pure aromatics. The yield in the operating conditions selected is always very high (Table 4.4).

In some cases (DMSO), a second extraction is used instead of extractive distillation, employing a paraffinic solvent that is then regenerated by distillation, and which is also used as a backwash.

Solvent extraction is suitable for treating virtually all varieties of feedstock, including the richest in benzene, although it appears illogical to dissolve most of this aromatic cut to release only a small part. The presence of a significant amount of olefins (about 1 per cent) can be tolerated by certain solvents, such as N-methylpyrrolidone and dimethylsulfoxide.

4.2.6.2 Extraction processes

A. Earliest industrial applications

a. Edeleanu process

This process, developed since 1910, employs liquefied sulfur dioxide as solvent. First applied to dearomatize kerosenes and gas oils, the initial technique was modified to obtain pure aromatics. An examination of the equilibrium diagrams shows that, theoretically, it is impossible to obtain aromatics in a purity greater than 67 per cent at -17.2°C , than 73 per cent at -29°C , using sulfur dioxide as solvent. However, thanks to a kerosene backwash, very pure products can be obtained with good yields, up to 98 per cent for benzene and toluene, and 95 to 97 per cent for C₈ aromatics.

b. Udex (Universal Dow Extraction) process

The first economic version of aromatics extraction, available industrially, was the Udex process, developed by Dow and licensed by UOP since 1952. Due to competition from new techniques, it has been practically abandoned since 1965, or its facilities altered and their production capacities increased.

The solvent used is diethyleneglycol (mp = 7.8°C , bp_{1.013} = 246°C , $d_{20}^{20} = 1.12$ ⁽²⁾, viscosity at 20°C 35.7 mPa · s, and at 100°C 2.5 mPa · s) or a mixture of glycols (diethyleneglycol and dipropyleneglycol), to which a certain amount of water is added for viscosity considerations and to open the diagram (88 to 92 per cent diethyleneglycol and 8 to 12 per cent weight of water, for example). This means that the system displays relatively low solvent power.

The solvent ratio is 6 to 8 by volume, and the extraction temperature is between 140 and 150°C . The operating pressure is about $0.9 \cdot 10^6$ Pa absolute, and the reflux ratio

(2) Specific gravity, 68.0/68.0.

TABLE 4.4
EXTRACTION PROCESSES, SOLVENT PROPERTIES AND PERFORMANCE

Company	Process	Solvent		Physical properties							Solvent ratio ⁽¹⁾	Yield (%)			
		Name	Formula	mp (°C)	bp _{1,013} (°C)	d ₄ ⁽¹⁾	t (°C)	μ (mPa.s)	t (°C) ⁽²⁾	B		T	X	C ₉	
Shell UOP	-	Sulfolane 0 to 5% Wt of water		27.8	287	1.260 1.200	30 100	10.3 2.5	30 100	3 to 6	99 to 99.9	98 to 99.5	96 to 98	-	
ARCO	-	id.	id.	id.	id.	id.	id.	id.	id.	id.	id.	id.	id.	id.	
Lurgi	Arosolven	N-methylpyrrolidone + water or ethylene glycol (40% Wt)		-24.4	202	1.027 1.005	25 50	1.65 1.30	25 30	3.5 to 6	99.9	99.5	95	60	
Union Carbide	Tetra	Tetraethylene glycol	$\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_4-\text{H}$	-6.2	328	1.130	20	60 1.8	20 150		99 to 100	98, to 99	94 to 96.5	65 to 96	
Koppers	Aromex	N-formylmorpholine + 2 to 5% of water (Wt)		20	244	1.150	15	8.13 2.45	20 70	4.5 to 6	99.8	99	96	-	
SNAM Progetti	Formex	id.	id.	id.	id.	id.	id.	id.	id.	5 to 6.5	100	99	95 to 98	-	
Hawa Baker	Aromex	Diglycolamine + 7% Wt of water	$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$	-9.4	221	1.060	20	31.8 8.5	20 50	4.5 to 6	100	99	97	76	

(1) Specific gravity t (°F)/39.2. (2) By weight based on feedstock.

is 1 to 1.5 by volume. The extract obtained contains about 15 per cent aromatics. This extract is flashed and the light effluent used as a reflux for the extraction column. The liquid effluent is distilled. Yields are as high as 99 per cent for benzene, 97 to 98 per cent for toluene, 90 to 94 per cent for C₈ aromatics, and 75 per cent for C₉ aromatics.

B. Currently available techniques

a. Processes with solvent regeneration by distillation or reboiling

The main techniques of this type and various characteristics of the solvents they employ are summarized in Table 4.4. Barring a few variants, the flow sheets are similar, and comprise the following steps:

- (a) Liquid/liquid extraction of aromatics in countercurrent flow between the feedstock and solvent, at a temperature ranging from 40 to 150°C depending on the solvent employed. The desired purity is obtained by recycling light paraffins containing a certain fraction of stripped benzene to the bottom of the reactor.
- (b) Aromatics enrichment of the extract by reboiling or extractive distillation, at a maximum temperature of about 150 to 200°C, with overhead production of light paraffins recycled to the extractor.
- (c) Solvent regeneration by distillation or reboiling, and its recycle.
- (d) Water washing of the raffinate and aromatics produced, and distillation of the aqueous solutions obtained to recover the stripped solvent in these effluents.

The equipment used for extraction itself may be of very different design:

- (a) The Shell process employs an extractor in which contact between the hydrocarbon phase and the solvent is achieved satisfactorily by agitation using systems with a central rotating shaft. In addition, a number of baffles opposes the continuous flow of one phase and the other. This type of extractor is familiar by the designation of RDC (Rotating Disk Contactor). The maximum diameter compatible with effective operation of the unit is about 3 m. For aromatics, extraction takes place between 50 and 100°C depending on the type of feed, and at a pressure of 0.3 to 0.4 . 10⁶ Pa absolute.
- (b) The Lurgi Arosolvan process uses a series of decanters (30) stacked on each other in a column (Fig. 4.7). Each component features the following:
 - A decantation zone fitted with stainless steel baffles. Starting with the effluent issuing from the upper stage, it separates a heavy phase and a light phase entraining part of the heavy phase, which rises to the upper level.
 - A baffle which separates the light and heavy phases arriving from the lower stage.
 - A mixing zone in which three streams are mixed: the light phase separated on the baffle of the element situated two stages below, the heavy phase decanted in the baffle zone, and the heavy phase separated on the baffle of the element concerned.

A pump sends this mixture to the next stage below in the decantation zone. The unit has one pump for each level. It is known by the designation of Mehner extractor and offers many advantages, including its ability to be used at very high capacity (up to 8 to 10 m in diameter).

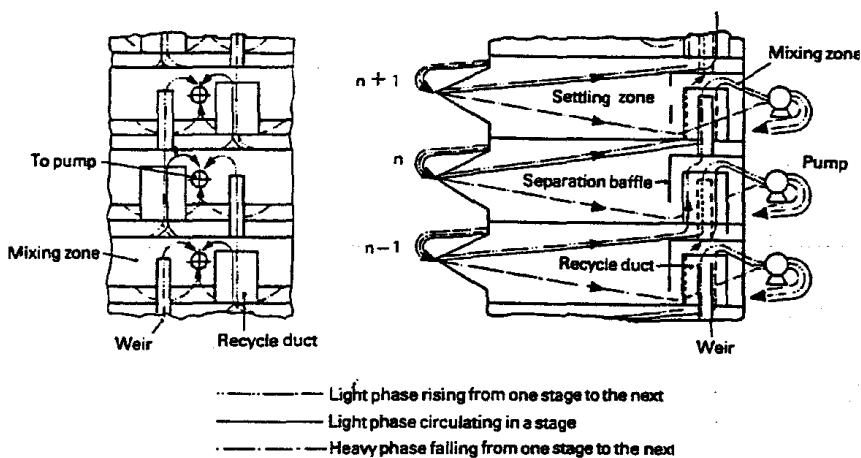


Fig. 4.7. Extraction of aromatics. Lurgi process.

For the extraction of aromatics, it operates at 60°C at a pressure close to atmospheric, with a backwash molar ratio of 0.2, based on the feed.

b. Extraction processes with solvent regeneration by reextraction

Two industrial processes of this type are currently available, developed by the following companies:

- IFP*, which presents a new version of its technique, and which employs dimethylsulfoxide (DMSO) as a BTX extraction solvent: $\text{CH}_3-\text{SO}-\text{CH}_3$. Its properties are the following: $\text{mp} = 18.4^\circ\text{C}$; $\text{bp}_{1.013} = 189^\circ\text{C}$; $d_4^{20} = 1.10^{(3)}$; $\mu(\text{mPa . s})$ at $25^\circ\text{C} = 1.99$; water in proportions up to 9 per cent.
- SNAM Progetti* which, in its Formex process adapted to the extraction of the heavier aromatics (xylenes and C_{9+}), employs N-formylmorpholine, also with water added.

The IFP process (Fig. 4.8) operates according to the following principle. The feedstock is treated in countercurrent flow with DMSO, pure or containing small amounts of water as an antisolvent, at a temperature of about 40°C (solvent to feedstock ratio: 4 by weight). Together with the aromatic, the solvent dissolves a small amount of undesirable hydrocarbons. These compounds are displaced by a backwash reflux (ratio ≥ 0.15 weight based on the feedstock), generally consisting of a paraffin, which is then easily separated by distillation. The fraction selected may be lighter (butane, ratio ≥ 0.35 weight based on the feedstock) or heavier (kerosene) than the products to be extracted. This

(3) Specific gravity, 68.0/39.2

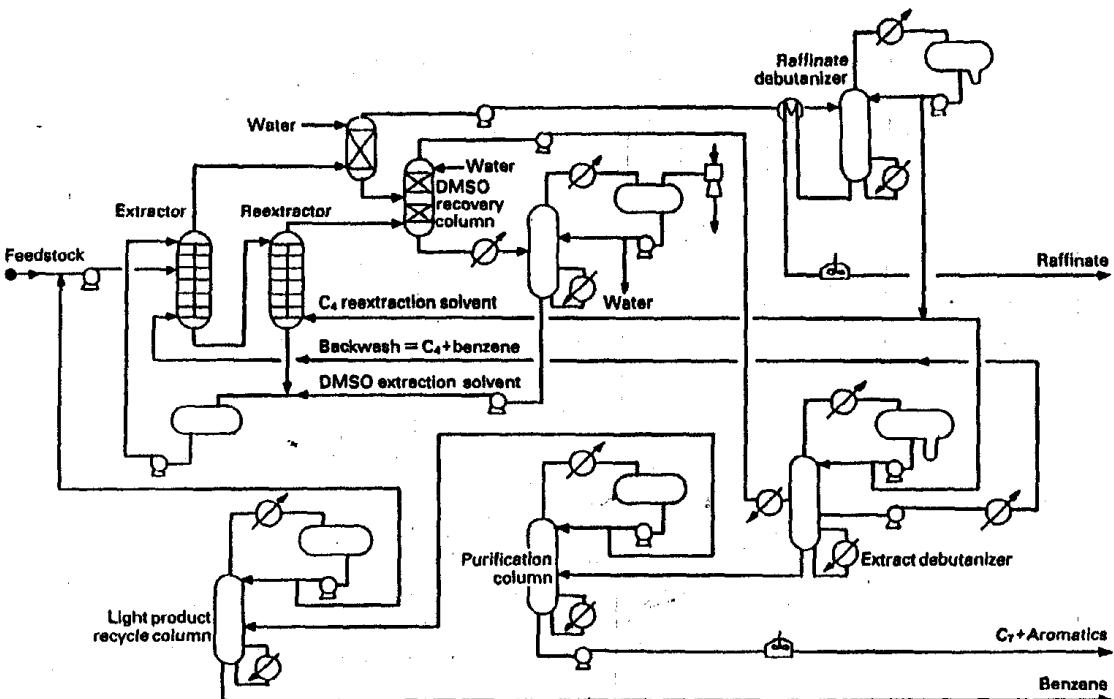


Fig. 4.8. Extraction of aromatics. IFP process.

reflux is sent to the bottom of the extractor. It may contain other light paraffins and some aromatics, depending on its source. The quantity of solvent and the water content, as well as the backwash ratio, depend on the feedstock composition, the yields and the purity required.

The solvent is regenerated in a second column, where the aromatics are reextracted by a paraffinic hydrocarbon, preferably the same as the reflux compound, namely butane, usually at a temperature of about 50°C and under sufficient pressure to ensure that the butane does not pass into the vapor phase. The aromatics are then recovered by simple fractionation of the paraffinic extract. While the reextraction solvent is directly recycled, they undergo prior distillation before their final separation, and the distillate, essentially consisting of paraffins and benzene, is returned with the feedstock to the initial extraction stage. Small fractions of DMSO (1 per cent of throughput) dissolved in the hydrocarbon phases are recovered by water washing, and concentrated under vacuum.

Table 4.5 provides one example of the results obtained by the DMSO process on a hydrogenated pyrolysis gasoline.

The Formex process, adapted to the treatment of heavier aromatic cuts, also operates with butane as a reextractive agent and a recovery rate as high as 98 per cent for xylenes.

TABLE 4.5
PERFORMANCE OF THE IFF EXTRACTION PROCESS WITH DMSO
ON A HYDROGENATED PYROLYSIS GASOLINE

Components	Feedstock	Raffinate	Extract	Yield (% Wt)
Benzene	34.0	0.2	33.8	99.5
Toluene	19.0	0.2	18.8	99
Xylenes	17.0	0.8	16.2	95
Non-aromatics	30.0	30.0	—	—
Total	100	31.2	68.8	

Benzene purity	crystallization temperature 5.5°C.
Sulfur content	1 ppm.
Other aromatics	100 ppm.
Non-aromatics	1,000 ppm.

Remark. Various other processes have also given rise to developments. These include the ONIA/ERAP Carmex technique (ONIA: *Office National des Industries de l'Azote*. ERAP: *Entreprise de Recherches et d'Activités Pétrolières*) Leuna's Mofex technique and Marathon's Simex technique etc.

4.2.6.3 Economic data

Tables 4.6a and 4.6b list some economic data on the main solvent extraction methods currently industrialized.

TABLE 4.6a
AROMATICS EXTRACTION. ECONOMIC DATA
(France conditions mid-1986)
PRODUCTION CAPACITY 200,000 t/year OF AROMATICS EXTRACTED

Company	UOP/Dow	Shell/UOP	Lurgi	IFP
Process	Udex	Sulfolane ⁽¹⁾	Arosolvan ⁽¹⁾	DMSO ⁽¹⁾
Battery limits investments (10 ⁶ US \$) ⁽²⁾	11.4	8.8	8.4	9.1
Initial solvent loads and miscellaneous (10 ⁶ US\$)	0.7	0.45	0.44	0.56
Consumption per ton of aromatics extracted				
Raw materials				
Feedstock (t)	2.00	1.65	1.45	1.45
By-products				
Raffinate (t)	1.00	0.65	0.45	0.45
Utilities				
Steam (t)	1.5	0.8	0.9	1.0
Electricity (kWh)	30	11	18	8
Cooling water (m ³)	40	35	3	17
Solvents and chemicals (US\$)	0.9	0.5	0.15	0.2
Labor (Operators per shift)	2	2	2	2

(1) New versions.

(2) Investments do not include BTX fractionation (see Table 4.1).

TABLE 4.6b
COMPOSITION OF FEEDSTOCK (a) AND RECOVERY RATE (b) (% Wt)

Process	Udex		Sulfolane		Arosolvan		DMSO	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Benzene	7.5	99+	6.5	99.8	34.0	99.8	34.0	99.5
Toluene	21.2	98	23.7	99.0	19.0	99.0	19.0	99.0
C ₈ aromatics	20.0	94	33.5	95.0	17.0	96.0	17.0	95.0
C ₉ - aromatics	0.9	75	0.1	60.0	0.2	70.0	0.2	—
Non-aromatics	50.4		36.2		29.8		29.8	
Total	100.0		100.0		100.0		100.0	

4.3 TREATMENT OF THE AROMATIC C₈ CUT

Catalytic reforming or aromizing and the separation techniques associated with them (solvent extraction, extractive distillation and conventional distillation) produce pure benzene and toluene, together with an aromatic C₈ cut containing, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, and also a C₉₊ cut.

4.3.1 Characteristics of the aromatic C₈ cut

The separation and purification of the different components of this cut raise a number of problems that are clearly identified by an examination of the physical properties of these compounds (Table 4.7).

It is obviously impossible to separate *m*-xylene and *p*-xylene by distillation, since their boiling points differ by only 0.8°C. However, this separation method is feasible to isolate *o*-xylene and ethylbenzene, although superfractionations are required. Furthermore, the melting point of *p*-xylene is much higher than that of the other C₈ compounds. This is why crystallization was initially employed to recover *p*-xylene from the mixture, which may be previously rid of ethylbenzene and *o*-xylene.

TABLE 4.7
PHYSICAL PROPERTIES OF C₈ AROMATICS

Isomer	Normal boiling point (°C)	Melting point (°)	<i>d</i> ₄ ²⁰⁽¹⁾
Ethylbenzene	136.2	-95	0.8670
<i>p</i> -xylene	138.3	+13.3	0.8611
<i>m</i> -xylene	139.1	-47.9	0.8642
<i>o</i> -xylene	144.4	-25.2	0.8802

(1) Specific gravity, 68.0/39.2.

4.3.2 Separation of ethylbenzene and *o*-xylene

4.3.2.1 Production of ethylbenzene by superfractionation

This technique was employed industrially for the first time by Cosden in 1957. Many variants have since been commercialized.

A. Principle

The low relative volatility of the ethylbenzene/xylenes system requires superfractionation of the aromatic C₈ cut, in other words operation with a large number of trays and a high reflux ratio.

The ethylbenzene recovery rate is usually over 95 per cent, and its purity greater than 99.8 per cent. The quality of the product obtained conditions that of its derivative, the styrene monomer, and its aptitude for polymerization. This depends on the presence of toluene or other aromatics in the feed, whose content must generally not exceed 0.3 per cent. This fractionation can only be calculated conveniently on a computer. The theoretical number of trays is as high as 330 for 95 per cent recovery. Since the efficiency of these trays approaches 85 per cent, about 390 real trays must be used with reflux ratios up to 80 to 90.

B. Industrial practice

The differences between these processes are essentially technological. In Cosden's initial version, a series of three 62 m columns is used, with a diameter of 4.6 m for a production capacity of 22,700 t/year.

The two latest variants are the following:

- (a) *Fluor*, with only two columns 87 m high, for a total number of real trays of 340 and a diameter of 6.1 m for a production capacity of 45,400 t/year.
- (b) *Union Carbide*, which claims to obtain ethylbenzene in a purity of 99.8 per cent with a recovery of 95.4 per cent from a feedstock containing 36.4 per cent ethylbenzene. The reflux ratio is 55, and the number of real trays is 410. The technological improvement is associated with the configuration of trays (perforated trays) with a spacing as small as 0.28 m. This requires two columns 60 m high and 6.2 m in diameter for an output of 72,000 t/year. The operating conditions at the top and bottom are as follows: temperature 163 and 204 °C, pressure ≈ 0.2 and $\approx 0.4 \cdot 10^6$ Pa absolute. The feedstock enters at tray 100 (Fig. 4.9).

Remark. Superfractionation is a costly operation. Hence, by analogy with the developments already achieved in the purification of paraffins, olefins and *p*-xylene, UOP offers a variant of the Sorbex technique to recover the ethylbenzene from a C₈ cut by adsorption on molecular sieves.

4.3.2.2 Production of *o*-xylene by distillation

The separation of *o*-xylene is easier than that of ethylbenzene. However, it is achieved by superfractionation of the C₈ cut in a column with 80 to 150 trays operating with reflux ratios of 7 to 15. These values depend on the recovery target, generally between 50 and 98 per cent, and the C₈ impurity content, which is in the range of 1 to 5 per cent.

Since *o*-xylene is obtained at the bottom, a second distillation is required to eliminate the C₉-aromatics which are also entrained, so as to obtain a product meeting commercial specifications. This is carried out in much less severe conditions: 40 to 60 trays, reflux ratio 1 to 2, depending on the content of heavy compounds (1 to 3 per cent) and the purity required in terms of these compounds (99 to 99.9 per cent).

4.3.2.3 Economic data

The construction of very large capacity units (300,000 t/year) for the alkylation of benzene by ethylene poses a serious competitor for the superfractionation of the ethyl-

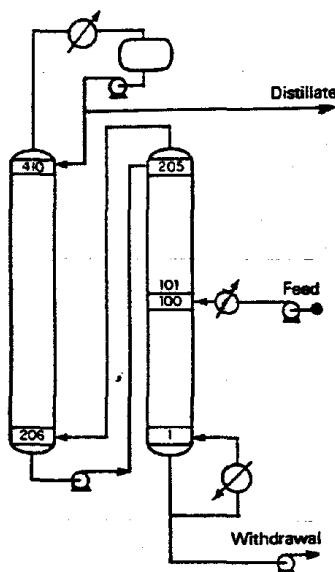


Fig. 4.9. Ethylbenzene separation by distillation. Union Carbide process.

TABLE 4.8
PRODUCTION OF ETHYLBENZENE AND o-XYLENE. ECONOMIC DATA
(France conditions, mid-1986)

Product	Ethylbenzene	o-xylene	
		Splitter	Purification
Material balance (t/year)			
Feedstock	325,000	422,500	22,500
Light ends	50,000	400,000	20,000
Heavy ends	275,000	22,500	2,500
Battery limits investments (10^6 US\$)	18.5	4.4	1.4
Consumption per ton of distillate			
Utilities			
Electricity (kWh)	165	6	10
Fuel (10^6 kJ)	40	1.5	2
Cooling water (m^3)	15	.3	5
Labor (Operators per shift)	1		0.5

benzene contained in the reformates. This is why it is often preferable to avoid this separation if the installations include an isomerization process capable of upgrading this compound to xylenes. However, an economic capacity threshold can be determined, above which distillation becomes profitable, and which varies inversely with the cost of the raw material. This threshold is currently at about 30,000 t/year.

Table 4.8 gives some economic data on the separations of ethylbenzene and *o*-xylene.

4.3.3 *p*-xylene separation

Industrially, *p*-xylene is obtained by crystallization or adsorption.

4.3.3.1 Crystallization

Crystallization was for many years the only industrial technique employed to separate *p*-xylene from its isomers.

A. Principle

p-xylene can be obtained in a high degree of purity by crystallization from an aromatic C₈ cut. Besides *p*-xylene, this cut contains *o*-xylene and ethylbenzene which, depending on the arrangements and the different steps in the treatment, are present either in the state of impurities if these compounds have been previously separated, or in substantial amounts if not, or if their recovery is only partial.

The crystallization temperature depends on the composition of the mixture to be treated. The cooling diagram shows that a eutectic exists between *p*-xylene and each of the other components of the mixture. In the case of the *m*, *p*-xylene binary system, the eutectic (E) contains 13 per cent *p*-xylene and melts at -52°C (Fig. 4.10). It separates two liquidus curves: ME in equilibrium with solid *m*-xylene, PE in equilibrium with solid *p*-xylene. Provided that the initial mixture contains more than 13 per cent *p*-xylene, crystals of pure *p*-xylene are obtained by cooling to -52°C, and a mother liquor, whose composition is that of the eutectic. However, it can be noticed that the existence of the eutectic leads to limited recovery, and that this recovery requires heat exchanges at low temperature.

In practice, the presence of other aromatics significantly affects the solid/liquid diagram of the mixture, but, as a first approximation, only the shape of the ME liquidus is modified. Indeed, as shown by the solubility curves of the different isomers in the aromatic C₈ solution, considered to be ideal (Fig. 4.11), *p*-xylene is the compound that crystallizes first as the temperature is lowered.

As a rule, if the amount of *o*-xylene and ethylbenzene present in the feedstock rises, the temperature of formation of the *m*, *p*-xylenes eutectic decreases, as well as its *p*-xylene content. Recovery is accordingly improved.

Thus, the temperature and composition of the eutectic can be calculated rapidly for a given feedstock, by restricting oneself to the analysis of the *m*, *p*-xylene binary mixture. This can be done by referring to Figs. 4.11 and 4.12, and determining the required temperature from the initial *m*- and *p*-xylene concentrations, and then determining the

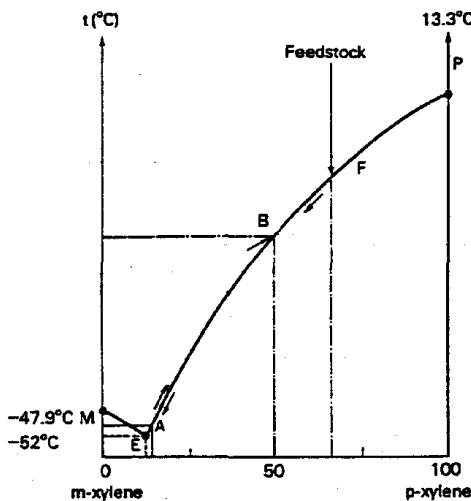


Fig. 4.10. *m*-xylene/*p*-xylene liquid/solid equilibrium.

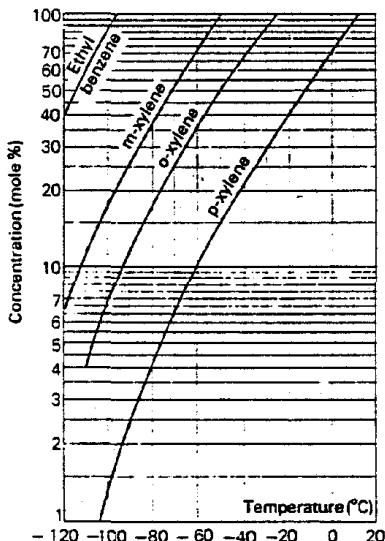
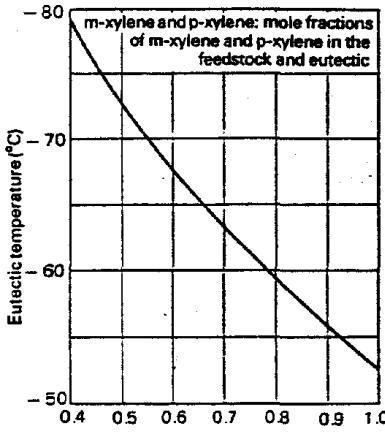


Fig. 4.11. Solubility temperature relationships of *C*₈ aromatics.



$$\left(\frac{\text{m-xylene}}{1.0-\text{p-xylene}} \right)_{\text{feedstock}} = \left(\frac{\text{m-xylene}}{1.0-\text{p-xylene}} \right)_{\text{eutectic}}$$

Fig. 4.12. Eutectic temperature according to feedstock composition (assumed to be reduced to *m*- and *p*-xylene only).

p-xylene recovery rate from the value obtained. As required, the results can be corrected to account for the formation of other binary or ternary eutectics.

B. Processes

As a rule (Fig. 4.10), techniques for crystallizing *p*-xylene consist in cooling the feedstock (F) to a temperature slightly higher than that of the eutectic (A). The crystals are separated by centrifugation or filtration. Theoretically pure, they are in fact wet by the mother liquor which is a solution rich in *m*-xylene. To purify this impure *p*-xylene, it is again melted and cooled to a temperature intermediate between those of the initial eutectic and the feed (B) (-20 to -30°C). The separated crystals are then wet by a solution rich in *p*-xylene, and their purity is about 99 per cent or more. To meet commercial specifications (minimum 99.5 per cent), auxiliary treatment is sometimes necessary. The mother liquor obtained in this second stage is recycled to the first crystallization step.

Various methods have been employed to improve the efficiency of the operation, particularly to facilitate the growth and separation of the crystals, and to make maximum use of refrigeration capacity. These methods differ in the following features:

- (a) Arrangement of the stages (drying, pretreatment, crystallizations and separations in series, supplementary purification, refrigeration cycles, recycles etc.).
- (b) The refrigerating method (flash of a liquefied gas in the medium to be crystallized, direct or indirect contacts, etc.).
- (c) The type, design and operating conditions of the equipment (absorber, crystallizers, heat exchangers, centrifuges, melters, etc.).
- (d) Heat recovery: recycle of the different fluids.

The first commercial facilities were built on techniques developed by *Oronite* (now *Chevron*) and *Humble-Oil*. Subsequently, the best known processes were those of *Chevron*, *Phillips*, which is no longer commercialized, *Amoco*, *Esso*, known by the designation of *Isofining*, and *Antar HRI* (*Hydrocarbon Research Inc.*). The latest have been proposed by *Krupp*, *Maruzen* and *ARCO* (*Atlantic Richfield Co.*).

Among the earliest techniques, some details can be provided on the *Phillips* process, whose originality resides in the use of a vertically pulsed crystallizer/purifier in the final phase (Fig. 4.13). In a first stage, the mixture of xylenes (containing 26 per cent *p*-xylene for example) is first rid of traces of water, cooled to -16°C, and introduced into a scraper-chiller, in which liquid ethane flows and in which crystallization takes place. The effluent exists at -53°C. The crystals and mother liquor are separated in a rotary filter, and the mother liquor serves to precool the feed. In a second stage, the solid fraction (containing about 65 to 68 per cent *p*-xylene) is again melted and crystallized at -18°C. After filtration, the new mother liquor is recycled to the first crystallization stage. In a final phase, supplementary purification is carried out in a pulsed column, in which the solid is washed in countercurrent flow by the melted product.

Among the latest processes are the schemes proposed by *ARCO*. In its standard version (Fig. 4.14), this process comprises the following stages:

- (a) Feedstock drying;
- (b) Precooling by direct contact with the mother liquor produced by subsequent

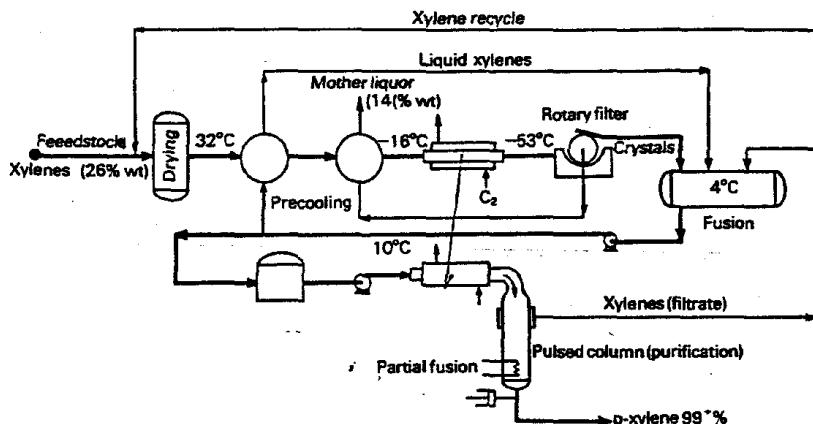


Fig. 4.13. Crystallization of *p*-xylene. Phillips process.

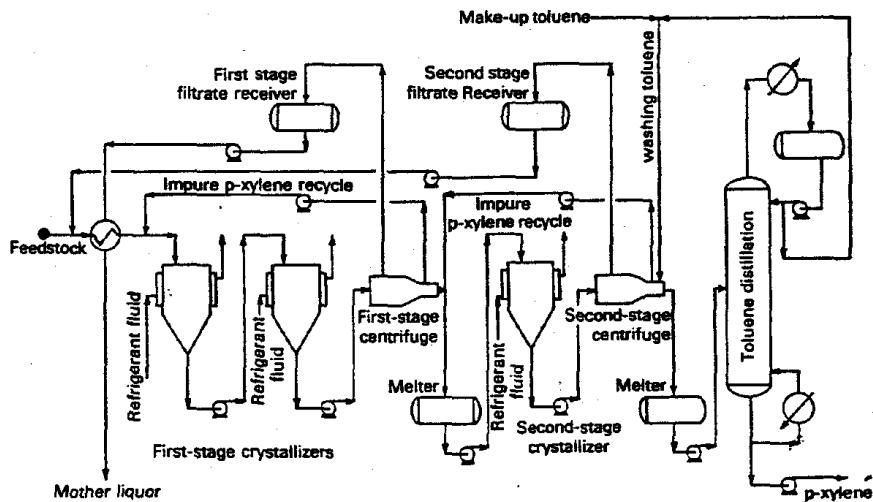


Fig. 4.14. Separation of *p*-xylene by crystallization. ARCO two-step process.

- separations, and passage into a series of two crystallizers operating at $-40/-50^{\circ}\text{C}$ and $-55/-70^{\circ}\text{C}$ respectively depending on the feedstock composition.
- Separation of *p*-xylene crystals by continuous centrifugation, in a purity of 85 to 90 per cent, from fines recycled to the feed and a mother liquor used for precooling.
 - Melting of impure *p*-xylene by steam, and recrystallization between -20 and 0°C in a single unit, by vaporization of liquid propane.
 - Final centrifugation yielding a mother liquor, fines and a cake washed by means of toluene to displace the wetting mother liquor.
 - Recovery by distillation of the toluene fixed on the solid and entrained with the fines before they are recycled.

This washing treatment is the original feature of the ARCO process. It allows better control of product purity (99 to 99.8 per cent) and, above all, helps to cut capital investment and operating costs by reducing the recirculation inventory stock by two-thirds.

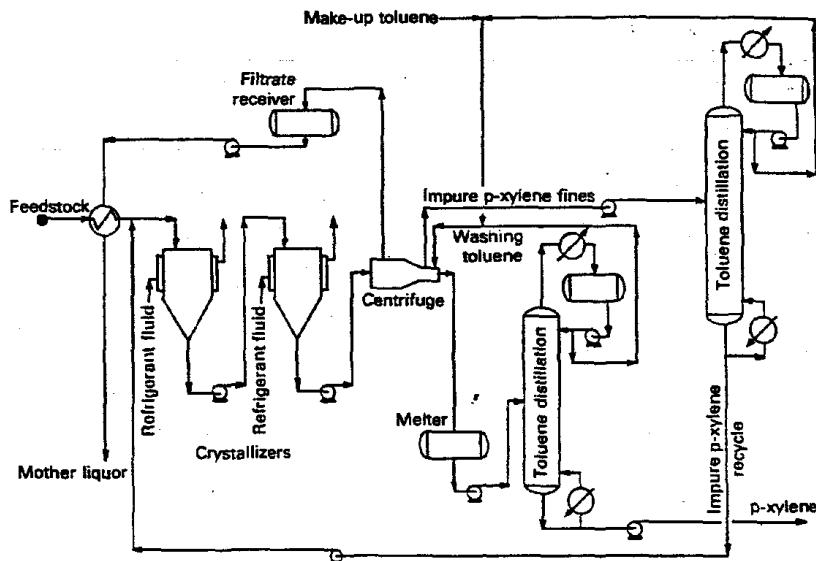


Fig. 4.15. Separation of *p*-xylene by crystallization. ARCO one-step process.

In its improved version (Fig. 4.15), this technique has only a single crystallization stage and one centrifugation stage, but requires optimization of the type of centrifuge employed and of the conditions of cake washing by toluene.

4.3.3.2 Selective solid adsorption

The separation of *p*-xylene by adsorption on molecular sieves is gradually supplanting crystallization. Among the various advantages this offers are much higher recovery ratios. Furthermore, combined with isomerization, it serves to reduce the treatment capacity by about 40 per cent for identical production of *p*-xylene.

A. Principle

As in chromatographic separation, the *p*-xylene contained in an aromatic C₈ cut must be retained preferentially on a solid and then recovered after displacement by an eluant. Type X or Y zeolites are preferably used to do this (0.9 ± 0.2 Na₂O, Al₂O₃, $w\text{SiO}_2$, $y\text{H}_2\text{O}$ with $3 < w < 9$ and $y < 8$) whose sodium ions have been substituted by metals, alone or in pairs, belonging to the alkali, earth alkali and rare earth groups etc., and especially by barium and potassium ions. The separation relies on the formation of association complexes in the presence of the substitution metals which, in pairs, display a certain synergy in their activity.

As a rule, the adsorbent is characterized by the following parameters:

- (a) Relative selectivities defined by equations such as:

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B}$$

where Y_A , Y_B and X_A , X_B are the contents of the products *A* and *B* in the adsorbed and fluid phases.

- (b) Adsorbent power: this increases to a certain degree with temperature, but mainly depends on the concentrations of the different compounds in the medium.
- (c) Pore volume.
- (d) Adsorption rate: this varies directly with the temperature and inversely with the dimensions of the sieve elements. As the latter decrease, however, the total pressure drop across the sieve bed rises.
- (e) Physical properties: bulk density, mechanical strength, distribution curve of solid particle dimensions, shape, thermal stability etc.
- (f) Chemical properties: structure, stability etc.

The *p*-xylene can be desorbed by raising the temperature or lowering the pressure, or by employing a desorbent. The latter may be an aromatic hydrocarbon with a boiling point lower than that of the feedstock, such as toluene, which is easily recovered by distillation, or, on the contrary, a heavier hydrocarbon, such as trimethylbenzenes, and diethyl and triethylbenzenes. In this case the advantage is to avoid the prior removal of non-aromatic compounds in the feedstock.

B. Processes

Two main industrial technologies using adsorption are currently available, marketed by UOP under the name of Parex, and Toray under the name of Aromax.

a. UOP Parex process

The process industrialized by *UOP* to recover *p*-xylene is one variant of the Sorbex technology for separating one component or a set of components from a mixture by selective adsorption on a solid. A pseudo-countercurrent is created in a system in continuous operation, between a liquid medium kept at a perfectly controlled temperature of about 120 to 175°C in the case of *p*-xylene, which flows downward in a column normally between 0.8 and 5.5 m in diameter, and the adsorbent distributed among several sections, generally twelve or more, to minimize pressure drops. It is normally preferable to mount two columns in series for greater operating continuity, by increasing the number of these stages.

Piping connections are positioned between each of the fixed sieve beds. As required, they allow fluid injection or effluent withdrawal, and, to do this, are equipped with multipurpose distributor systems, designated for uniform dispersion or collection over the entire cross-section of the column. The fictional upward displacement of the sieve is simulated by means of a rotary valve that causes a gradual change in the injection and withdrawal points.

In a simple scheme, this valve has sixteen outlets which bring each of the twelve zeolite stages in contact either with the fresh C₈ feed, or with the eluant, and with the steps in the treatment of the *p*-xylene rich extract and the raffinate containing the other aromatics. A recovery pump at the bottom of the column re-injects the fluid at the top, ensuring continuous liquid countercurrent flow. All these operations must be strictly controlled and programmed.

At a given moment, given the number of injections and withdrawals selected, it is possible to schematize the distribution curves of the different compounds adsorbed on the sieve, namely *p*-xylene (A), other C₈ (B) and desorbent (D), and to distinguish four zones along the height of the column. Using the example in Fig. 4.16, one can thus interpret the operation as follows:

- (a) Zone I or adsorption zone, bounded by the raffinate B + D withdrawal and feed A + B injection points. The solid on which D primarily and some B are adsorbed

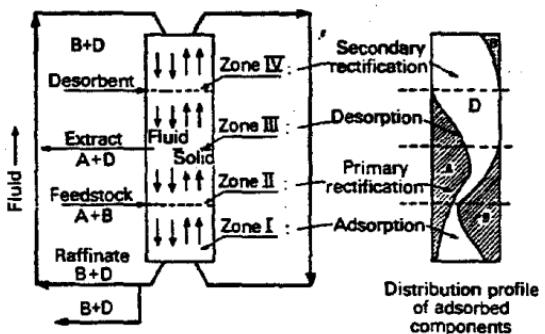
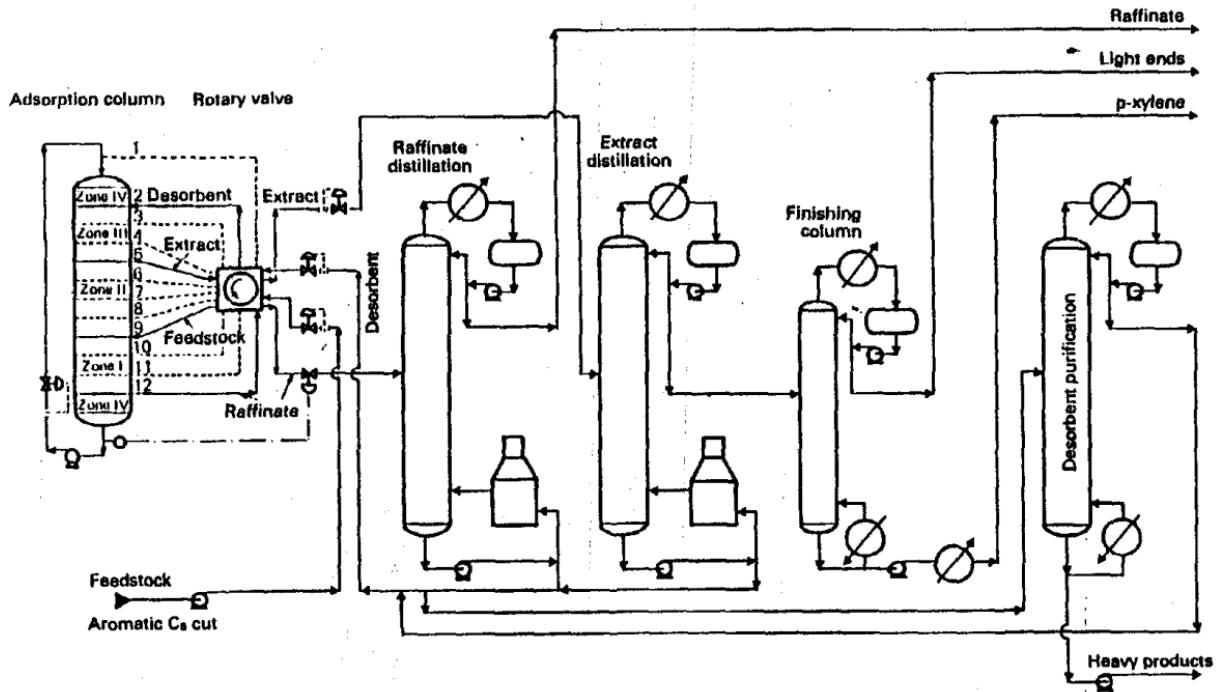


Fig. 4.16. Operating principle of UOP Parex process for the manufacture of *p*-xylene.

A. *p*-xylene; B. Other C₈; D. Desorbent.

Fig. 4.17. Separation of *p*-xylene by adsorption. UOP Parex process.

penetrates into this section. As it rises, the sieve is enriched in A, which chiefly replaces D. By correlation, as it descends, the fluid becomes depleted of A.

- (b) Zone II or primary rectification zone, bounded by the feed A + B injection and extract A + D withdrawal points. As it advances, the solid, which contains A, B and D, encounters a fluid that is increasingly rich in eluant. B is thus displaced until it disappears completely.
- (c) Zone III or desorption zone, bounded by the extract A + D withdrawal and desorbent D injection points. The sieve on which A and D are adsorbed encounters desorbent D which totally displaces A.
- (d) Zone IV or secondary rectification zone, bounded by the desorbent D injection point and the raffinate B + D withdrawal point at the bottom of the column, picked up by the circulation pump and sent to the top of the adsorber. The solid meets a mixture B + D that is increasingly rich in B, making D available to displace A.

The eluant contained in the extract and raffinate can be separated by distillation (Fig. 4.17).

The Parex process can handle feeds from different sources: C₈ cut from solvent extraction, mixture of C₈ aromatics from extraction and from isomerization in the

TABLE 4.9
PERFORMANCE OF THE PAREX PROCESS ACCORDING TO FEEDSTOCK

Source of feedstock	Solvent extract ⁽¹⁾	Solvent extract ⁽²⁾ and isomerate	Reformate
Feedstock composition (% Wt)			
Toluene	0.9	0.6	—
Ethylbenzene	18.9	13.7	18.4
<i>o</i> -xylene	0.9	15.8	15.9
<i>m</i> -xylene	55.2	43.5	39.7
<i>p</i> -xylene	25.0	18.4	17.4
Non-aromatics	—	8.0	8.6
Total	100.0	100.0	100.0
Parex extract composition (% Wt)			
Toluene	—	0.7	—
Ethylbenzene	0.2	—	0.4
<i>o</i> -xylene	—	—	0.1
<i>m</i> -xylene	0.4	—	0.3
<i>p</i> -xylene	99.4	99.3	99.2
Total	100.0	100.0	100.0
<i>p</i> -xylene recovery rate (%)	95.0	92.0	84.5
Residual <i>p</i> -xylene in the raffinate (% Wt)	1.9	1.8	4.2

(1) With total prior separation of *o*-xylene.

(2) With partial prior separation of *o*-xylene from isomerate.

presence of a precious metal catalyst, previously rid of diolefins and olefins by clay treating and of toluene by distillation, C₈ reformate cut rich in aromatics, previously fractionated to separate light and heavy products, also subjected to clay treating, mixture of C₈ cuts from reforming and isomerization.

A light desorbent (toluene) can be used with the first type of feed. With the others, heavy eluants are preferable (diethylbenzene and more specifically *p*-diethylbenzene or a 70/30 mixture of *p*-diethylbenzene and C₁₁ to C₁₃ paraffins, etc.). Sieve life is about 5 years.

Table 4.9 provides an example of the performance of the Parex process for C₈ cuts from extraction and reforming.

b. *Toray Aromax process*

Toray conducts adsorption in the liquid phase in a horizontal column with a series of stages that are totally isolated from each other and filled with molecular sieves. In steady state conditions, considering the instantaneous injection and withdrawal points at the different levels of the column, three zones can be distinguished (Fig. 4.18):

- (a) A separation zone, in which the *p*-xylene is adsorbed selectively. It is limited on one side by the fresh C₈ cut feed entry point, and on the other by the withdrawal of the raffinate depleted of *p*-xylene.
- (b) An enrichment zone, whose ends correspond to the feed injection and the withdrawal of the *p*-xylene rich extract. It also comprises a reflux, consisting mainly of *p*-xylene, whose function is to improve the purity of the extract by displacing the less adsorbable compounds.
- (c) A desorption zone lying between the extract withdrawal point and the eluant injection point.

As in the Parex process, the desorbent in the raffinate and extract is recovered by distillation and recycled. Countercurrent solid/liquid flow is also simulated by gradually altering the role of each of the column stages by means of a set of simple automatic injection and withdrawal valves, whose controls are programmed. This has the effect of progressively displacing the different zones from one end of the column to the other, and of achieving a degree of continuous production in this manner.

In the Aromax process, the adsorbent can be easily loaded, unloaded or regenerated at the level of each stage. Its total life is about 10 years. The operation takes place at a temperature below 200°C at less than 2 . 10⁶ Pa absolute. The number of stages can be increased by placing two or more horizontal adsorbers in series, depending on the type and volume of the feed to be treated and the performance required.

Table 4.10 indicates some typical performance figures.

4.3.3.3 Economic data

Table 4.11 a helps to compare the economics of the most important *p*-xylene adsorption and crystallization processes.

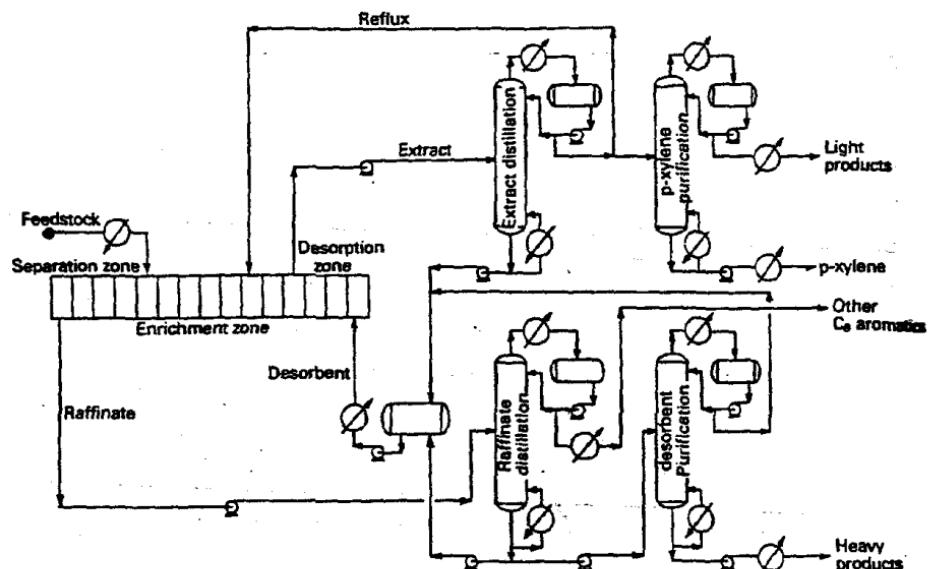


Fig. 4.18. Separation of *p*-xylene by adsorption. Toray Aromax process.

TABLE 4.10
PERFORMANCE OF THE AROMAX PROCESS

Composition (% Wt)	Feedstock	Extract	Raffinate
Light compounds	8.2	—	10.6
Ethylbenzene	14.9	0.4	18.3
<i>o</i> -xylene	13.3	—	17.3
<i>m</i> -xylene	45.5	0.1	51.8
<i>p</i> -xylene	18.5	99.5	2.0
Total	100.0	100.0	100.0
<i>p</i> -xylene recovery rate (%)	≥ 92		

TABLE 4.11 a
SEPARATION OF *p*-XYLENE. ECONOMIC DATA
(France conditions, mid-1986)

Type of separation	Adsorption			Crystallization			
Company	UOP	Toray	ARCO standard	ARCO modified	Krupp	Amoco	Phillips
Capacity (10 ³ t/year)	100	100	100	100	300	50	50
Battery limits investments (10 ⁶ US\$)	13.1	15.8 ⁽¹⁾	14.9	13.1	31.5	9.6	13.1
Initial loads (10 ⁶ US\$)							
Adsorbent	3.0	4.0					
Desorbent	1.0		—	—	—	—	—
Miscellaneous	—						
Yield (%)	92		63				
Consumption per ton of <i>p</i> -xylene							
Feedstock (t)	5.90 ⁽²⁾		8.40 ⁽²⁾		7.65 ⁽²⁾	8.45	6.40
Utilities							
HP steam (t)	0.08	1.0	0.35	0.40	0.15	0.45	0.35
MP steam (t)	1.0	—	—	—	—	—	—
LP steam (t)	—	—	0.55	0.40	—	—	—
Electricity (kWh)	100	315	590	550	350	380	470
Cooling water (m ³)	—	12	80	60	70	125	55
Fuel (10 ⁶ kJ)	10.5	18	—	—	—	—	—
Adsorbent (US\$)	7	4.5					
Desorbent (US\$)	1	1					
Refrigerants (kg)	—	—	5	5	5	5	5
Labor (Operators per shift)	2	2	2.5		2.5	2.5	2.5

(1) Conditions in Japan.

(2) See Table 4.11 b.

TABLE 4.11 b
UNIT FEEDSTOCK COMPOSITION (% Wt)

Separation	Adsorption	Crystallization	
Process	UOP	ARCO	Krupp
Non-aromatics	8.0	3	4.2
Toluene	0.6	1	0.7
Ethylbenzene	13.7	16	11.0
<i>o</i> -xylene	15.8	18	19.0
<i>m</i> -xylene	43.5	44	45.2
<i>p</i> -xylene	18.4	18	19.9
Total	100.0	100	100.0

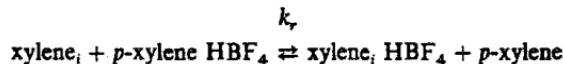
4.3.4 Direct separation of *m*-xylene

Given the problems raised by the presence of *m*-xylene in the separation of a high yield of *p*-xylene at the required degree of purity, one possibility consists in isolating *m*-xylene selectively. In this way, in treating the aromatic C₈ cut, it is no longer necessary in principle to resort to crystallization or adsorption to recover the *p*-xylene, and each of the isomers can then be obtained in the pure state by distillation.

Among the different alternatives proposed, only the technique developed by *Mitsubishi Gas Chemical* (formerly *Japan Gas Chemical*) has been commercially implemented.

4.3.4.1 Principle

This process achieves the extraction of *m*-xylene by means of HF-BF₃. It exploits the complexing properties of boron trifluoride on aromatic C₈ compounds, and the particular ability of *m*-xylene to form the most stable complex. Subsequently, this isomer, added to a mixture of C₈ aromatics which does not contain it, displaces the other components from their respective complexes, and the composition of the medium depends on the values of the equilibrium constants, or $k_r = 100$ for *m*-xylene, 2 for *o*-xylene, 0.14 for ethylbenzene, when *p*-xylene constitutes the reference element 1, in the following exchange reaction:



By adjusting the amount of boron trifluoride, introduced in gaseous form in hydrofluoric acid in contact with the organic phase, it is therefore possible to extract the *m*-xylene from an aromatic C₈ cut after agitation. The HF-BF₃ solvent is also an isomerization catalyst whose activity is related to the operating conditions, so that the combination of extraction and isomerization (see Section 4.4.2.2) offers a number of economic advantages.

4.3.4.2 Practical implementation (Fig. 4.19)

Mitsubishi Gas Chemical proposes two alternatives for upgrading the aromatic C₈ cut, according to whether or not the *m*-xylene can be commercialized directly. The simplest, or "once-through" process, does not include an isomerization stage. The more general process includes this possibility, so that the following sections can be distinguished:

- (a) *m*-xylene extraction: this is carried out at about 0°C in a multi-stage liquid/liquid extractor, equipped with a system to remove the heat liberated by the formation of the complex at the inlet into the unit, or about 40 kJ/mol of complexed C₈. The hydrocarbon feed must be dry (molecular sieves) and devoid of polar compounds, in order to avoid excessive corrosion and high solvent losses. To improve selectivity, the medium is diluted by the addition of a hydrocarbon. The exchange reactions take place in the different stages of the extractor, so that the purity of

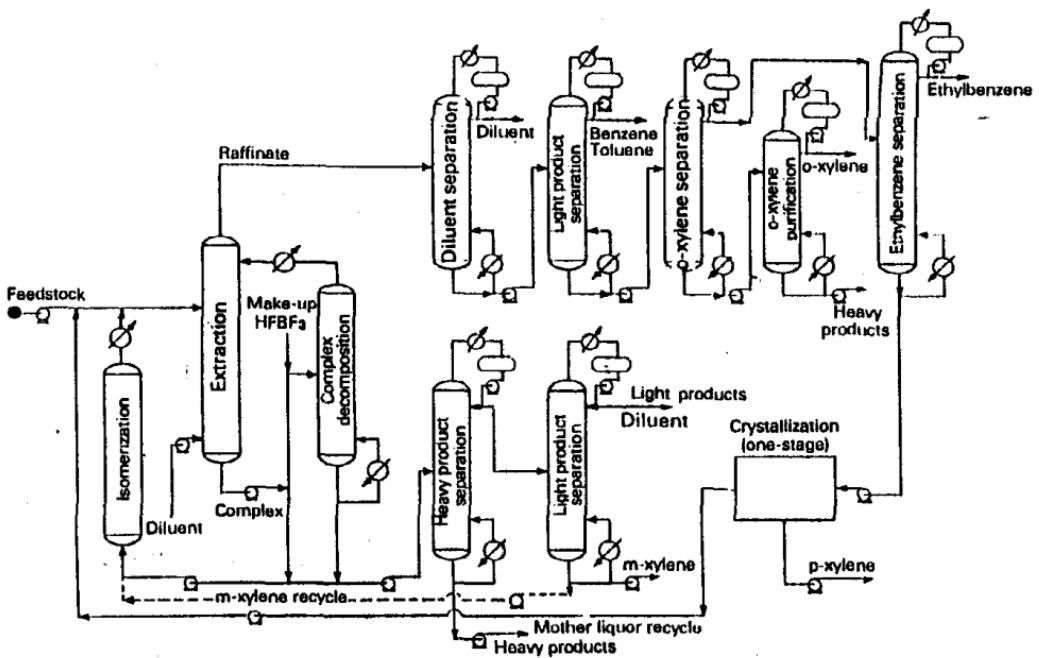


Fig. 4.19. Direct extraction of *m*-xylene. Mitsubishi Gas Chemical process.

m-xylene in the extract is greater than 99 per cent in relation to xylenes. Loss in the raffinate is less than 0.2 per cent.

- (b) Recovery of *m*-xylene from the complex: the complex is decomposed by raising the temperature, causing vaporization of the fluorinated compounds that are recycled to the extraction step. This operation takes place in a unit similar to a distillation column. The *m*-xylene is then rid of the heavy compounds and desorbent, which is also recycled to the extractor. Losses by the disproportionation reaction to *C*₇ and *C*₉, or by isomerization can be reduced to 0.2 per cent by adjusting the residence time.
- (c) Raffinate treatment: the scheme presented by Mitsubishi Gas Chemical includes the separation of a certain fraction of desorbent which is recycled, and of lighter components such as benzene and toluene. This split raffinate can be used to produce ethylbenzene and *o*-xylene by superfractionation, and, using a single crystallization stage, to produce *p*-xylene in the required purity (see Section 4.3.3.1).
- (d) *m*-xylene isomerization (see Section 4.4.2.2).

TABLE 4.12
MITSUBISHI GAS CHEMICAL PROCESS. ECONOMIC DATA
(France conditions, mid-1986)

Operation	Once-through	General
Material balance		
Feedstock, C ₈ cut (t/year) (<i>ox</i> 20%, <i>mx</i> 40%, <i>px</i> 20%, <i>eb</i> 20%)	200,000	300,00
Products (t/year)		
<i>o</i> -xylene (98.5% min.)	59,000	116,000
<i>m</i> -xylene (99% min.)	40,000	—
<i>p</i> -xylene (99.5% min.)	60,000	120,000
Ethylbenzene (99.7% min.)	40,000	60,000
Light and heavy compounds	1,000	4,000
Battery limits investments (10⁶ US\$)	35	58
Initial loads		
Hydrofluoric acid (t)	0.17	0.25
Boron trifluoride (t)	0.05	0.075
Diluent (t)	0.07	0.10
Consumption per ton of feed:		
Chemicals and catalyst		
Hydrofluoric acid (kg)	0.02	0.02
Boron trifluoride (kg)	0.06	0.06
Diluent and miscellaneous (kg)	ε	ε
Utilities		
Steam (t)	(-)1.17	(-)0.75
Electricity (kWh)	80	105
Cooling water (m ³)	80	105
Fuel (10 ⁶ kJ)	10	11
Refrigeration (10 ⁶ kJ)	1.0	1.7
Labor (Operators per shift)	6	6

4.3.4.3 Economic data

Table 4.12 provides economic data on the two variants of the Mitsubishi Gas Chemical process.

4.4 AROMATICS CONVERSION PROCESSES

The following aromatics conversion techniques have produced developments reaching the industrial level:

- (a) Hydrodealkylation.
- (b) Isomerization.
- (c) Dismutation and transalkylation.

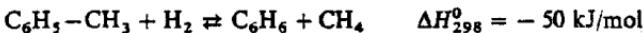
4.4.1 Hydrodealkylation

This is designed to produce benzene from toluene, whose upgrading from the chemical standpoint is often difficult, and possibly from heavier aromatics available in surpluses, or sometimes from complete C₅₊ cuts.

4.4.1.1 Reactions involved

In dealkylation by hydrogen (hydrodealkylation), the essential reaction is the removal of alkyl groups fixed to the benzene ring, in the form of methane. If the operation is properly conducted and if the conversion is completed by recycling the unconverted aromatics, the products obtained are benzene and various light hydrocarbons, chiefly methane. Any non-aromatics contained in the feed, for example in the direct treatment of a pyrolysis C₅₊ cut without prior solvent extraction, are decomposed into light paraffins (methane). This serves to obtain high purity benzene, but entails high consumption of hydrogen. Sulfur compounds are partly converted to H₂S.

The main reaction is therefore the following:



(-105 kJ/mol for xylenes).

The most important side reactions are:

- (a) Formation of heavy aromatics (diphenyl).
- (b) Hydrogenation of benzene rings and their destruction with the production of methane.
- (c) Decomposition of paraffins and naphthenes to methane.
- (d) Carbon formation.

On the whole, the reactions involved are highly exothermic ($\Delta H = -190$ to -230 kJ/mol for hydrocracking), except for the production of heavy aromatics, which is slightly endothermic, and the decomposition of methane to carbon and hydrogen. They take place at elevated temperature, about 650°C , and, depending on each case, are favored (hydrogenation) or not (decomposition, coke formation) by an increase in pressure, which is optimally about 5 to $6 \cdot 10^6$ Pa absolute.

Some reactions, such as hydrogenation, are highly sensitive to the presence of the metallic elements of the walls. This catalysis can be inhibited by recycling part of the H_2S that is also formed during hydrodealkylation. From the kinetics standpoint, the main reaction is a first order reaction with respect to the hydrocarbon, and of the 0.5 order with respect to hydrogen.

The high temperature at which the conversion occurs makes cooling necessary within the reactor itself, by injection of the cold product, in order to prevent an excessive elevation in temperature, which favors decomposition above 750°C , among other reactions.

4.4.1.2 Processes

Processes are of two types, catalytic and thermal. However, apart from the operating conditions, their flow sheets are identical. Depending on the feedstock, a simplified version is available with dealkylation alone, and another more elaborate version, which includes pretreatment of the pyrolysis C_{5+} cut intended to convert the diolefins, stable sulfur compounds, nitrogen and oxygen compounds, etc. by selective hydrogenation.

A. Basic hydrodealkylation flow sheet (Fig. 4.20)

Make-up and recycle hydrogen are mixed with the toluene feedstock and the unconverted alkylaromatic recycle stream. The mixture is preheated by heat exchange with the effluent from the reaction section, raised by passage through a furnace to the incipient conversion temperature required, and introduced into the reactor. The latter, which is empty or contains catalyst beds (usually two), must be designated to withstand high pressures, thermal shocks, and hydrogen diffusion through the heated walls. This precludes the use of a single stainless steel shell that could be raised to a temperature of 600 to 700°C .

Current technology calls for the superposition of three envelopes:

- An outer wall of 1.1/4 Cr . 1/2 Mo steel capable of withstanding the internal pressure at 200°C , clad with stainless steel.
- A refractory brick lining, whose inner and outer faces are raised to about 700 and 200°C respectively, capable of withstanding thermal shocks.
- A thin stainless steel inner casing designed to keep the refractory brick in place.

Between the catalyst beds or in the axis of the shell, cooling is often provided by means of hydrogen recycle, for example, for better control of the temperature rise, which must not be more than 50 to 75°C between the reactor inlet and exit. The reaction section effluent is cooled, sometimes quenched by a recycle, and sent to a high pressure separator where the hydrogen is recovered. This is recycled after passage through a toluene absorber, to rid it of traces of entrained aromatics, after purification or purge.

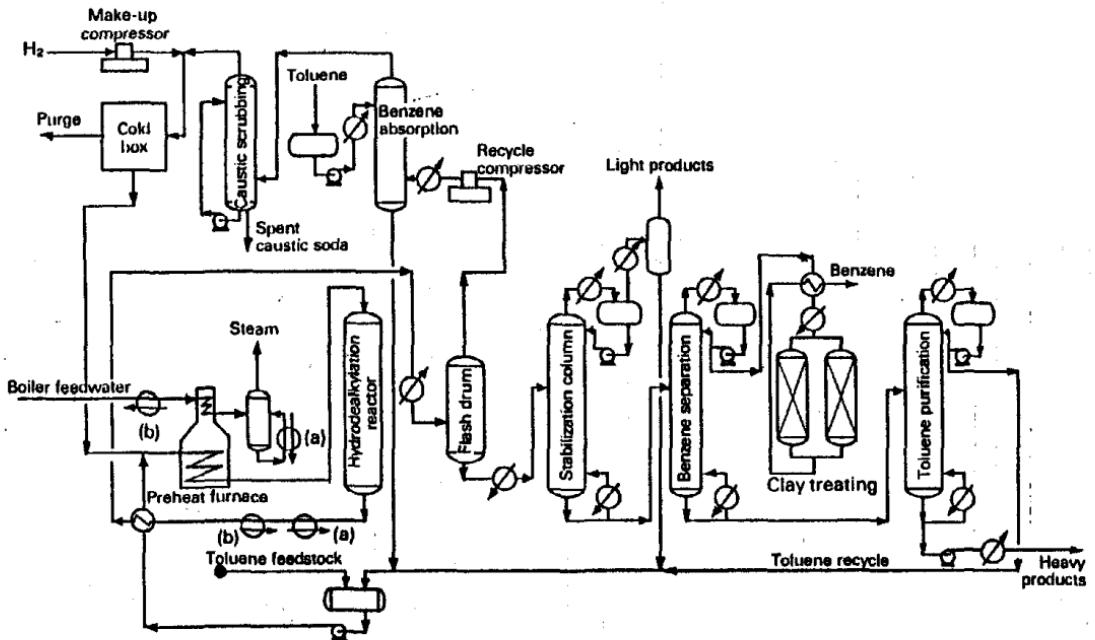


Fig. 4.20. Hydrodenalkylation of toluene.

The liquid product is sent to a stabilization column to eliminate light products and then to a column to separate unconverted toluene. The benzene distillate undergoes clay treating before being upgraded.

The benzene yield in relation to the toluene used varies from 95 to more than 98 molar per cent depending on the type of process. Its purity is relatively high, 99.9 to 99.99 per cent, with a melting point above 5.4°C and a sulfur and thiophene content less than 1 ppm.

Hydrogen may be obtained from various sources, including catalytic reforming, electrolysis, coke oven, steam reforming and partial oxidation, etc. Pretreatment is sometimes required to remove carbon oxides and sulfur impurities (caustic scrubbing). Hydrogen recycle depends chiefly on its purity. Sometimes, to avoid excessive losses in the purge, the methane it contains is removed by cryogenics. Pretreatment is also carried out on the recycle to limit the amounts of H₂S returned to the reactor.

B. Catalytic processes

The main techniques of this type were developed by the following companies:

- (a) *Shell* with the Bextol process.
- (b) *UOP* with the Hydeal technique, developed jointly with *Ashland*.
- (c) *Houdry*, which offers three variants: Detol (dealkylation of toluene and alkyl-aromatics in general), Litol (purification by selective hydrogenation and partial dealkylation of a light coke oven gasoline), and Pyrotol, which combines the above two techniques to some degree, for the selective hydrogenation and complete dealkylation to benzene of the components of the BTX fraction of a C₅₊ pyrolysis gasoline.
- (d) *BASF* (*Badische Anilin und Soda Fabrik*).

A number of other companies have also developed catalytic hydrodealkylation techniques.

Most of these processes employ chromium oxide based catalysts (10 to 15 per cent weight) deposited on alumina. The average operating conditions are approximately as follows: reactor inlet temperature 620°C, maximum temperature 700 to 720°C, pressure $4.5 \cdot 10^6$ Pa absolute, H₂/hydrocarbon molar ratio at reactor inlet: 6, LHSV 1 h⁻¹. The yield for a toluene feed is more than 97 molar per cent and once-through conversion reaches an average of 70 molar per cent. Catalyst life is at least two years. The carbon deposit that accumulates with time requires a progressive increase in temperature, from 620°C at the start of the run to 650°C at the end at the reactor inlet, as well as an annual regeneration by controlled combustion using an oxygenated gas.

C. Thermal processes

The main companies marketing these processes are the following:

- (a) *Atlantic Richfield (ARCO)* and *Hydrocarbon Research Inc (HRI)* with the HDA technique. The reactor has a system of quench gas injections at six levels, with temperature regulation between 665 and 735°C.
- (b) *Mitsubishi* and *Chiyoda* with the MHC (Mitsubishi Hydrocracking) process distinguished by a special reactor design. The heat generated by conversion is used

to produce high-pressure steam ($4 \cdot 10^6$ Pa absolute). It is unnecessary to carry out intermediate quench, or to add inert to control the temperature.

(c) *Gulf Oil*, which has developed the THD (Thermal Hydro Dealkylation) process.

The average operating conditions of these techniques are substantially as follows: reactor inlet temperature 620°C; maximum temperature 730 to 750°C; pressure $4.3 \cdot 10^6$ Pa absolute; average residence time 25 to 30 s; H₂ to hydrocarbon molar ratio at reactor inlet = 4; once-through conversion 75 per cent; minimum purity of recycle hydrogen ≥ 50 to 60 per cent volume. The benzene obtained is a high purity product, and the yields, depending on whether or not heavy products (diphenyls, dibenzyls etc.) are recycled, vary from 97 to 99 molar per cent.

D. Remarks

a. Comparison of catalytic and thermal processes

Theoretically, the use of a catalyst helps to operate in less severe conditions and to achieve higher once-through conversion and selectivity, and hence also to improve the

TABLE 4.13

HYDRODEALKYLATION OF TOLUENE (AND XYLEMES), ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100,000 t/YEAR OF BENZENE

Type of process	Catalytic		Thermal			
	UOP	Houdry	HRI	Mitsubishi	Gulf	
Process	Hydeal	Detol	HDA	MHC	THD	
Battery limits investments (10^6 US\$) ⁽¹⁾	7.9	8.2	8.4	10.2	18.4	7.9
Initial loads (catalyst/clay) (10^6 US\$)	0.15	0.2	0.01	0.01	—	—
Consumption per ton of benzene						
Raw materials						
Toluene (t)	1.198	1.185	1.209	1.194	0.853	1.237
Xylenes (t)	—	—	—	—	—	0.610
C ₉ + aromatics (t)	—	—	—	—	0.507	—
Pure hydrogen (kg) or Hydrogenated gas (kg)	27 255	35 360	26 250	34 360	58 300	35 360
By-products						
Fuel gas (kg)	470	540	460	545	620	540
Utilities						
Steam (t)	(—) 0.5	(—) 2.25	1.1	0.6	0.8	(—) 0.6
Electricity (kWh)	105	90	85	145	70	40 ⁽²⁾
Fuel (10^6 kJ)	5.2	9	3.3	3.8	5.0	3.8
Cooling water (m ³)	5	5	8	45	15	4.2
Process water (m ³)	—	—	—	1.5	0.8	—
Catalysts and miscellaneous (US\$)	0.70	0.44	0.09	0.17	1.05	0.09
Labor (Operators per shift)	2	2	2	2	2	2

(1) Including clay treatment, benzene distillation, cryogenic purification of hydrogen.

(2) Not including hydrogen purification.

yield (originally 97 to 98 per cent against 95 to 96 per cent) and the final purity of the benzene. It also facilitates the conversion of heavy alkylaromatics. From the economic standpoint, these advantages are normally reflected by lower investment and operating cost.

In fact, the two types of process display substantially identical operating conditions and performance, since temperature is the essential parameter for improving the already high yields. Consequently, the use of a conventional catalyst entails additional investment cost or operating expenses during the purchase of the initial or replacement loads, and a drop in productivity resulting from the unit shutdowns required for regeneration and replacement.

TABLE 4.14

**HYDRODEALKYLATION OF A PYROLYSIS GASOLINE. ECONOMIC DATA
(France conditions, mid-1986)**
PRODUCTION CAPACITY 100,000 t/YEAR OF BENZENE

Company.....	Houdry	HRI	Mitsubishi
Process.....	Pyrotol	HDA	MHC
Feedstock composition (% Wt)			
C ₅	9	8	12
C ₆ -C ₈ non-aromatics	20	11	21
Benzene	32	19	27
Toluene	15	51	18
C ₈ aromatics	14	8	14
C ₉ + aromatics	8	19	6
C ₉ + non-aromatics	2	8	2
Total	100	100	100
Battery limits investments (10 ⁶ US\$) ⁽¹⁾	13.1	14.0	14.9
Initial loads (10 ⁶ US\$).....	0.5	0.1	0.1
Consumption per ton of product			
Raw materials			
Gasoline (t)	1.860	1.360	1.950
Pure hydrogen (kg)	75	55	60
Hydrogenated gas (kg)	150	305	125
By-products			
Fuel gas (kg)	650	625	625
C ₅ - light compounds (kg).....	190	30	165
C ₉ - heavy compounds (kg).....	165	10	280
Utilities			
Steam (t)	(-)0.3	-	(-)0.5
Electricity (kWh)	125	110	110
Fuel (10 ⁶ kJ)	4.2	2.1	4.6
Cooling water (m ³).....	5	3	30
Boiler feedwater (m ³).....	-	0.4	0.1
Catalysts and miscellaneous (US\$)	2.1	0.7	0.9
Labor (Operators per shift).....	3	3	3

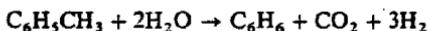
(1) Complete installations: pretreatment, fractionation, hydrogen and benzene purification included.

b. Production of xylenes and naphthalene

Most hydrodealkylation processes can be adapted to produce xylenes or naphthalene from heavier feeds. For example, two Hydeal units exist producing naphthalene. Two other specific processes for naphthalene manufacture can be added to the list of techniques already mentioned, the catalytic Union Oil of California Unidak process and the Standard Oil of Indiana thermal process.

c. Steam dealkylation

Dealkylation processes are big hydrogen consumers. Many investigations have been and are being conducted to replace it with steam according to the following main reaction, which would occur in the presence of a catalyst based on precious metals on alumina, around 500 to 550°C, and at $0.5 \cdot 10^6$ Pa absolute:



The reaction also produces carbon monoxide resulting from the equilibrium between carbon dioxide and hydrogen.

4.4.1.3 Economic data

Indications are given in Tables 4.13 and 4.14 for the main industrial processes. They vary widely according to the type of feed considered (toluene, aromatics blends, pyrolysis gasolines etc.) and the composition and conditions of supply of the hydrogen gas employed.

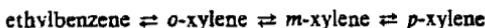
4.4.2 Xylene isomerization

In a conventional scheme comprising the separation of ethylbenzene and *o*-xylene by distillation, and of a large fraction of *p*-xylene by crystallization or nearly completely by adsorption, a mother liquor with a high *m*-xylene content remains after these operations. It can be upgraded as a solvent or employed in high octane gasolines. Depending on market requirements, however, this C₈ cut can be used to boost the production of *o*-xylene and *p*-xylene by catalytic isomerization.

4.4.2.1 Reactions

Isomerization can be carried out in the liquid or vapor phase in the presence of a catalyst. The systems proposed were initially of the Friedel and Crafts type, using aluminum chloride, followed by HF-BF₃ complexes. Subsequent use was made of heterogeneous acid catalysis, developed in reforming, and chiefly of dual-function catalysts containing noble metals and operating in the presence of hydrogen. More recently, investigations have been conducted into the use of Y-type and X-type zeolites exchanged by rare earths (REX : Rare Earth Exchanged Zeolites) and modified.

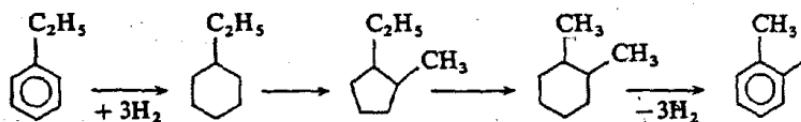
Isomerization leads to an equilibrium between the four C₈ aromatics. This results from the succession of conversions in the following order:



Depending on the type of catalyst employed and the medium in which isomerization takes place (presence of hydrogen, for example), a number of side reactions tend to develop:

- (a) Aromatics hydrogenation.
- (b) Naphthene dehydrogenation.
- (c) Aromatics disproportionation reaction.
- (d) Aromatics dealkylation.
- (e) Hydrocracking of saturated compounds.

Whereas the mutual isomerization of xylenes appears to take place by the transfer of the CH_3 group according to a conventional carbonium ion mechanism, ethylbenzene isomerization is more complex and requires the presence of hydrogen. To interpret this factor, it is assumed that the conversion comprises the production of C_5 and C_6 naphthenes as intermediates, according to the following reaction:



Hence the isomerization of ethylbenzene is possible in the case of polyfunctional catalysts controlled by a partial pressure of hydrogen. According to some authors, a similar mechanism is also involved for the mutual conversion of xylenes.

From the thermodynamic standpoint, since the reaction shift in favor of *p*-xylene formation is slightly exothermic, a change in temperature only has a limited effect on the composition of the C_8 aromatics mixture at equilibrium. This is shown by Fig. 4.21.

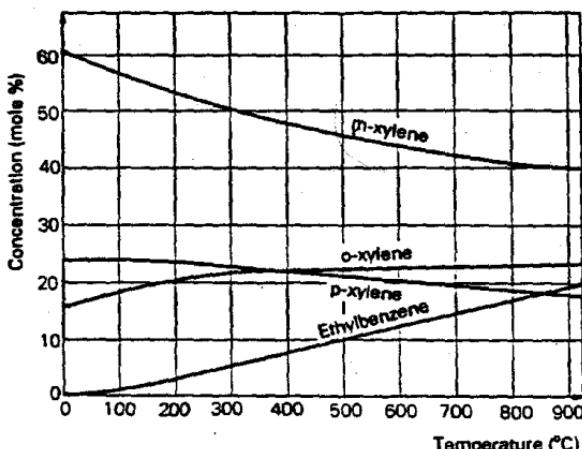


Fig. 4.21. Equilibrium composition of C_8 aromatics
(at $P = 0.1 \cdot 10^6 \text{ Pa}$ absolute).

4.4.2.2 Processes

Industrial vapor phase techniques enjoy a virtual monopoly today. However, interest is now being revived in liquid phase processes, after a long period of neglect.

A. Liquid phase processes

Low temperatures favor the production of *p*-xylene. According to Fig. 4.21, its equilibrium concentration in the C₈ aromatics mixture is a maximum at around 80°C, and then slowly decreases.

a. Friedel-Crafts type catalysts

These are halogenated acids, metallic halogenides or a mixture of both, forming complexes with aromatics, AlCl₃—HCl, BF₃—HF, etc. They act according to the following principle:

- (a) Isomerization takes place in the acid phase, but the mutual solubility of the acid and xylenes is low.
- (b) The halogenide has the effect of yielding a complex with the aromatics and, if it is present in sufficient quantity, tends to increase the size of the reaction phase in which isomerization takes place.

Since the complexes formed with *p*-xylene and *o*-xylene are less stable than that obtained with *m*-xylene, they are salted out in the organic phase when *m*-xylene is in excess, facilitating their separation. However, these catalysts present the drawback of not isomerizing ethylbenzene, which yields an unstable complex, and of favoring certain side reactions, particularly dismutation to benzene and diethylbenzenes.

At the industrial level, the processes employing these catalyst systems were first abandoned quickly in favor of vapor phase techniques. In 1968, *Mitsubishi Gas Chemical* commercialized a technique employing the BF₃—HF mixture, both as an extractant and an isomerization catalyst. This is achieved by a simple elevation in temperature to about 100°C (see Section 4.3.4).

b. Zeolites

Mobil Chemical has developed a xylene isomerization process called LTI (Low Temperature Isomerization) which, in the liquid phase, uses special zeolites as catalysts (ZSMS), commercialized by the designation AP (Aromatics Processing). These systems are more active than those of the REX type, which are generally proposed for vapor phase operation.

In the Mobil process, conversion takes place in the absence of hydrogen, at a pressure of $3 \cdot 10^6$ Pa absolute, and a temperature that rises progressively with time, from 200 to 260°C. The catalyst, whose LHSV is 3 h^{-1} in normal operating conditions, has a life of two years. Intermediate regenerations, designed to burn the coke deposited, are carried out as soon as the temperature reaches 260°C. To minimize dismutation reactions, toluene is used as a diluent at a rate of 10 to 12 per cent weight of the reactor feed.

Ethylbenzene is not involved in the equilibrium between the different aromatic C₈ compounds. It is not formed from them, nor is it destroyed, if the initial concentration is low. Hence, to reduce equipment size and to facilitate *p*-xylene recovery, it is preferable to remove it first by superfractionation to a content less than 10 per cent.

The overall xylene yield of the operation is estimated at over 98 per cent with an approach to the equilibrium content for *p*-xylene of 95 to 98 per cent.

B. Vapor phase processes

Depending on the type of catalyst employed and the medium in which it operates (presence or absence of hydrogen), vapor phase processes are divided into three main types:

- (a) Silica alumina or promoted alumina, operating without hydrogen.
- (b) Noble metal on silica alumina with hydrogen atmosphere.
- (c) Non-noble metals used in the presence of hydrogen.

They are also differentiated by other characteristics, especially the operating conditions, and the frequency and method of regeneration of the catalyst system.

a. Silica alumina or promoted alumina catalysts

These catalysts are silica-aluminas whose cracking and disproportionation power has been altered by steam treatment, the use of an inhibitor, or of aluminas containing a halogenated compound or fluorine. They are very rugged, are employed without hydrogen and hence cannot isomerize ethylbenzene, which is therefore cracked or transformed by a disproportionation reaction into benzene and C₁₀ aromatics. Consequently, they can only be used with feeds poor in ethylbenzene. However, no naphthenic hydrocarbons are formed.

Isomerization takes place between 400 and 500°C, at 0.1 to 2 · 10⁶ Pa absolute, in adiabatic reactors. Since a coke deposit rapidly appears during the conversion, operations are conducted in cycles. One or two reactors are in operation, with another in regeneration. Regeneration normally includes three steps: steam purge, combustion of the coke deposited by means of a gas containing an inert and oxygen whose content must be perfectly controlled, and a new steam purge to reduce the cracking activity of the catalyst. The complete cycle time (reaction and regeneration) depends on the process concerned. It also depends on the amount of ethylbenzene present in the feed. It varies in practice from 10 to 24 hours to 3 to 4 days. Total catalyst life is estimated at about two years.

Various processes have been developed by *Chevron*, *Shell*, *Sinclair*, *Southern Petrochemical*, etc., and particularly by *ICI (Imperial Chemical Industries)*, *Maruzen* (XIS process), which operates in the presence of steam at a ratio of 0.05 to 0.15 mol/mol of xylenes feedstock, and *ARCO*, which proposes the permanent regeneration of its catalyst by using the moving bed technology. These processes are usually combined with a *p*-xylene recovery technique, generally by crystallization. The isomerization yield depends on the ethylbenzene content at the reactor inlet and on the desired target product, either *p*-xylene alone or *o*- and *p*-xylenes simultaneously.

Mobil has developed a process similar to its LTI technique called MVPI (*Mobil Vapor Phase Isomerization*). It operates in vapor phase above 350°C in the absence of hydrogen. It uses ZSM11 zeolite as catalyst and is adapted to transform feedstock with a high ethylbenzene content. Ethylbenzene is disproportionated into benzene and para-diethylbenzene.

b. Catalysts based on supported noble metals

Operating conditions of catalyst systems

These systems consist of platinum deposited on silica alumina or on alumina activated by a halogen or a halogenated compound. They operate in the presence of hydrogen, enabling them to isomerize ethylbenzene. Depending on each case, and especially on the content of this hydrocarbon in the reactor feed, use can be made of different catalyst systems, for example a silica alumina containing 0.5 to 0.6 per cent weight of platinum, or a promoted alumina operating with 0.3 to 0.4 per cent weight of platinum. However, the injection of chlorine into the hydrogen recycle loop to maintain the activity of the catalyst is liable to cause substantial corrosion.

Also depending on circumstances, the conversion takes place between 300 and 500°C, and usually between 400 and 480°C, at a pressure between 1 and $3 \cdot 10^6$ Pa absolute. The hydrogen to hydrocarbon molar ratio is about 8 to 10, and the LHSV is 1 to 2 h^{-1} . Since the isomerization reaction is slightly exothermic in the shift towards *p*-xylene production, it is carried out in adiabatic reactors.

The presence of hydrogen theoretically allows the conversion of the ethylbenzene to xylenes. In practice, the ethylbenzene is not converted if its content in the reactor feedstock is less than 8 per cent weight, a value corresponding to the thermodynamic equilibrium around 410°C. Above this concentration, it can be shown experimentally that the amount converted in relation to this threshold, called the "approach to equilibrium", does not depend on the ethylbenzene content, but on that of naphthenic C₈ compounds present in the reaction medium. For example, it may be 40 per cent with 6 molar per cent of these saturated cycles, and over 70 per cent with 10 per cent.

These naphthenes result from hydrogenation side reactions that take place as the unit operates, and which subsequently maintain a stationary concentration of these compounds. The same applies to other side reactions, such as hydrogenation, hydro-dealkylation and dismutation, which lead to the formation of paraffins and aromatics (benzene, toluene, C₉, etc.). Thus, it can be considered that the total loss of C₈ aromatic rings depends only on the approach to equilibrium for *m*-xylene, namely the treatment severity. Indeed, everything takes place as if, unaware of the source of the by-products, the other xylenes and the ethylbenzene are not involved. A correlation to determine once-through losses (2 to 4 per cent weight), namely the once-through yield (96 to 98 per cent weight), can therefore be established with the knowledge of only the *o*- and *p*-xylene contents in the feed, while the *m*-xylene, with which these losses are associated, is obtained by difference (Fig. 4.22). The calculation is more complex in practice, and takes account of the approach to equilibrium for the different C₈ aromatics, catalyst performance (LHSV), and the operating conditions (severity factor).

Since the isomerization unit is incorporated in a loop comprising the recycle of unemployed C₈ aromatic compounds, the total yield of the operation is related to the products that are effectively upgraded (*o*- and *p*-xylenes) on the basis of the make-up feed. Hence the overall yield is actually only about 90 per cent weight, as shown by Table 4.15 a.

The calculation of the loop is discussed in simplified form in Section 4.5. It is based on the adoption of an approach to equilibrium of ethylbenzene with 60 per cent weight on the average, and a C₈ aromatic ring retention ratio of 97 per cent weight.

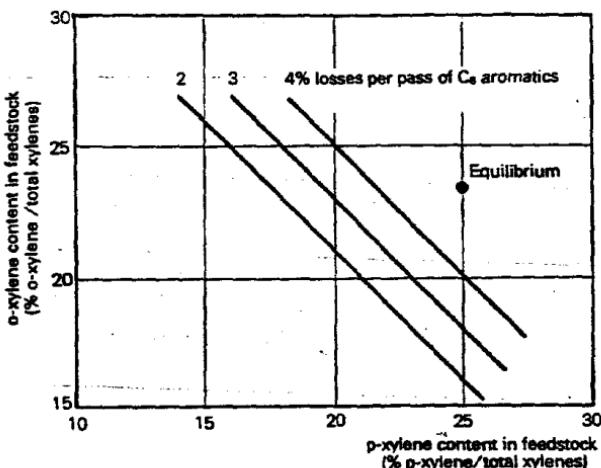


Fig. 4.22. Losses of aromatic C₈ rings in the isomerization of xylenes on catalysts based on supported noble metals.

Another aspect of this type of process is to allow the hydrocracking of the saturated compounds initially present. Normally, the catalysts employed easily withstand contents of about 15 per cent weight, but, by adjusting the operating conditions and by providing additional hydrogen consumption, it is possible to treat petrochemical fractions with much higher concentrations of saturated compounds.

Overall catalyst life is about 3 to 5 years, with regeneration every 6 to 18 months by combustion of the coke deposits formed with oxygen-poor air. Run length is related to the activity of the catalyst system, mainly toward ethylbenzene, whose approach to equilibrium decreases much faster with time than for the other C₈ aromatics. This effect towards *m*-xylene, a majority hydrocarbon in the feedstock, is corrected by a progressive increase in the temperature which, on the other hand, is unfavorable to the formation of naphthalenes, and hence to the conversion of ethylbenzene. Thus, the approach to equilibrium for this hydrocarbon drops even faster, going from 90 to 100 per cent at the beginning of the run to 30 to 35 per cent at the end. The ethylbenzene concentration in the loop increases substantially by recycle, and this proportionally decreases that of *p*-xylene. In practice, if the *p*-xylene content at the bottom of the deheptanizer is less than 18 per cent weight, the unit is normally shut down, the recirculation stock eliminated, and the catalyst regenerated.

Processes

The main processes employing this type of catalyst are the following:

- (a) Octafining by *Engelhard*, with a silica alumina support.
- (b) Isomar by *UOP*, which employs chlorinated alumina.
- (c) Isarom by *IFP*, operating on fluorinated alumina.

A new generation of catalyst systems based on precious metals appeared recently, consisting of platinum deposited on a composite support containing a certain proportion of a zeolite, probably mordenite. These catalysts are those of the Toray Isolene II, Engelhard Octafining II (O-750), and Leb Leuna Verke Aris (K8830) processes. Their activity is twice as high, allowing the doubling of the LHSV and operation with an H₂ to hydrocarbon molar ratio of 4 instead of 8 to 10.

Such a catalytic system has also been developed by *Mobil* with its MHTI process (Mobil High Temperature Isomerization). It uses platinum deposited over a low acid ZSM5 zeolite and is well adapted to feedstock having a high paraffins and ethylbenzene content. Paraffins are cracked and ethylbenzene hydrodealkylated.

The operating flow sheet of the installations is substantially the same from one technique to another, and is illustrated by Fig. 4.23 for the Octafining process. The C₈ cut to be treated and the hydrogen are preheated by heat exchange with the reactor effluent and passage through a furnace. After cooling, the reaction products undergo flash under pressure, to allow recycle of the hydrogen, which is first purged and then recompressed. The light hydrocarbons are then separated by distillation.

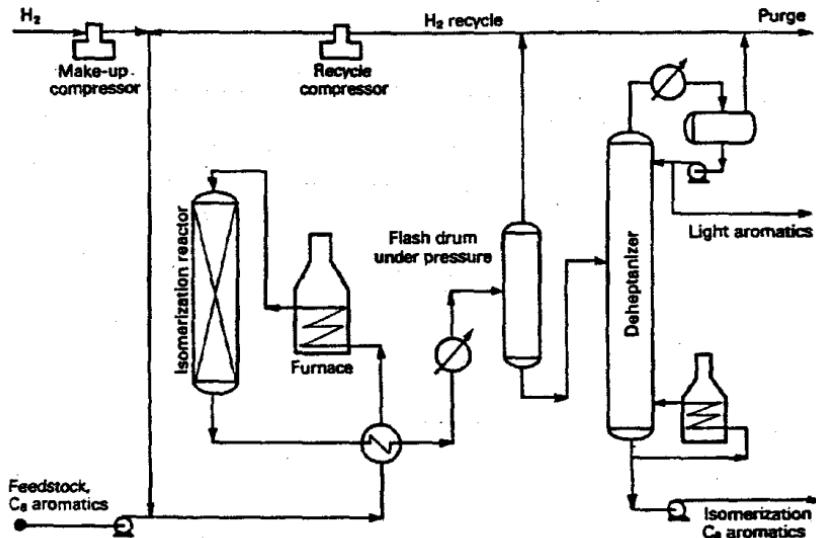


Fig. 4.23. Isomerization of C₈ aromatics. Octafining process.

Tables 4.15 a and 4.15 b provide an idea of the performance of the Octafining process and of the Isomar catalyst for different ethylbenzene contents in the feed.

c. Catalysts based on non-noble metals

These catalysts appeared on the market more recently. Derivatives of the catalysts used in hydrocracking, they are controlled by a hydrogen pressure, like systems based on noble metals. Ethylbenzene can hence be converted theoretically. In fact, it is only

TABLE 4.15a

PERFORMANCE OF OCTAFTINING PROCESS
ACCORDING TO FEEDSTOCK AND FINAL PRODUCTS

Ethylbenzene content of feedstock	Low	Medium	High	
Final products	<i>o</i> -xylene and <i>p</i> -xylene	<i>p</i> -xylene	<i>p</i> -xylene	<i>o</i> -xylene and <i>p</i> -xylene
Composition of fresh feedstock (% Wt)				
Ethylbenzene	5.0	16.0	31.0	
<i>p</i> -xylene	23.0	18.0	10.0	
<i>m</i> -xylene	50.0	44.0	56.0	
<i>o</i> -xylene	22.0	22.0	3.0	
Total	100.0	100.0	100.0	
Hydrogen (100% Wt)	0.3	0.7	0.8	0.5
Products (% Wt)				
<i>p</i> -xylene	44.0	86.9	80.3	44.0
<i>o</i> -xylene	50.4	—	—	43.1
C ₁ to C ₅ paraffins	2.1	4.1	7.1	4.3
C ₆ -naphthalenes	1.0	3.1	3.4	2.2
Benzene	0.8	2.1	3.6	3.1
Toluene	0.6	1.4	1.7	0.8
C ₉ to C ₁₆ aromatics	1.4	3.1	4.7	3.0
Total	100.3	100.7	100.8	100.5
Presumed separation yield per pass (%)				
<i>p</i> -xylene	60	60	60	60
<i>o</i> -xylene	80	—	—	80

slightly converted, and is neither isomerized nor cracked. As a rule, the quantity of by-products formed is around 1 per cent.

The catalyst is regenerable, but can be employed for more than one year without regeneration. The temperature at the beginning of the run reaches 370°C, and is gradually increased, up to 450°C at the end of the run, to maintain the activity of the catalyst system. The pressure ranges from 1.5 to 3 · 10⁶ Pa absolute, the LHSV between 0.5 and 3 h⁻¹, and the hydrogen to hydrocarbon molar ratio at the reactor inlet between 3 and 8.

The operating principle of an installation is substantially the same as with catalysts containing noble metals. The main processes proposed industrially are the following:

- (a) Isoforming by Esso Research and Engineering.
- (b) Isomer by UOP.
- (c) Isolene I by Toray.

In the last two processes, depending on the ethylbenzene content in the feed, use is made of one or the other of the two types of catalyst proposed, containing noble or non-noble metals.

TABLE 4.15 b

PERFORMANCE OF ISOMAR CATALYST ACCORDING TO FEEDSTOCK COMPOSITION⁽¹⁾ AT THE ISOMERIZATION REACTOR INLET

Case Composition (% Wt)	1 ⁽¹⁾		2 ⁽¹⁾		3 ⁽¹⁾		4 ⁽¹⁾	
	Feedstock ⁽³⁾	Effluent						
C ₁ -C ₈ paraffins		1.4		1.2		1.8		
C ₅ -C ₇ naphthenes		0.9		0.9		1.0		
C ₈ naphthenes		7.7		7.8		7.5		
Total non-aromatics	0.1	10.0	0.2	9.9	0.4	10.3	9.6	12.5
Benzene and toluene	—	0.3	0.4	0.4	0.1	0.8	0.6	1.0
C ₈ aromatics	99.9	89.1	99.4	89.3	99.5	88.3	89.8	85.9
C ₉ aromatics	—	0.6	—	0.4	—	0.6	—	0.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
p-xylene	12.1	22.7	14.0	22.4	14.3	24.0	2.4	22.2
m-xylene	75.3	57.7	74.0	58.7	73.1	55.5	71.6	54.4
<i>o</i> -xylene	12.6	19.6	12.0	18.9	12.6	20.5	26.0	23.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ethylene in % of C ₈ aromatics	5.2	5.8	23.7	17.7	43.2	26.7	18.4	12.8
Ethylene converted to xylenes (%)	—	0.0	—	33.1	—	45.4	—	56.6
Retention rate of C ₈ aromatics (%)	—	96.9	—	97.7	—	96.3	—	96.0

(1) Average temperature 400°C, LHSV 2 h⁻¹.(2) Estimated values corresponding to an aromatic C₈ cut, from which p-xylene has been separated by adsorption (Parex) and whose initial composition is as follows: 18.3% ethylbenzene, 19.9% *o*-xylene, 38.4% *m*-xylene, 18.3% p-xylene, 5.1% saturated C₈ and LHSV ≥ 2.8 h⁻¹.

(3) Not including hydrogen.

TABLE 4.16 a
ISOMERIZATION OF XYLEMES. MATERIAL BALANCES.
PROCESSES OPERATING IN THE PRESENCE OF NOBLE METALS

Isomerization process	Obtaining	Isomar	Isolene	-
Process holder	ARCO	UOP	Toray	IFP
Associated p-xylene separation technique	Crystallization	Parex	Aromax	Crystallization
Production capacity of complete installation (t/year)				
p-xylene	100,000	100,000	100,000	300,000
<i>o</i> -xylene	25,000	25,000	25,000	-
Material balance per ton of <i>p</i> - and <i>o</i> -xylenes				
C ₈ cut feedstock: (1) To loop (2) To isomerization	(1)	(2)	(1)	(2)
Quantity (t)	1.55	3.80	1.20	4.00
Composition (% Wt)				
Ethylbenzene	19.2	-	18.3	16.5
<i>o</i> -xylene	21.0	-	19.9	19.1
<i>m</i> -xylene	40.2	-	38.4	52.4
<i>p</i> -xylene	19.1	-	18.3	1.8
Miscellaneous	0.5	-	5.1	10.2
Hydrogen gas (t)	0.07	-	0.11	0.18
Co-products and by-products (t)				
Mixed xylenes	0.40	-	-	-
Fuel gas	0.12		0.29	0.20
Heavy aromatics	0.09			0.09
Light aromatics	0.06		0.02	0.04
Recycle rate (ratio of loop recycle to fresh feedstock)	≈ 2.75	-	≈ 3	≈ 7.7

TABLE 4.16 b
ISOMERIZATION OF XYLEMES. ECONOMIC DATA,
(France conditions, mid-1986)
PROCESSES OPERATING IN THE PRESENCE OF NOBLE METALS

Technology	ARCO	UOP	Toray	IFP
Investments				
Battery limits investments (10 ⁶ US\$)	9.6	10.5	11.4	26.3
Initial catalyst loads (10 ⁶ US\$)				
Support	0.45	0.45	0.55	1.75
Precious metals ⁽¹⁾	1.75	0.50	0.90	2.20
Consumption per ton of <i>p</i> - and <i>o</i> -xylenes				
Hydrogen (100%) (kg)	8.5	10	8	12
Catalyst ⁽¹⁾ (US\$)	25	6	6	6
Utilities				
HP steam (t)	-	-	1.0	1.05
Electricity (kWh)	220	60	145	225
Fuel (10 ⁶ kJ)	7.5	3.3	2.5	6.7
Cooling water (m ³)	6	-	5	8
Labor (Operators per shift)	3	3	3	3

(1) Platinum at 7,000 US\$ kg.

Remarks:

- (a) Depending on the ethylbenzene content in the feedstock, the following relative values are obtained as a first approximation:
 - Ethylbenzene content (% Wt) 10 20 30
 - Battery limits investments .. 0.85 1 1.15
 - LHSV h⁻¹ .. 0.75 1 1.25
- (b) If from a single feedstock (ethylbenzene content 20% Wt) it is desired to produce either *p*-xylene alone or a mixture of *o*- and *p*-xylenes, the following relative values are obtained:
 - *c*-xylene *p*-xylene ratio 1.0 0.25 0

TABLE 4.16 c
ISOMERIZATION OF XYLEMES. "MARUZEN" PROCESSES. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 100.000 t/year of *p*-XYLENE

Ethylbenzene content of feedstock i% Wt)	5	20
Investments		
Battery limits investments (10^6 US\$)	8.8	14.9
Initial catalyst loads (10^3 US\$)	0.25	0.35
Material balance per ton of <i>p</i>-xylene		
C ₈ cut feedstock (t)		
To isomerization	7.3	7.6
To loop	1.17	1.22
Fuel gas (t)	0.015	0.025
Heavy aromatics (t)	0.10	0.12
Light aromatics (t)	0.14	0.20
Consumption per ton of <i>p</i>-xylene		
Catalyst (US\$)	4.4	5.3
Utilities		
LP steam (t)	(-)2.0	(-)2.1
MP steam (t)	1.30	1.35
Electricity (kWh)	45	65
Fuel (10^6 kWh)	0.01	0.02
Cooling water (m ³)	25	25
Process water (m ³)	0.15	0.15
Labor (Operators per shift)	3	3

4.4.2.3 Economic data

Tables 4.16 a, b and 4.16 c provide some economic data on the isomerization processes employing noble metal base catalysts, and on techniques operating in the absence of hydrogen, including the Maruzen process in particular, for which only data concerning the crystallization/isomerization unit are usually available.

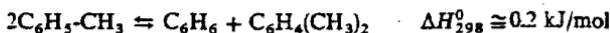
4.4.3 Toluene dismutation

This technique, whose industrial development is recent, serves to increase the availability of benzene and of mixed xylenes, at the expense of toluene. Combined with the separation of *p*-xylene by crystallization or adsorption, or with isomerization, it can be used to produce additional quantities of *o*- and *p*-xylenes without increasing the reformate tonnage to be treated.

4.4.3.1 Reactions

On the industrial scale, the toluene disproportionation reaction is carried out in the vapor or liquid phase, in the presence of a solid catalyst. The catalyst systems employed

were originally of the Friedel-Crafts type, silica aluminas, dual-functional or zeolites. The main reaction is the following:



If trimethylbenzenes are also present in the feed, the following *transalkylation* reaction occurs simultaneously:



This conversion can be exploited to adjust the benzene to xylenes ratio by introducing C₉ aromatics, which are separated during the treatment of the aromatic C₈ cut. Although hydrogen is not theoretically necessary, its presence limits coke formation, especially for vapor phase operations. These coke deposits on the catalyst require regeneration and hence operation in cycles.

Several side reactions may also take place:

- (a) Dealkylation of toluene to benzene and methane.
- (b) Disproportionation of xylenes to toluene and trimethylbenzenes, if the C₉ aromatics content is initially low.
- (c) Disproportionation of trimethylbenzenes to xylenes and durene (1,2,4,5-tetramethylbenzene).

From the thermodynamic standpoint, Figure 4.24 shows the change in the equilibrium molar composition at 750°K of the mixture of methylbenzenes produced, in accordance with the type of feedstock. The variable is in fact the ratio between the methyl groups and the initial benzene rings, ranging from 1 for toluene alone to 2 for xylenes.

According to Fig. 4.24, in the case of pure toluene, the residual content of this compound in the mixture obtained is 42 per cent at equilibrium. Hence the maximum

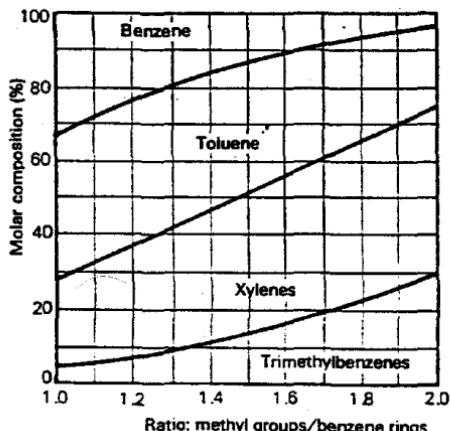


Fig. 4.24. Molar composition of methylbenzenes at equilibrium at 750°K.

once-through conversion is necessarily less than 58 per cent, requiring the recycle of large amounts of unconverted reactant for the units. These calculations do not account for the influence of the ethyl groups (ethylbenzene and ethyltoluene), because their presence does not significantly change the compositions at equilibrium.

4.4.3.2 Processes

Three main techniques have already been or are undergoing industrialization. Two of them operate in the vapor phase, and the third in the liquid phase.

A. Vapor phase toluene dismutation processes

These processes are the Atlantic Richfield Co. (ARCO) "xylene plus" process, operated since 1968 in Houston, Texas, and Toyo Rayon's Tatoray process, commercialized with the assistance of UOP.

In the Arco technique, conversion takes place in the absence of hydrogen, at a pressure close to atmospheric conditions ($0.2 \cdot 10^6$ Pa absolute) and a temperature that rises gradually during the run from 480 to 520°C. Subsequently, the catalyst, similar to those employed in catalytic cracking, which is a modified silica-alumina (mordenite doped with nickel) without noble metal, is rapidly poisoned by the coke, and must therefore be regenerated frequently. The moving bed technology is therefore employed.

In the Tatoray process, the H₂ to hydrocarbon mole ratio at the reactor inlet is between 5 and 20, and the hydrogen concentration in the recycle gases is greater than 70 per cent volume. The catalyst, called T81, is a zeolite with a transition metal. It operates at $3 \text{ to } 4 \cdot 10^6$ Pa absolute, at a temperature of about 410°C at the beginning of the run, and 470°C at the end. The regenerations, performed by combustion of the coke deposits by a 98/2 per cent volume mixture of nitrogen and oxygen, are less frequent due to the presence of hydrogen, and overall catalyst life is longer than two years. It is also possible to operate in a fixed bed. The existence of ethyl groups may also exert a detrimental effect on catalyst activity.

In these two versions, the conversion flow sheet (Fig. 4.25) is as follows:

- (a) The fresh and recycle toluene feed, with recycle and make-up hydrogen added, is preheated by heat exchange with the reactor effluent and passage through a furnace. The products obtained, previously cooled, are first subjected to flash to separate the hydrogen gas and recycle it after purge and recompression. The separation train then comprises a stabilization column, followed by benzene distillation, with clay treating if necessary, and that of toluene and xylenes. Unconverted trimethylbenzenes can also be recovered to recycle them and add them to a fresh aromatic C₉ feed, which is itself added to the toluene feed.
- (b) Depending on the process, and in the most favorable conditions, the yield of the operation reaches 95 to 97 molar per cent of benzene and xylenes. It lies closer to 90 to 92 molar per cent in practice.
- (c) By exploiting the transalkylation of trimethylbenzenes, it is theoretically possible to vary the xylenes to benzene ratio in wide proportions, and thus to adjust the output of the facilities to match market needs. The maximum xylene yield, nearly 40 per cent (mol) in the reactor effluent, is obtained with an initial trimethylbenzenes concentration of about 50 per cent.

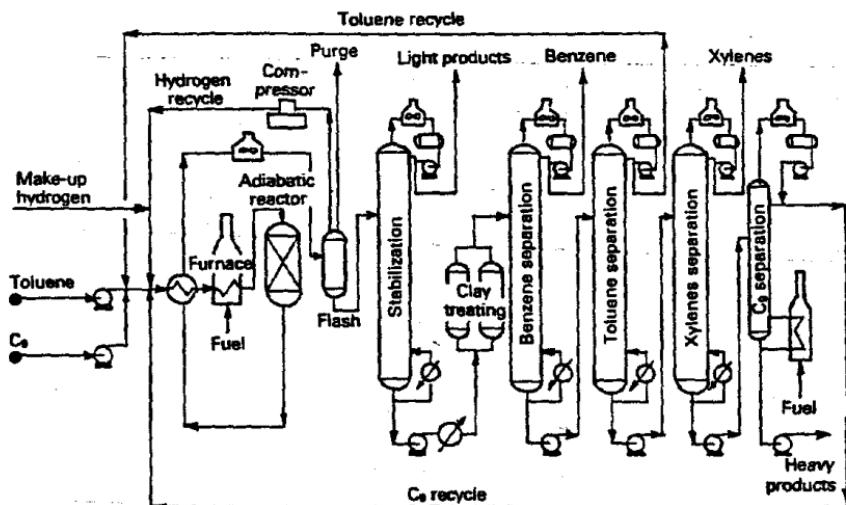


Fig. 4.25. Toluene dismutation. Tatoray process.

B. Liquid phase toluene dismutation

Certain zeolites display specific properties for the treatment of aromatics. *Mobil Chemical* uses them as catalysts (designated AP) to conduct the benzene dismutation reaction in moderate operating conditions, by the Mobil LTD (Mobil Low Temperature Disproportionation) process. Conversion takes place in the liquid phase, in the absence of hydrogen, at a pressure of $4.5 \cdot 10^6$ Pa absolute, and a temperature that is raised progressively with time from 260 to 315°C, to maintain catalyst activity.

The catalyst system a ZSM5 zeolite, which operates with a LHSV of 1.5 h^{-1} , has an overall life of 1.5 years. Infrequent intermediate regenerations by controlled combustion are required to remove the coke deposits formed. These operations are carried out when the reaction temperature reaches 315°C.

The flow sheet principle is similar to those of vapor phase techniques, with the additional possibility of recycling the trimethylbenzenes. The aromatics yield of the operation is greater than 95 molar per cent.

4.4.3.3 Economic data

The dismutation of toluene is similar to hydrodealkylation from the technical and economic standpoints. It offers the following advantages:

- (a) Simultaneous and flexible production of benzene and xylenes.
- (b) Higher aromatics yields.

- (c) No or low hydrogen consumption, which means lower compression costs (investment and energy expenditure).
- (d) More moderate operating temperature and pressure.

On the other hand, it presents the following drawbacks:

- (a) Recirculation of large volumes of unconverted toluene, increasing investment.
- (b) More complex separation train.

Table 4.17 lists the economic characteristics of the Tatoray and ARCO processes.

TABLE 4.17
TOLUENE DISMUTATION. ECONOMIC DATA
(France conditions, mid-1986)

Process	Tatoray		ARCO		
Mole % of C ₉ aromatics in feedstock	4	20	0	40	60
Xylenes/benzene mole ratio	1	2	1	5	7.5
Feedstock capacity (t/year)	100,000	135,000	100,000	190,000	300,000
Battery limits investments (10 ⁶ US\$) Initial catalyst loads (10 ⁶ US\$)	10.5 0.7 ⁽¹⁾	14.0 0.9 ⁽¹⁾	13.7 0.3	15.8 0.35	17.5 0.45
Material balance					
Feedstock					
Toluene (t)	1.000	1.000	1.000	1.000	1.000
C ₉ aromatics (t)	0.050	0.330	—	0.870	1.960
Make-up hydrogen (100%) (kg)	5	5	—	—	—
Products					
Benzene (t)	0.425	0.345	0.390	0.225	0.250
Xylenes (t)	0.585	0.940	0.530	1.520	2.550
C ₉ aromatics (kg)	15	25	45	30	45
Light compounds (kg)	30	25	35	95	115
Consumption per ton of feedstock toluene					
Utilities					
Steam (t)	1.5	2.1	—	—	—
Electricity (kWh)	120	170	70	95	125
Fuel (10 ⁶ kJ)	2.9	4.6	7.1	10.0	15.5
Cooling water (m ³)	3	4	110	180	245
Catalyst (US\$))	1.8	1.8	0.9	1.0	1.4
Labor (Operators per shift)	2	2	2	2	2

(1) Estimated life 3 years.

4.5 AROMATIC LOOP, SIMPLIFIED BALANCE

The production schemes shown in Section 4.1 may comprise an aromatic loop to maximize the production of *o*- and *p*-xylenes at the expense of *m*-xylene. The two variants in Fig. 4.2 are resumed in Figs. 4.26 a and 4.26 b, which show only the units of the aromatic loop. This loop may or may not be preceded by ethylbenzene separation, as required.

4.5.1 Data and parameters of the balance

The following products are produced:

$$\begin{aligned} Q_o &= \text{*o*-xylene,} \\ Q_p &= \text{*p*-xylene,} \\ \text{Possibly } S &= \text{solvents.} \end{aligned}$$

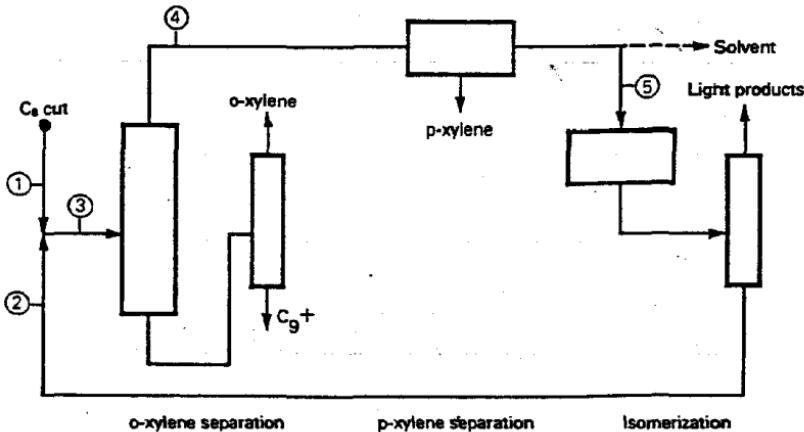


Fig. 4.26 a. Aromatic loop. Variant A.

Material Balance (Feedstock = 1)

Line	1	2	3	4	5
EB	X_E	q_E	$X_E + q_E$	$X_E + q_E$	$X_E + q_E$
OX	X_O	$0.22 q_X$	$X_O + 0.22 q_X$	$(X_O + 0.22 q_X)(1 - \rho_O)$	$(X_O + 0.22 q_X)(1 - \rho_O)$
PX	X_P	$0.22 q_X$	$X_P + 0.22 q_X$	$X_P + 0.22 q_X$	$(X_P + 0.22 q_X)(1 - \rho_P)$
MX	X_M	$0.56 q_X$	$X_M + 0.56 q_X$	$X_M + 0.56 q_X$	$X_M + 0.56 q_X$
Total	1	$q_E + q_X$	$1 + q_E + q_X$	$1 + q_E + q_X - \frac{Q_o}{Q_i}$	$1 + q_E + q_X - \frac{Q_o + Q_p}{Q_i}$

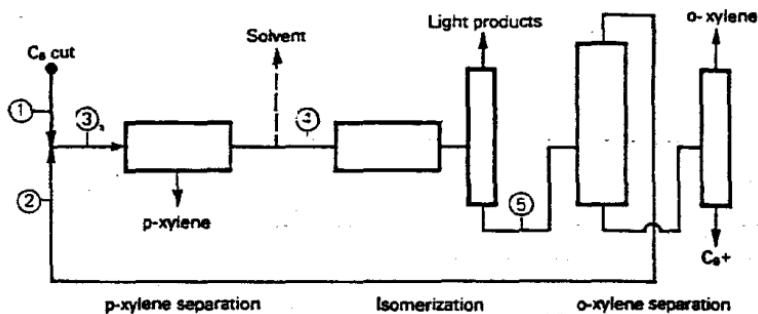


Fig. 4.26 b., Aromatic loop. Variant B.

Material Balance (Feedstock = 1)

Line	1	2	3	4	5
EB	X_E	q_E	$X_E + q_E$	$X_E + q_E$	q_E
OX	X_O	$0.22 q_X (1 - \rho_O)$	$X_O + 0.22 q_X (1 - \rho_O)$	$X_O + 0.22 q_X (1 - \rho_O)$	$0.22 q_X$
PX	X_P	$0.22 q_X$	$X_P + 0.22 q_X$	$(X_P + 0.22 q_X) (1 - \rho_P)$	$0.22 q_X$
MX	X_M	$0.56 q_X$	$X_M + 0.56 q_X$	$X_M + 0.56 q_X$	$0.56 q_X$
Total	1	$q_E + q_X - \frac{Q_O}{Q_i}$	$1 + q_E + q_X - \frac{Q_O}{Q_i}$	$1 + q_E + q_X - \frac{Q_O + Q_P}{Q_i}$	$q_E + q_X$

The feedstock entering the loop is assumed to be known:

X_E = per cent weight ethylbenzene,

X_O = per cent weight *o*-xylene,

X_P = per cent weight *p*-xylene,

X_M = per cent weight *m*-xylene.

The residual contents of C₉- and non-aromatics are ignored.

Production is determined by two main parameters:

ρ_P = *p*-xylene yield of the separation operation: this depends on the process employed (adsorption, crystallization), and its value can be determined accordingly,

ρ_O = *o*-xylene yield of the distillation operation: this parameter depends essentially on the Q_O/Q_P ratio and is calculated by balance.

The balance can be adjusted by two other parameters:

Q_i = amount of C₈ cut sent to the loop,

R = recycled isomerization effluent.

The writing can be simplified by considering the reduced recycle amount r , itself divided into two parts:

$$q_E = \text{reduced amount of ethylbenzene recycled}, \\ q_X = \text{reduced amount of xylenes recycled},$$

and corresponding to a C₈ cut feed make-up of 1.

4.5.2 Hypotheses for the balance around isomerization

The simplified isomerization balance has two distinct terms:

- (a) Ethylbenzene conversion to xylenes: α (estimated at 60 per cent), the remainder being recycled (q_E).
- (b) Isomerization of converted ethylbenzene and xylenes, yielding the following average composition⁽⁴⁾:
 - . o-xylene 22 per cent weight.
 - . p-xylene 22 per cent weight.
 - . m-xylene 56 per cent weight.

The xylene isomerization yield is 97 per cent, the remainder being cracked with the formation of lighter products (benzene, gas).

4.5.3 Production of o- and p-xylenes, variant A

a. Material balance (Fig. 4.26 a)

The balance is calculated for a unitary amount of feed.

b. Isomerization balance

Ethylbenzene conversion:

$$\text{EB recycled} : (1 - \alpha)(X_E + q_E) = q_E \quad (4.1)$$

Hence

$$\text{EB converted} : \alpha(X_E + q_E) = X_E \quad (4.2)$$

Isomerization of converted ethylbenzene and xylenes:

$$[X_E + (X_O + 0.22q_X)(1 - \rho_O) + (X_P + 0.22q_X)(1 - \rho_P) + X_M + 0.56q_X] \\ \times 0.97 = q_X \quad (4.3)$$

c. Relative production of o- and p-xylenes

$$\frac{(X_O + 0.22q_X)\rho_O}{(X_P + 0.22q_X)\rho_P} = \frac{Q_O}{Q_P} \quad (4.4)$$

(4) For greater accuracy, refer to the diagram in Fig. 4.21, which gives the equilibrium composition as a function of temperature.

d. Resolution of the system of equations

Equation (4.2) gives q_E .

Equations (4.3) and (4.4) contain two unknowns ρ_o and q_x . They are of the second degree, but the product $(X_o + 0.22q_x)\rho_o$ can be eliminated between the two equations, leaving one equation for q_x .

Equation (4.4) gives ρ_o .

The production of *p*-xylene $Q_p = Q_i(x_p + 0.22q_x)\rho_p$ serves to calculate Q_i .

Recycle is $R = Q_i \cdot r = Q_i(q_E + q_x)$.

4.5.4 Production of *o*- and *p*-xylenes, variant B

Figure 4.26 b gives the material balance.

Equations (4.1) and (4.2) remain unchanged.

Equations (4.3) and (4.4) become:

$$[X_E + X_o + 0.22q_x(1 - \rho_o) + (X_p + 0.22q_x)(1 - \rho_p) + X_M + 0.56q_x] \times 0.97 = q_x \quad (4.3')$$

$$\frac{0.22q_x\rho_o}{X_p + 0.22q_x)\rho_p} = \frac{Q_o}{Q_p} \quad (4.4')$$

The equations are resolved in the same way as above.

The difference between these two variants is related to the separation of *o*-xylene, which takes place on a smaller feed, but with a higher yield. This variant is especially interesting if the demand for *o*-xylene is much smaller than the demand for *p*-xylene. Thus a maximum of *o*-xylene can be isomerized to *p*-xylene, with only a part of the isomerization effluent sent for distillation.

Remark. The foregoing calculations are valid for situations normally encountered, in which demand for *p*-xylene is greater than for *o*-xylene. If not, the value of ρ_o obtained may be higher than 1. A technically feasible maximum value of ρ_o is therefore set, and the value of ρ_p that helps to adjust the balance is calculated. Low values of ρ_o or ρ_p may correspond to low yield operation, or to the diversion of part of the effluent, which therefore does not go to the separation unit.

4.6 USES AND PRODUCERS

Tables 4.18 and 4.19 provide an indication of the average commercial specifications for benzene, toluene and xylenes, in mixtures or individually.

Tables 4.20, 4.21 and 4.22 list the uses, sources, production, capacities and consumption for these different products in 1984, for Western Europe, the United States, Japan and the world. Some data are given for 1986.

TABLE 4.18
AVERAGE COMMERCIAL SPECIFICATIONS OF BTX

Product	Benzene	Toluene	Mixed xylenes	
Distillation range (°C)	0.6-0.8	0.6-0.8	5	10
Melting point (°C)	5.4-5.5	—	—	—
Specific gravity (15.5/15.5°C)	0.883-0.886	0.869-0.872	0.860-0.870	0.860-0.875
Color (Pt-Co) max.	20	20	20	20
Acid wash color max.	2	2	6	6
Free acidity	None	None	None	None
Total sulfur (ppm) max.	1	4	10-15	10-15
H ₂ S.....	None	None	None	None
Non-aromatics (% Wt) max.	0.2	0.2	—	—
Benzene/toluene (% Wt) max.	0.05	0.2	—	—
C ₈ aromatics (% Wt) max.	—	0.02	—	—
Residue (mg/100 ml) max.	2	5	10	10

TABLE 4.19
AVERAGE COMMERCIAL SPECIFICATIONS OF XYLEMES

Characteristics	<i>o</i> -xylene		<i>p</i> -xylene		<i>m</i> -xylene
Purity (% Wt)	96.0	99.0	99.1	99.4	95.4
Distillation range (°C)	2	1	1	1	1
Melting point (°C)	—	-25.5	—	13.1	—
Specific gravity (15.5/15.5°C)	≈0.885	0.882-3	0.867-8	0.865-6	≈0.869
Color (Pt-Co) max.	20	20	20	20	20
Acid wash color max.	2	2	1	1	—
Bromine number max.	200	200	200	200	—
Total sulfur (ppm) max.	10-15	10-15	10-15	10-15	10-15
Free acidity	None	None	None	None	None
Copper corrosion	None	None	None	None	Passable
C ₈ aromatics (% Wt) max.	3.0	{ 0.9	0.8	0.55	} 4.4
Other aromatics (% Wt) max.	0.8		0.1	0.05	
Non-aromatics (% Wt) max.	0.2	0.1	—	—	0.2

TABLE 4.20
BENZENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
Alkylbenzenes	5	3	3	5
Chlorobenzenes	2	3	3	3
Cumene (phenol)	21	19	13	19
Cyclohexane	15	15	21	17
Ethylbenzene (styrene)	47	55	55	49
Maleic anhydride	3	—	2	2
Nitrobenzenes (aniline)	6	5	3	4
Miscellaneous	1	6	6	1
Total	100	100	100	100
Sources (% product)				
Catalytic reforming	15	50	34	29
Coal	7	5	21	12
Hydrodealkylation	16	24	3	20
Steam cracking	62	21	42	39
Total	100	100	100	100
Production (10 ⁶ t/year)	5.0	4.5	2.2	17.3
Capacity (10 ⁶ t/year)	6.8	7.3	2.8	24.8
Consumption (10 ⁶ t/year)	5.3	5.3	2.1	17.5

(1) Biphenyl, fumaric acid, resorcinol.

(2) In 1986 the worldwide production capacity of benzene was $25.7 \cdot 10^6$ t/year with the following distribution:

United States	7.4	Western Europe	6.8	Middle East	0.5
Canada	0.8	Eastern Europe	4.4	Japan	2.7
Latin America	1.3	Africa	0.2	Asia and Far East	1.6

TABLE 4.21
TOLUENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
Chemicals	98	61	65	81
Gasoline	2	39	35	19
Total	100	100	100	100
Chemical uses (% product)				
Disproportionation	15	—	—	12
Hydrodealkylation	36	78	18	50
Caprolactam	4	—	—	2
Phenol	6	1	—	2
Solvent	21	6	60	22
Toluene diisocyanates	8	12	10	7
Miscellaneous	10	3	12	5
Total	100	100	100	100
Sources (% product)				
Catalytic cracking	70	86	43	77
Coal	1	1	10	4
Steam cracking	29	13	47	19
Total	100	100	100	100
Production (10 ⁶ t/year)	2.2	2.4	0.8	9.3
Capacity (10 ⁶ t/year)	3.1	5.0	1.4	14.8
Consumption (10 ⁶ t/year)	2.4	2.9	0.8	9.5

(1) Benzoic acid, benzylchloride, cresols, p-methyl styrene, nitrotoluenes, phthalates.

(2) In 1986 the worldwide production capacity of toluene was $15.5 \cdot 10^6$ t/year with the following distribution:

United States	5.1	Western Europe	3.1	Middle East	0.5
Canada	0.7	Eastern Europe	2.7	Japan	1.4

TABLE 4.22
PRODUCTION AND CONSUMPTION OF MIXED XYLEMES, *o*-XYLENE AND *p*-XYLME IN 1984

Geographic areas	Western Europe			United States			Japan			World		
Uses (% product) of mixed xylenes												
Isomers	84			95			86			83		
Solvents	16			4			13			13		
Miscellaneous ⁽¹⁾	—			1			1			4		
Total	100			100			100			100		
Sources (% product) of mixed xylenes												
Catalytic reforming	73			97			82			85		
Coal	1			—			2			1		
Disproportionation	10			—			—			5		
Steam cracking	16			3			16			9		
Total	100			100			100			100		
Products ⁽³⁾	Mixed xylenes	<i>o</i> -xylene	<i>p</i> -xylene	Mixed xylenes	<i>o</i> -xylene	<i>p</i> -xylene	Mixed xylenes	<i>o</i> -xylene	<i>p</i> -xylene	Mixed xylenes	<i>o</i> -xylene	<i>p</i> -xylene
Production (10^6 t/year)	1.9	0.53	0.91	2.8	0.32	1.94	1.4	0.15	0.62	9.6	1.4	3.9
Capacity (10^6 t/year) ⁽²⁾	2.8	0.72	1.15	5.1	0.47	2.32	1.7	0.22	0.67	15.0	2.6	5.9
Consumption (10^6 t/year)	2.2	0.60	0.85	2.8	0.40	1.64	1.3	0.15	0.70	9.4	1.4	3.9

(1) Gasoline.

(2) In 1986 the worldwide production capacity of mixed xylene was $15.6 \cdot 10^6$ t/year with the following distribution:

United States ... 5.1 Western Europe ... 2.8 Middle East 0.3

Canada 0.4 Eastern Europe.... 2.6 Japan 1.7

Latin America..... 1.1 Africa 0.3 Asia and Far East .. 1.3

(3) 99% of *o*-xylene is used to synthesize phthalic anhydride and the remaining 1% shared among solvents, lubricant additives and bactericides.

99% of *p*-xylene is converted to monomers for polyesters (in the United States 57% to dimethylterephthalate and 42% to pure terephthalic acid) and the remaining 1% is used to produce herbicides (dimethyltetrachloroterephthalate), pesticides, solvents, *p*-xylene...

Production capacities of pure *m*-xylene in 1984 were the following: in Western Europe = $40 \cdot 10^3$ t/year (Italy, *Saras Chimica, Sarach*); in the United States = $80 \cdot 10^3$ t/year ($105 \cdot 10^3$ t/year in 1985, *Amoco Chemicals, Texas City, Tx.*) and in Japan = $55 \cdot 10^3$ t/year (*Mitsubishi Gas Chemical, Mizushima*). *m*-xylene is mainly used to produce isophthalic and to a lesser extent 5-t-butyl-2,4,6-trinitro *m*-xylene (perfume), isophthalonitrile (fungicide, guanamine resin), *m*-xylene diamine, isophthaloylchloride, *m*-toluic acid (insecticide), *m*-xylene diamine, xylenols, 2,4- and 2,6-xylidene (dyes)...

Chapter 5

ACETYLENE

5.1 THEORETICAL CONSIDERATIONS

Acetylene $\text{HC} \equiv \text{CH}$ ($d_4^{20} = 1.089$ ⁽¹⁾, $\text{bp}_{1.013} = 87.8^\circ\text{C}$) is a flammable gas, soluble in acetone and many polar solvents. It is an unstable compound whose explosive decomposition can occur spontaneously if its partial pressure in a mixture exceeds $0.14 \cdot 10^6 \text{ Pa}$ absolute.

Of all hydrocarbon compounds, acetylene is the one whose formation is the most endothermic. A glance at Fig. 2.1 (Section 2) shows that it is thermodynamically possible to prepare it from all the saturated or olefinic hydrocarbons, which become unstable in relation to it above 1200°K .

5.1.1 Thermodynamic aspects

Acetylene synthesis is dominated by three major problems associated with its thermodynamic properties.

A. *Choice of raw material*

Acetylene can be produced from coal or from hydrocarbons. The coal route, involving calcium carbide as an intermediate, was the only one practised industrially until the late 1930s, when acetylene was the basic product for the organic chemical industry. Since about 1940, coal has been supplanted by methane and other hydrocarbons. Methane is a widely available raw material: ethane, propane and butane are more advantageously converted to the corresponding olefins than to acetylene.

As shown by Table 5.1, the acetylene yield declines as the molecular weight of the hydrocarbon increases. The quantity of heat required also decreases, but this advantage is accompanied by difficulties of a kinetic nature: many by-products are formed.

(1) Specific gravity, 68.0-39.2

TABLE 5.1
PRODUCTION OF ACETYLENE FROM LIGHT HYDROCARBONS
(AUTOTHERMAL OXYGEN REACTOR, PREHEATING 400°C)

Feedstock	CH ₄	C ₂ H ₆	C ₃ H ₈
Acetylene yield			
% Wt of unburned hydrocarbon	55	48	40
% Wt of feedstock	23	26	24
Heat of reaction (kJ/mol C ₂ H ₂)	418	334	318
Sensible heat of reactants (kJ/mol C ₂ H ₂)	920	552	527
Total heat (kJ/mol C ₂ H ₂)	1,338	886	844
Mole ratio O ₂ /C ₂ H ₂	3.9	3.1	2.6

B. Transfer of energy required for the reaction at the elevated temperature defined by thermodynamics

Since the energy of activation of the acetylene formation reaction is greater than that of its decomposition reaction quickly raising the reaction medium to elevated temperature results in the increased production of acetylene. The following heating methods are used to achieve this:

- (a) Contact with a hot solid: the gas is introduced into an externally heated tube, or heat is transferred indirectly by passage over a solid raised to high temperature.
- (b) *In situ* production of combustion gas and partial oxidation of the feedstock.
- (c) Electric discharge.
- (d) Use of a plasmogenic fluid.

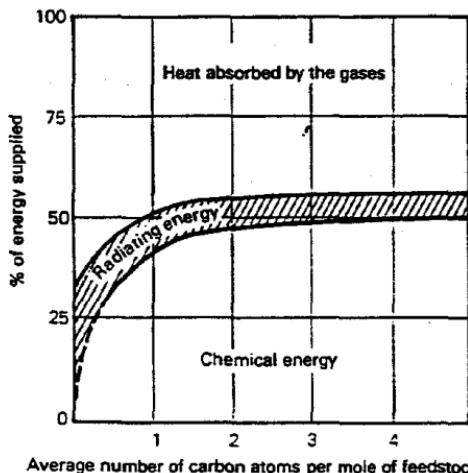


Fig. 5.1. Heat balance of an acetylene production reactor.

C. Very short residence time to limit decomposition

The analysis of changes in the reaction medium with time shows that the reaction must be interrupted to prevent the acetylene formed from decomposing. This is achieved by rapidly cooling the medium by the injection of a cold fluid (quench). To ensure that this necessary operation does not result in an excessive loss of energy, recent techniques attempt to limit the drop in temperature by causing the heat of the system to be absorbed by a hydrocarbon, which can produce upgradable products (ethylene) by steam cracking. As shown in Fig. 5.1, 50 to 60 per cent of the energy supplied in an acetylene production unit is dissipated in the quench operation and can be recovered at a high temperature, provided that a number of acetylene extraction and purification problems can be solved.

5.1.2 Practical consequences

Industrial processes for the manufacture of acetylene from hydrocarbons are distinguished by the heating technique.

(a) Thermal processes with direct heat transfer:

- . Electric arc: *Hüls, Du Pont.*
- . Plasma : *Du Pont, Hüls, UCC (Union Carbide Co.), Cyanamid.*

(b) Thermal processes with indirect heat transfer:

- . Contact masses: *Wulff.*
- . Steam at 2000°C: *Kureha.*

(c) Autothermal processes in which the combustion of part of the feed provides the heat required for the cracking reaction of the remainder. Among these techniques are the BASF (*Badische Anilin und Soda Fabrik*) technique (Sachsse Bartholomé) starting with naphthas, processes using a submerged-flame, including BASF using crude oil and SBA using methane, and the Hoechst HTP (High Temperature Pyrolysis) technology, in which cracked gases are burned to furnish the heat required for the reaction.

5.2 ACETYLENE MANUFACTURE FROM COAL CALCIUM CARBIDE PROCESS

5.2.1 Reactions involved

In this method, lime (calcium oxide) is reduced by carbon (coke or anthracite):



The process takes place in an electric furnace between 2200 and 2300°C. The calcium carbide obtained is then hydrolysed to produce acetylene:



5.2.2 Process description

5.2.2.1 Calcium carbide manufacture

Calcium carbide is manufactured today in a closed furnace⁽²⁾ lined internally with refractory bricks and equipped with three electrodes positioned in a triangular layout, fabricated *in situ* with coke and lime fines from the processes (Sodeberg electrodes). These electrodes are suspended vertically above the furnace and introduced progressively into the lime/coal mixture, in which they cause partial fusion and mutual reaction. They are continuous, but usually have hollow cores to allow the injection of raw material fines from the feed or dust removal (Knapsack plant). They are supplied with three-phase a.c. power at a voltage of 100 to 250 V, with a current density less than 10 A/cm² of electrode surface area. Due to the reaction's poor energy efficiency, electricity consumption may be as high as 3.3 kWh/kg of carbide.

Calcium carbide in the molten state is drawn off from one or more (up to 6) tap holes in the base of the furnace. It is collected in crucibles, where it cools for one to two hours and is then emptied for subsequent crushing and screening (Fig. 5.2).

The production of calcium carbide is accompanied by the evolution of a large amount of carbon monoxide (400 m³/t). This gas contains on the average (per cent volume): CO = 70, CO₂ = 10, N₂ = 9, H₂ = 7 and CH₄ = 2, together with dust. Older installations burned it at the surface of the furnace, but modern units employ it as a fuel in auxiliary installations.

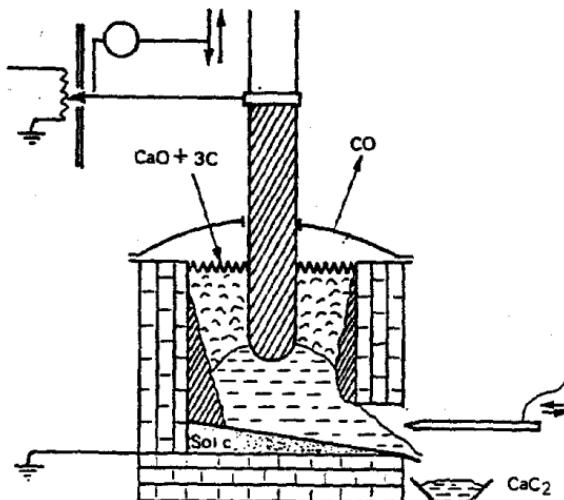


Fig. 5.2. Carbide furnace.

(2) Average unit power 50 MWe, maximum power 70 MWe.

5.2.2.2 Calcium carbide hydrolysis

This reaction is highly exothermic and requires stringent temperature control to prevent the acetylene from decomposing. Two types of unit are distinguished, called wet or dry generators, depending on whether the residual lime is extracted in the form of a milk containing about 10 per cent weight of lime or in the form of hydrated lime without excess water. Wet generators are mainly used to produce dissolved acetylene: they include systems for dropping carbide into water (carbide-to-water system), falling water (water-to-carbide system) and contact (carbide immersion or water displacement). Dry generators are chiefly used in large-capacity installations for the chemical industry; the water to calcium carbide weight ratio is about 1.1.

Figure 5.3 illustrates a process to manufacture acetylene from calcium carbide. The carbide is introduced by a screw conveyor into a perforated horizontal cylinder housed in a concentric envelope. Water is sprayed inside the internal shell. The acetylene formed passes upstream through the screw conveyor to a scrubbing tower, where a new water spray carries off most of the solids conveyed by the gas. The residual lime and carbide impurities are removed by a screw conveyor to a sludge receiver. The acetylene is cooled to -10°C to condense most of the water. It is then purified by contact with dilute sulfuric acid in a liquid-liquid absorber, and then with sodium hypochlorite prepared by the action of chlorine on caustic soda, to remove impurities. The acetylene is then cooled to 0°C for the more complete separation of moisture. The final product nevertheless still contains 0.4 per cent by weight of water, which is suitable for most uses. More intensive dehydratation can be achieved by passage over silicagel.

The residual lime can be upgraded as a fertilizer or for the manufacture of cement, or recycled to the process. Recycle lime is raised to 1100°C by the burned gases from the electric furnace, cooled to around 180°C , and iron particles eliminated in a magnetic separator. Recycling cannot be complete, because it leads to the accumulation of impurities in the electric furnace. It is normally limited to a value between 40 and 60 per cent weight of the lime produced.

The manufacture of acetylene from calcium carbide is marked by the need to handle large amounts of solids. In fact, although the yield of the hydrolysis reaction is practically quantitative, the manufacture of 1 t of acetylene requires 3.1 t of carbide with a purity of 80 per cent weight.

5.3 ACETYLENE MANUFACTURE FROM HYDROCARBONS. THERMAL PROCESSES WITH DIRECT HEAT TRANSFER

5.3.1 Electric arc processes. The Hüls process (Figs. 5.4, 5.5 and 5.6)

The originality of the process resides in the use of a high-power (8200 kW) electric arc furnace supplied with direct current electricity. The Hüls arc furnace consists of a vertical tube surmounted by an injection chamber, into which the gas is introduced

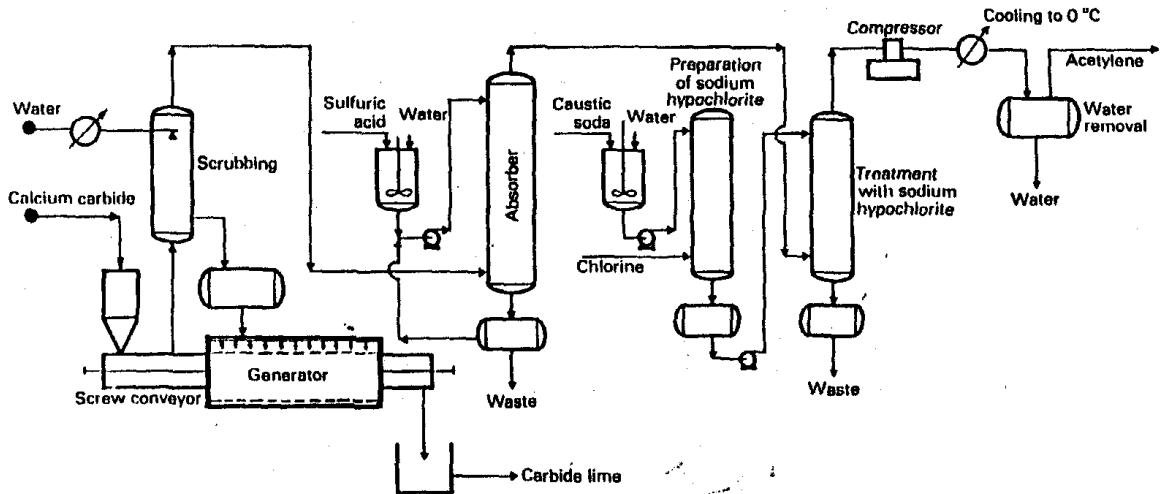


Fig. 5.3. Acetylene manufacture from calcium carbide.

tangentially to create a vortex motion designed to make the temperatures in the reactor uniform.

The main characteristics are the following:

Power	8500 kW
Voltage	7000 V
Current	1200 A
Quantity treated	2000 m ³ /h of gaseous hydrocarbons
Temperature	1000 to 1500°C
Field intensity	70 V/cm
Residence time	2/1000 s

The reactor is cooled by water circulation. Quench at the furnace exit is provided by water spray or by hydrocarbons, which are cracked into olefinic compounds.

The purification section comprises:

- Removal of carbon particles using a cyclone separator and water scrubber.
- Separation of aromatic compounds and heavy polymers by treatment with water and with an aromatic oil.
- Dissolution of most of the acetylene in water under pressure ($1.8 \cdot 10^6$ Pa absolute).

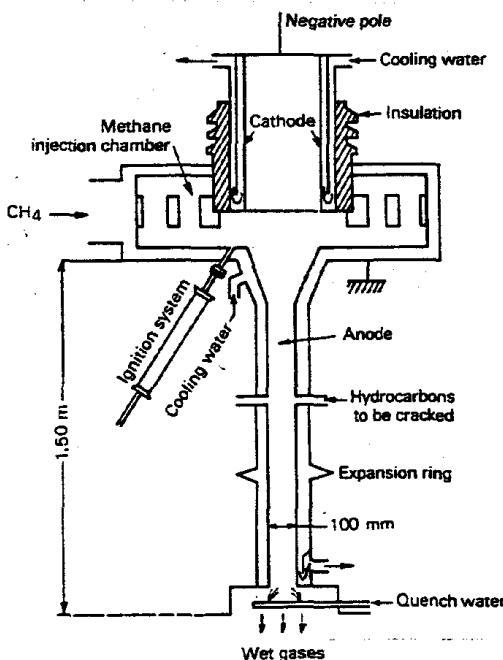


Fig. 5.4. Acetylene synthesis. 8500 kW arc furnace. Hüls process.

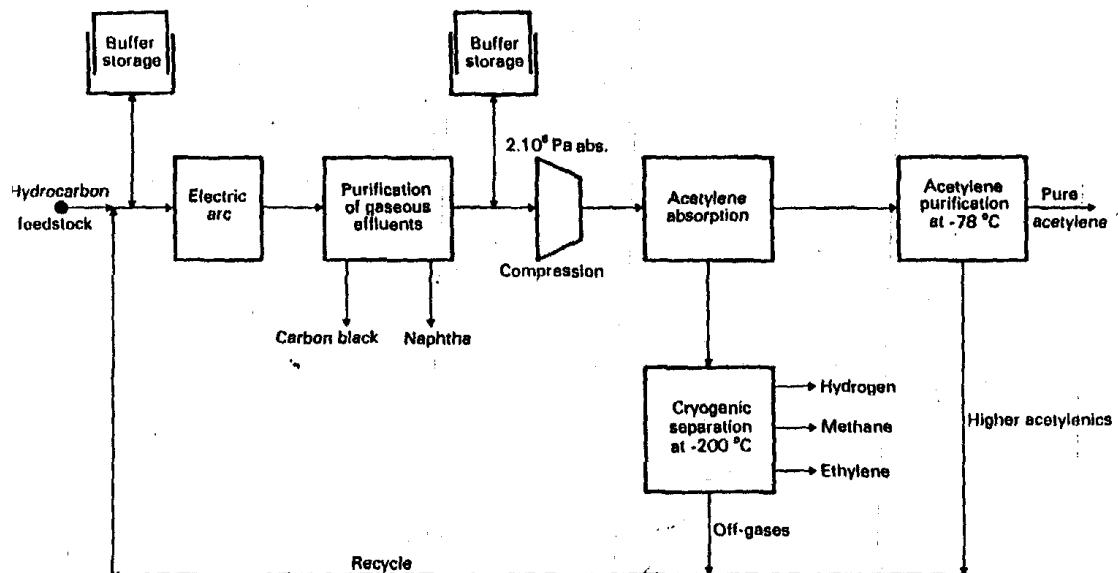


Fig. 5.5. Acetylene manufacture from hydrocarbons by electric arc treatment. Basic scheme.

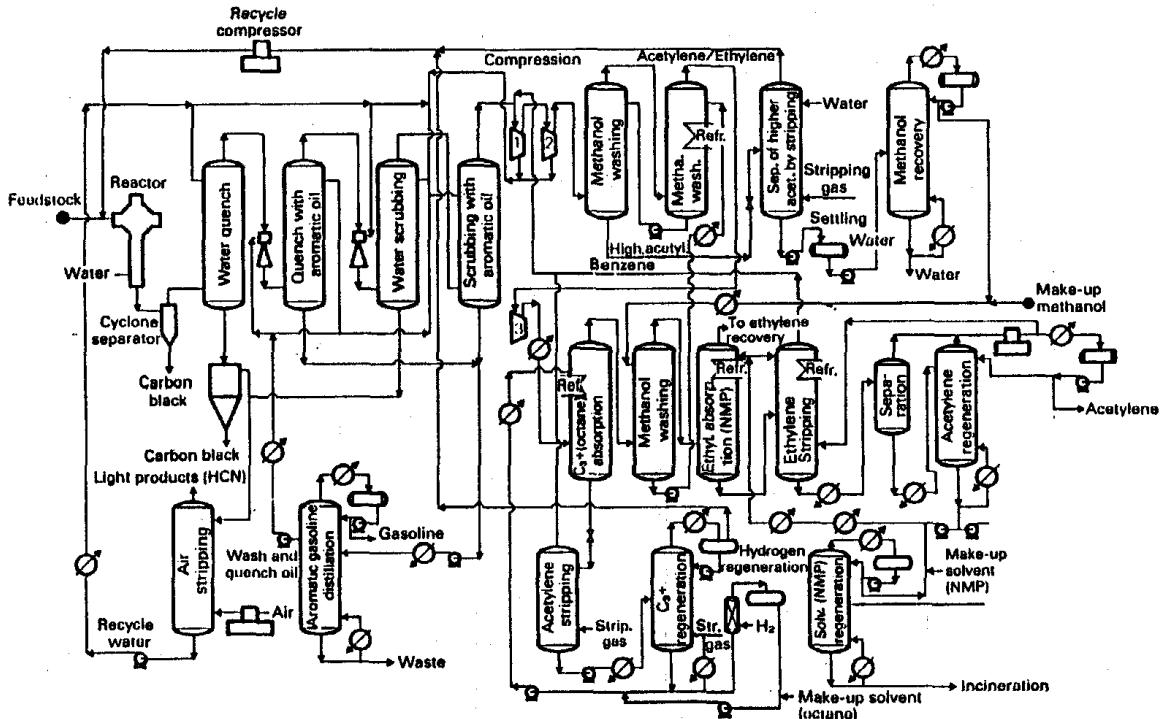


Fig. 5.6. Acetylene manufacture from hydrocarbons by electric arc treatment. Hills process.

- (d) Progressive decompression of this solution, which furnishes a gas containing 10 per cent volume of heavy acetylenic compounds, subsequently eliminated by cooling to -80°C , and finally by scrubbing with a methanol/benzene mixture.

The acetylene product collected has a purity of 97 per cent weight.

A wide variety of furnace charges are employed. The weight yield of acetylene produced from a medium-range naphtha is about 35 per cent. *Chemische Werke Hüls* has built a plant at Recklinghausen (West Germany) with 19 arc furnaces with a capacity of 120,000 t/year of acetylene, 50,000 t/year of ethylene and $420 \cdot 10^6 \text{ m}^3/\text{year}$ of hydrogen. The annual consumption of the plant is 1,440,000 MWh, or approximately that of a town with a population of 400,000.

5.3.2 Other electric arc processes

Various technologies employing an electric arc have been used to improve the *Hüls* process, by trying to reduce the cost of the electrical installations or to improve the heat transfer to the gas to be pyrolysed.

Du Pont de Nemours operated a 28,000 t/year plant employing the *Hüls* process, modified by the use of a rotating magnetic field. This unit, built in 1963, was shut down in 1968. *Romchim*, in Borzesti in Romania, operates an 8000 t/year plant with an electric arc process, employing the BASF N-methylpyrrolidone extraction process to recover the acetylene.

5.3.3 Plasma processes

The high temperatures required for the manufacture of acetylene can be obtained by thermal plasmas, using arc and high frequency systems. In arc systems, the ionization of a gas (argon, hydrogen etc.) is achieved by its passage through an electric arc ignited and maintained between a thermo-emissive cathode and an anode which serves as a nozzle. In high frequency systems, the gas is ionized by passage through a silica tube, which may be placed in a solenoid conveying a high frequency current, generally between 5 and 60 MHz. Several pilot plants have been tested in the United States, the URSS and West Germany.

Among the arc plasmas, those of *Hoechst* and *Hüls* employ hydrogen in a system supplied with hydrocarbons ranging from methane to crude oil. The acetylene and ethylene yield is as high as 80 per cent weight, with an H_2 to CH_4 molar ratio of 0.5. *Hüls* has developed an industrial pilot plant of this type in Marl, in West Germany, which will employ coal.

In the United States, *AVCO (Wulff-Acetylene Company)*, in cooperation with *GAF (General Anilin and Film Co.)*, has also built an experimental pilot plant to manufacture acetylene from coal with a high volatile matter content. The coal is fluidized in hydrogen produced in the process, and introduced into an electric arc. The cracked gases are quenched by a hydrocarbon stream. The effluent is rid of coal particles, compressed to $0.3 \cdot 10^6 \text{ Pa}$ absolute, treated with N-methylpyrrolidone to remove H_2S and HCN, and

then with caustic soda to remove CO_2 . It is then compressed to $1.5 \cdot 10^6$ Pa absolute, and again extracted with N-methylpyrrolidone to absorb the CS_2 , and then the acetylene.

In this process, the production of 1 t of acetylene consumes 2.5 t of coal and 8000 kWh of electricity.

5.4 ACETYLENE MANUFACTURE FROM HYDROCARBONS. THERMAL PROCESSES WITH INDIRECT HEAT TRANSFER

5.4.1 Wulff process (Figs. 5.7 and 5.8)

Since the first demonstration plant built in 1952 at Maywood, California, with a capacity of 500 t/year, operated by the *Wulff-Acetylene Company*, the process has grown considerably in the United States and in Western Europe. At present, for technical reasons connected with the excessive production of soot, and economic reasons stemming from the rising price of naphtha, most of these units have had to be shut down.

The reactor comprises a stack of carborundum pieces drilled with small-diameter holes to allow the gases to pass through. The assembly, surrounded by refractory bricks, is enclosed in a metal envelope. Furnace operation is cyclic. The refractory stack is first heated by the combustion in air of a fuel oil (feed or other fuel). The hydrocarbons to be cracked are then decomposed by absorbing the heat stored during the previous period. A gas chamber at each end of the furnace introduces and recovers the gases evolved during cracking. Openings for the introduction of the fuel are provided at the center, as well as a burner designed to build up the initial temperature when the installation is started up.

The cycle comprises four periods in practice:

- (a) Heating phase. The air enters the furnace through one of the ends (for example, right), is heated through the refractory bricks to 980 to 1100°C, and reaches the fuel injection chamber. Combustion raises the temperature to 1200 to 1370°C. The gases removed at the left exit at 315°C after having heated the refractory stack.
- (b) Cracking phase. The vaporized feedstock enters through the left and flows towards the right, up to the center, where the vapors are raised to 1200 to 1370°C. The cracked gases exit at the right at a temperature of 315°C. Residence time is about 0.1 s.
- (c) Heating phase. This is identical to the first, but the fluids flow in the reverse direction.
- (d) Cracking phase. This is identical to the second phase, with fluid flow reversed.

The cycle lasts one minute, and the carbon deposited is eliminated during the heating phases by combustion. Cracking can be conducted under vacuum (50 kPa absolute) or in the presence of steam.

The gases are quenched at the furnace exit by water or a water:hydrocarbon mixture, rid of tars (Cottrell electrostatic precipitator) and compressed before being sent to the

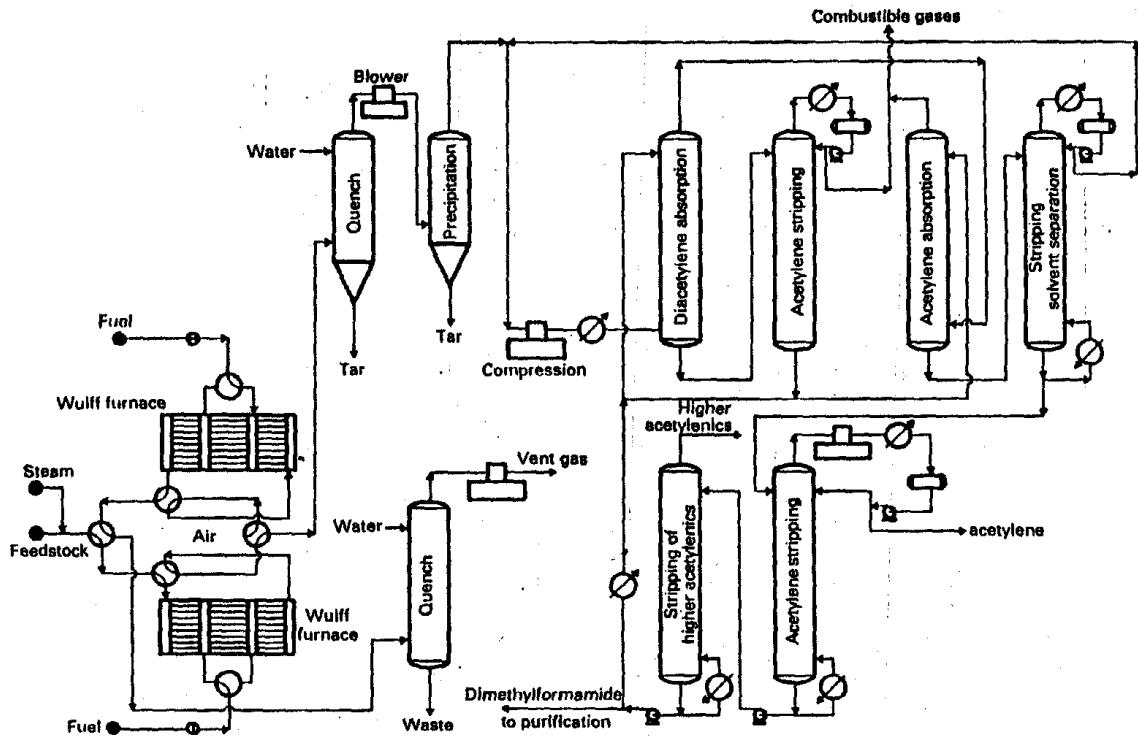


Fig. 5.7. Acetylene manufacture. Wulff process.

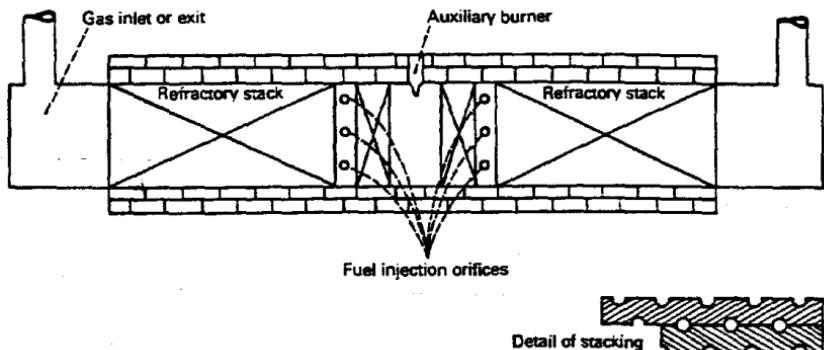


Fig. 5.8. Acetylene manufacture. Wulff process reactor.

purification section. This unit is designed to remove the heavy acetylenic compounds, such as diacetylene, by solvent treatment (for example with acetonylacetone). The acetylene is then absorbed selectively and thus separated from the light gases employed as a fuel or a hydrogen source. A stabilization column eliminates the last traces of carbon monoxide, ethylene, methane and hydrogen. After the acetylene is removed by heating, the absorption solvent is regenerated by separating methylacetylene and various heavy products. As required, the ethylene may or may not be recovered from the gases leaving the acetylene absorber, by a cryogenic method or by absorption.

The feedstocks employed may range from ethane to gas oil. The most favorable today for the process economics is ethane.

5.4.2 Kureha process

Kureha crude oil steam cracking technology was developed jointly with *Union Carbide* for the manufacture of ethylene (see Section 2.1.3.4). By operating at very high temperature and with very short contact times (0.003 to 0.010 s), approximately equal amounts of acetylene and ethylene can be produced from a number of crude oils. This is illustrated by Table 5.2 for Indonesian and Arabian crudes, cracked in the presence of steam at 2000°C, in a steam to feed weight ratio of about 3, and with residence time of 0.005 s. In these conditions, the temperature at the reactor exit before quench reaches 1150°C.

Figure 5.9 provides a glance at the flow sheet of the Kureha process. The crude oil, preheated to 300°C by heat exchange with the combustion flue gases, is introduced into the reactor, into the top of which a stream of superheated steam at 2000°C is injected. This is produced in two furnaces of the regenerative type, lined internally with ceramic and packed with pebbles partly impregnated with zirconium oxide in the high temperature zone, and partly with alumina in the lower temperature. The steam in the two generators circulates in countercurrent flow with the air combustible gas mixture. The

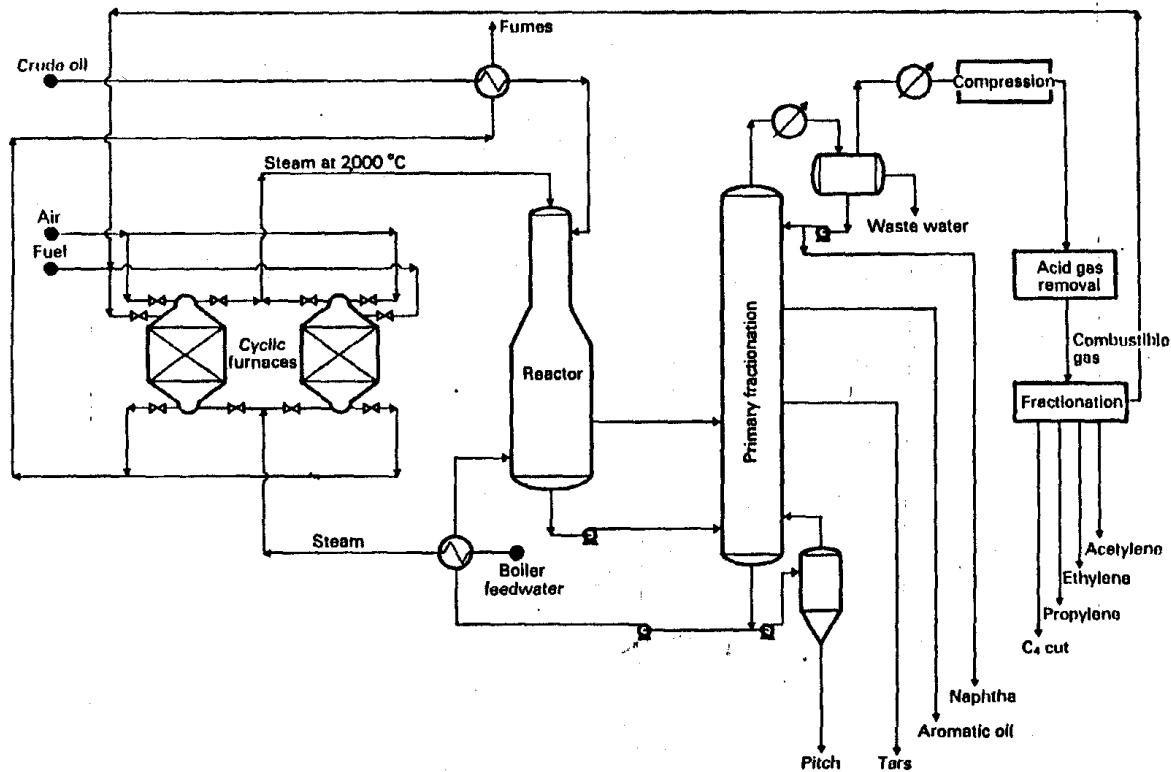


Fig. 5.9. Acetylene manufacture. Base scheme of reaction section of Kurcha process.

olid oxides of one of the furnaces are first heated by combustion of the gas during the heating phase. Once this operation has been completed, the combustible mixture is sent to the second generator, while the steam is introduced into the first, where it absorbs the sensible heat of the oxide pebbles.

TABLE 5.2
KREHA STEAM CRACKING EFFLUENT COMPOSITION
(% Wt of feedstock)

Components	Borneo crude	Arabian crude
CH ₄	15.7	13.7
C ₂ H ₂	21.5	17.7
C ₂ H ₄	20.4	18.6
C ₃ H ₆	0.8	0.7
C ₄ H ₆	0.5	0.5
Benzene fraction	6.0	5.0
Naphthalene fraction	5.0	4.0
Tars	7.0	6.0
Pitches	13.0	25.0

The liquid and gaseous effluents obtained are quenched and sent to a primary fractionation column, which produces an oil at the bottom, partly used as a quenching fluid, and pitch, tars and a naphthalene-rich aromatic oil at the side withdrawals. Naphtha and lighter fractions are recovered at the top of the column. After compression, the different fractionation operations required on the light products are identical to those of conventional steam cracking, while the only significant difference relates to the acetylene recovery unit, which is larger.

5.5 ACETYLENE MANUFACTURE FROM HYDROCARBONS: AUTOTHERMAL PROCESSES

These processes, which employ the partial combustion of the feedstock to supply the heat required by the reaction, can treat raw materials ranging from methane to middle distillates. They differ in the design of the burner and the choice of the acetylene extraction solvent.

5.5.1 Operating principle

As a rule, the main operations are designed to meet specific requirements.

A. Reactor

The reactor must satisfy the following conditions:

- (a) Create the combustible feed oxygen mixture without causing backfire in the gas intake ducts.
- (b) Produce a stable flame front by regulating the gas flow rate.
- (c) Prevent carbon deposition on the walls by the injection of steam at specific locations of the burner.
- (d) Cause the rapid cooling of the gases, by the injection of a cold fluid dispersed in fine droplets.

B. Purification steps

The purification steps include:

- (a) Cooling of the gases by the injection of a cold fluid (water or oil) which entrains part of the carbon black.
- (b) Elimination of the last traces of carbon black by filtration or scrubbing.
- (c) Compression of the gases to a value such that the partial pressure of acetylene does not exceed $0.14 \cdot 10^6$ Pa absolute: this serves to prevent the explosive decomposition of acetylene into its elements.
- (d) Absorption of carbon dioxide by a solvent or alkaline solution.
- (e) Elimination of unconverted hydrocarbons.
- (f) Selective dissolution of acetylene followed by its desorption.
- (g) Recovery of acetylene or hydrogen from the by-products.
- (h) Regeneration of the solvents employed.

5.5.2 Industrial production

5.5.2.1 BASF process (Fig. 5.10)

The hydrocarbon (methane or naphtha) and oxygen are preheated before introduction into a combustion chamber where, after passing through a venturi, they enter the burner block fitted with a hundred or so channels. Small amounts of oxygen introduced in countercurrent flow enhance the stability of the flame. The oxygen to hydrocarbon ratio is regulated so that part (about one-third) of the hydrocarbon is burned, and the remainder cracked. The gas formed is quenched with water at a level of the combustion chamber corresponding to the maximum acetylene production. The coke formed is withdrawn and separated.

After scrubbing with oil and the removal of polymers and naphthalene, the gaseous effluent is compressed. It is then sent to the extraction section employing N-methylpyrrolidone as solvent.

The burner employed in BASF's first plant by *IG Farben* at Oppau (West Germany) during the Second World War was of the Sachsse type. Simultaneously, *Union Carbide* developed a similar facility, which was commissioned in 1950. Subsequently, *SBA* (Société

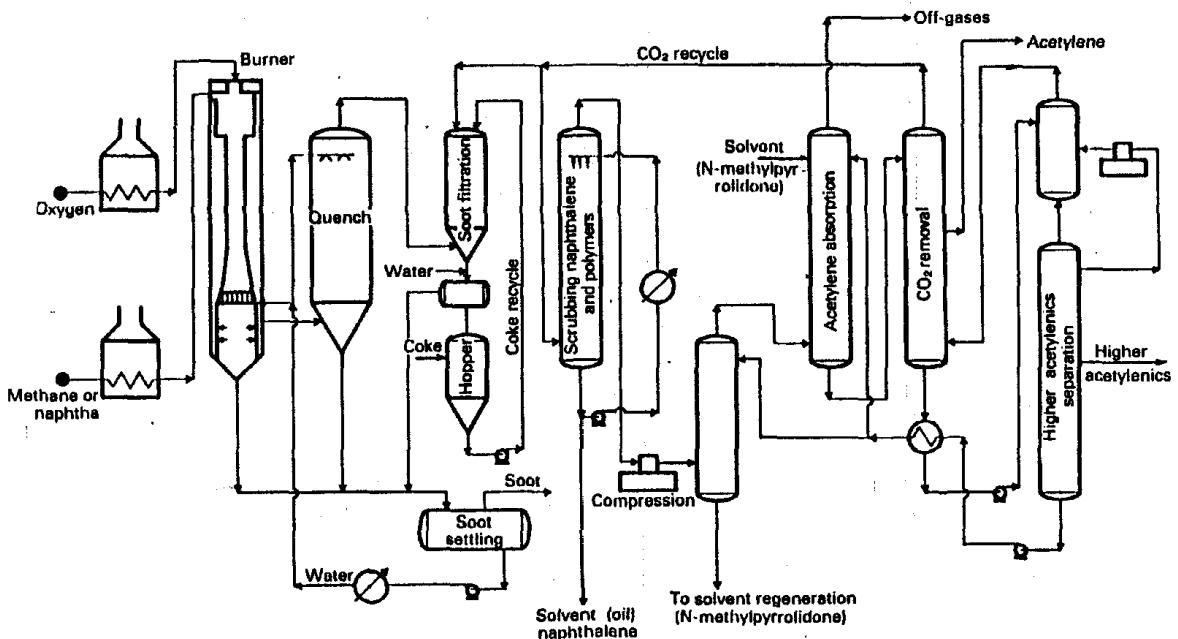


Fig. 5.10. Acetylene manufacture. BASF process for autothermal combustion of hydrocarbons.

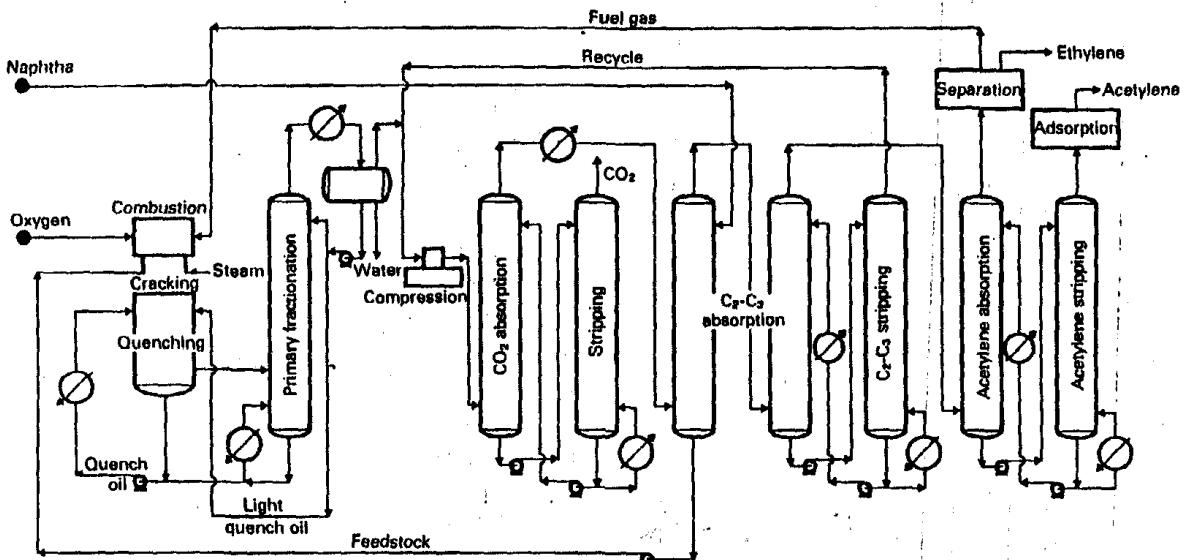


Fig. 5.11 Simultaneous production of acetylene and ethylene by autothermal combustion of hydrocarbons. Hoechst HTP process.

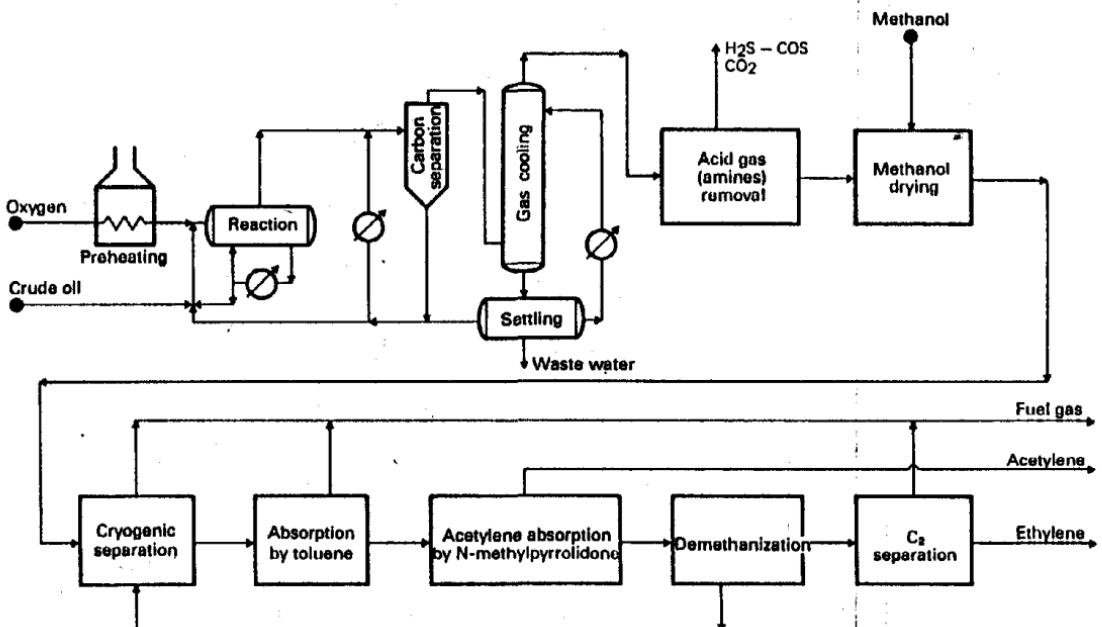


Fig. 5.12. Acetylene manufacture by autothermal combustion of hydrocarbons.
BASF submerged flame process.

Belge de l'Acétylène) developed another burner, identical in its principle, but different in design. In Italy, *Montecatini* tested an identical system to that of *BASF*, but operating under pressure.

5.5.2.2 Hoechst HTP process (Fig. 5.11)

The HTP (High Temperature Pyrolysis) process employs a burner in which the combustion of cracked gases (CO , H_2 and CH_4) with oxygen raises the temperature to 2700°C . This device is followed by a cracking reactor, at whose inlet the injection of steam lowers the temperature to 2300°C . The naphtha is then injected in the hot combustion gases where pyrolysis takes place, reducing the reactor exit temperature to 1300°C . After contact for 0.002 to 0.003 s, the gases are quenched by the injection of oil produced in the process and recycled. The heat absorbed by this fluid is used to produce steam. The gases are separated from the heavy fractions, cooled to about 50°C and compressed at $3 \cdot 10^6 \text{ Pa}$ absolute. They are rid of CO_2 by absorption followed by neutralization, after which the different hydrocarbons are fractionated. Acetylene and ethylene are produced in a weight ratio ranging from 30/70 to 70/30.

5.5.2.3 BASF submerged-flame process (Figs. 5.12 and 5.13)

The submerged-flame technique developed by *BASF* represents the latest development in autothermal processes. Within a liquid hydrocarbon, a flame creates a sufficiently high temperature in its vicinity to cause the formation of light products, including acetylene. The gases are quenched in the cold zones of the liquid, and the carbon black formed is sent with the hydrocarbon to the burner. The reactor can operate under pressure with any hydrocarbon compound, without the substantial production of carbon black. The weak point of the device is the control of the burner, which is difficult to achieve due to the high gas flow velocity (Fig. 5.13).

Table 5.3 lists the main characteristics of the best known autothermal processes.

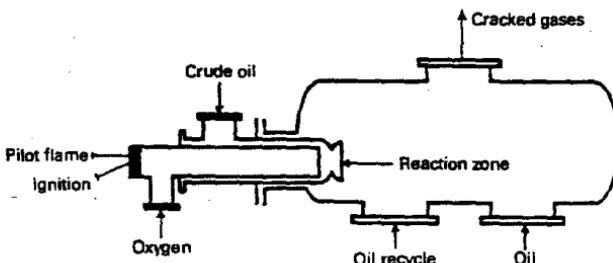


Fig. 5.13. Acetylene manufacture by autothermal combustion of hydrocarbons. Scheme of the *BASF* submerged flame reactor.

TABLE 5.3
ACETYLENE PRODUCTION. CHARACTERISTICS OF THE MAIN AUTOTHERMAL PROCESSES

Company	Feedstock	Products	Burner	Quench	Carbon black elimination	Compression	Solvents	Solvent purification
BASF	Natural gas. Naphtha.	Acetylene: purity 99.8 % total yield 30 %. Ethylene.	O ₂ /hydrocarbon ratio: 0.6. Separate preheating of the two gases at 650 °C. The hydrocarbon preheating furnace is of nickel free steel and guarantees high space velocities to prevent the formation of carbon.	Water for methane feedstock. Aromatic oil for naphtha feedstock.	Water and moving carbon bed.	0.8 to 1.10 ⁶ Pa absolute.	N-methyl-pyrrolidone.	Flash under low pressure.
BASF	Crude oil, residues.	Acetylene 50%. Ethylene 50%.	Submerged flame.	Immediate by liquid surrounding flame.			N-methyl-pyrrolidone.	
SBA	Naphtha, LPG, O ₂ .	Acetylene: purity 99.6%. Ethylene.	Two types of burner: One adapted to the pyrolysis of methane and completely metallic, the second adapted to the pyrolysis of heavier hydrocarbons, similar to the Eastman reactor.	Water (90 °C).	Water and oil.	0.1 to 1.2.10 ⁶ Pa absolute.	Aqueous ammonia for CO ₂ . Liquid ammonia (30°C) for C ₂ H ₂ . Methanol or kerosene for C ₃ .	Steam treatment. Distillation.
Montecatini	Natural gas.	Acetylene: purity >99%; yield 23% weight of feedstock.	Burner similar to the second type of the SBA process, operating at 0.4.10 ⁶ Pa absolute, thus allowing higher capacity, better recovery of latent heat from off-gases, and limitation of the energy costs of compression before purification.	Water.	Water.	1.3.10 ⁶ Pa absolute.	Methanol (0 °C).	Distillation.
Hoechst	From methane to middle distillates, O ₂ .	Acetylene: purity 98.8%; yield 40% weight for methane feedstock. Ethylene: purity 99.9%; yield 50 to 44% for distillate feedstock.	All metal burner. Gas injection tangential to the wall to favor mixing. Oxygen introduced tangentially to the wall is sent into the hot gases at the same time as superheated steam.	Cooling in a steam generator system.		Moderate pressure.	Own solvent.	Simple regeneration at low temperature.

Other processes: Gremenko (URSS), Hydrocarbon Research, Phillips, Union Carbide.

5.6 ACETYLENE MANUFACTURE BY EXTRACTION FROM STEAM-CRACKED C₂ CUTS

Acetylene is obtained in steam-cracked gases, at the rate of 0.5 to 2.5 per cent weight in relation to the feed. This content may be higher if the raw material is heavier. Thus, a number of methods under development attempt to convert the total crude or heavier fractions, to produce ethylene as well as significant amounts of acetylene. One such process is the ACR (Advanced Cracking Reactor) technology developed by *Union Carbide*, *Kureha* and *Chiyoda*. In this process, the feedstock is introduced for 20 milliseconds in a plasma generated by the combustion of a liquid or gaseous fuel in the presence of oxygen. Superheated steam injected into the combustion products cools the gases to about 2000°C, and serves as a diluent for the hydrocarbon feed introduced into the reactor. The effluents are quenched by the injection of heavy oil. Using a light Arabian crude, the product gas contains 31.8 per cent weight of ethylene and 4.2 per cent of acetylene.

The Dow process also uses a high temperature plasma to crack whole crudes or heavy fractions. It produces 22 to 29 per cent weight of ethylene, and about 2.5 per cent of acetylene.

In routine practice, the acetylene is selectively converted to ethylene during the hydrogenation treatment applied to the steam-cracked C₂ cut after its separation, partly to meet commercial specifications, and partly to upgrade the starting raw material most effectively by recycling the ethane, a preferential ethylene precursor.

The overproduction of ethylene in certain geographic areas and, all things considered, the strong demand for acetylene at its high price level, could normally justify its recovery from the steam-cracked C₂ cut for economic reasons. Given the slight differences in boiling points between the constituents of these effluents, and the pronounced tendency displayed by acetylenic compounds to polymerize, this separation cannot be achieved by simple distillation or even superfractionation. A feasible alternative is solvent extraction, particularly with dimethylformamide.

In principle, the flow sheet of such a facility (Fig. 5.14) comprises the cooling of the C₂ cut in gaseous form, followed by its countercurrent passage into an absorption column (20 trays), where the solvent flows, and which operates at about $2 \cdot 10^6$ Pa absolute. The extract, containing nearly all the initial acetylene, is sent to a stripping column (25 trays), operating at $0.105 \cdot 10^6$ Pa absolute to remove the other absorbed gases, which are recycled to the previous column after recompression. A desorber (25 trays) then separates the dimethylformamide at the bottom and the acetylene at the top (Fig. 5.11).

The main license holders are *Linde*, *Lummus* and *Monsanto*. These facilities are in operation in Western Europe (*DSM* : *Nederlandse Staats Mijnen*, *Erdöl-Chimie* etc.) and the United States (*Union Carbide*).

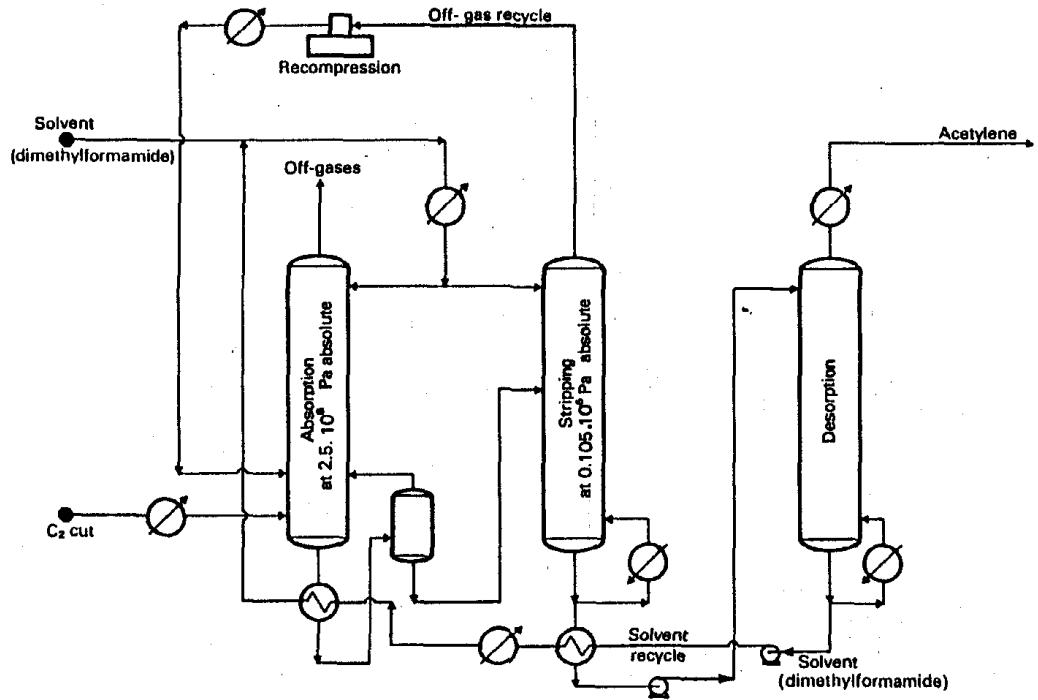


Fig. 5.14. Acetylene manufacture by extraction from steam-cracked C₂ cuts.

5.7 ECONOMIC DATA

The sharp rise observed between 1973 and 1986 in the cost of fossil energies, especially crude oil, has contributed to a considerable increase in the price of ethylene, so that the competition it has exerted on acetylene for several decades could subsequently disappear. The situation was especially favorable to processes using electricity as an energy source, and nuclear-generated electricity could be highly advantageous in periods of slack demand. In certain countries, this situation could also favor technologies using cheap coal as a local raw material.

A number of syntheses using acetylene, by their very nature (simplicity of the reaction in a single step, high yield and selectivity etc.), were favored over their counterparts employing ethylene. These included, for example, the manufacture of vinyl chloride or acetate. Inasmuch as resources became available to fund the corresponding investments, such a substitution could be considered in the long term.

Table 5.4 shows the influence of electricity expenditures on the cost price of acetylene for the five main processes examined above. Among them, the electric arc processes and techniques based on calcium carbide are those that benefit most from the advantages of electricity, and guarantee some independence of the acetylene price from that of petroleum products.

Table 5.5 gives economic data concerning the main acetylene manufacturing processes.

Table 5.6 lists some economic data on the Kureha process.

TABLE 5.4
INFLUENCE OF ELECTRICITY EXPENSES ON ACETYLENE COST PRICE
(mid-1982)

Process	Share of electricity in utilities (%)	Share of utilities in cost price (%)
Wulff	2	16
Hüls	12	34
BASF (gas)	85	3
BASF (submerged flame)	92	16
Calcium carbide	99	32

5.8 USES AND PRODUCERS

Table 5.7 provides an idea of the average commercial specifications for acetylene manufactured from calcium carbide or hydrocarbons.

Table 5.8 lists the main uses of acetylene, production, capacities and consumption in Western Europe, the United States and Japan in 1984.

TABLE 5.5
ACETYLENE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)

Process	Coke via calcium carbide	Natural gas partial combustion	Arc natural gas	Arc coal	Ethane pyrolysis	C ₂ cut extraction
Typical technology	—	BASF ⁽¹⁾	Hüls	AVCO-GAF ⁽²⁾	Wulff	Linde
Capacity (t/year)	50,000	50,000	50,000	50,000	50,000	5,000
Battery limits investments (10 ⁶ US\$)	63	61	102	109	89	7.9
Consumption per ton of acetylene						
Raw materials						
Natural gas (10 ⁶ kJ)	—	210	85	—	—	—
Ethane (t)	—	—	—	—	3.3	—
Butanes (t)	—	—	0.7	—	—	—
Coal (t)	0.03	—	—	3.4	—	—
Graded coke (t)	1.9	—	—	—	—	—
Lime (t)	4.9	—	—	—	—	—
Steam-cracked C ₂ cut (t)	—	—	—	—	—	100
Oxygen (t)	—	5.0	—	—	—	—
By-products						
Hydrogen (kg)	—	—	300	—	—	—
Ethylene (t)	—	—	0.3	—	—	99
BTX (kg)	—	50	—	—	—	—
Gasoline (kg)	—	—	150	—	—	—
Pyrolysis residue (kg)	—	—	50	—	—	—
Carbon black and char (kg)	—	—	350	1,500	—	—
Hydrogen cyanide (kg)	—	—	—	100	—	—
Carbon disulfide (kg)	—	—	—	60	—	—
Utilities						
Steam (t)	—	(—) 5.5	2.0	6.0	14.0	8.5
Electricity (kWh)	10,500	150	14,000	11,000	130	2,800 ⁽³⁾
Fuel (10 ⁶ kJ)	—	(—) 90	(—) 8	(—) 17	(—) 7	—
Refrigeration at 0°C (10 ⁶ kJ)	—	—	—	—	—	15
Cooling water (m ³)	100	70	180	500	350	600
Process water (m ³)	4	1	—	—	1	—
Nitrogen (m ³)	35	2	—	50	—	—
Chemicals and catalysts (US\$)	16	2	14	11	5	—
Ammonia (kg)	—	—	—	—	3	—
Sulfuric acid (kg)	55	130	—	—	—	—
Chlorine (kg)	40	—	—	—	—	—
Caustic soda (100%) (kg)	—	30	—	3	3	—
Solvents						
N-methylpyrrolidone (kg)	—	3	1	7	—	—
Diethanolamine (kg)	—	—	—	5	—	—
Dimethylformamide (kg)	—	—	—	—	6	3
Labor (Operators per shift)	25	15	12	15	10	0.5

(1) With quench heat recovery. (2) With water quench. (3) With recycle compressor.

TABLE 5.6

PRODUCTION OF ACETYLENE AS A BY-PRODUCT OF THE MANUFACTURE OF ETHYLENE
BY THE KUREHA CRUDE OIL STEAM CRACKING PROCESS. ECONOMIC DATA
(France conditions, mid-1986)

Ethylene capacity (t/year)	500,000
Battery limits investments (10^6 US\$)	315
Consumption per ton of ethylene	
Raw materials	
Crude oil (t)	3.36
Oxygen (t)	1.75
By-products	
Acetylene (t)	0.12
Propylene (t)	0.28
C ₄ cut (t)	0.15
C ₅ + gasoline (t)	0.43
Medium fuel oil (t)	0.44
Heavy fuel oil (t)	0.13
Vacuum residue (t)	0.20
Utilities	
Steam (t)	1.60
Electricity (kWh)	105
Cooling water (m ³)	420
Chemicals and catalysts (USS)	20
Labor (Operators per shift)	15

TABLE 5.7
AVERAGE COMMERCIAL SPECIFICATIONS

Origin	From carbide	From hydrocarbon
Acetylene (% vol min.)	98	99.1
CO ₂ (ppm) max.	—	500
O ₂ (ppm) max.	250	300
Higher acetylenics (ppm) max.	Traces	3,100
Nitrogen (ppm) max.	10,000	1,500
Propadiene (ppm) max.	Traces	4,000
Benzene (ppm) max.	—	100
Phosphines (ppm) max.	Traces	—
Arsines (ppm) max.	3	—

TABLE 5.8
ACETYLENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
1,4-butanediol and derivatives	6	31	—
Vinyl acetate monomer	16	—	—
Vinyl chloride monomer	26	33	—
Miscellaneous chemicals ⁽¹⁾	28	7	71
Metal cutting and welding	24	29	29
Total	100	100	100
Source (% product)			
By-products ⁽²⁾	7	19	—
Calcium carbide	7	20	100
Natural gas ⁽³⁾	86	61	—
Total	100	100	100
Production (10 t/year)	425	140	120
Capacity (10 t/year)	480	170	180
Consumption (10 t/year)	420	135	115

(1) Acetylene black, acetylenic diols and alcohols (methylbutynol, ethylcynol, propargyl alcohol...), acrylic acid and esters, acrylonitrile, chlorinated solvents, isoprene, vinyl ethers, vinyl fluoride...

(2) Steam cracking of natural gas liquids, naphtha or gas oil and refinery off-gases.

(3) Electric arc, partial oxidation and Wulff process.

Chapter 6

MONOMERS FOR THE SYNTHESIS OF ELASTOMERS

6.1 BUTADIENE

Butadiene ($\text{bp}_{1.013} = -4.413^\circ\text{C}$, $d_4^{20} = 0.6211$)⁽¹⁾ has become a major petrochemical product thanks to the development of its copolymers with styrene and acrylonitrile. The earliest processes for manufacturing butadiene started with acetylene and formaldehyde (Germany, the Reppe process), or produced it by the aldolization of acetaldehyde (Germany), or by the dehydration and dehydrogenation of ethanol (USSR, United States: *Union Carbide*).

Manufacturing processes today employ petroleum raw materials. In Europe and Japan, butadiene is obtained entirely by extraction from steam-cracked C_4 cuts (see Section 3.1.2). In the United States, it is also produced by the dehydrogenation of butane and particularly of butenes contained in C_4 cuts from catalytic cracking.

6.1.1 Direct catalytic dehydrogenation

Butadiene obtained by dehydrogenation still accounted for one-fifth of world output in 1981, but, by 1990, it appears that this synthesis method will have virtually disappeared. The operation was first carried out on butenes, and then on butane in two steps with passage through the intermediary of butenes, and finally in a single step.

6.1.1.1 Catalytic dehydrogenation of butenes (Fig. 6.1)

A. Operating conditions

Butenes are only obtained in mixtures (25 to 45 weight per cent) in C_4 cuts containing *n*-butenes, isobutene, *n*-butane and isobutane (see Tables 2.11 and 2.28 in Section 2). To achieve a satisfactory return from dehydrogenation operations, the *n*-butenes concen-

(1) Specific gravity, 68.0 39.2.

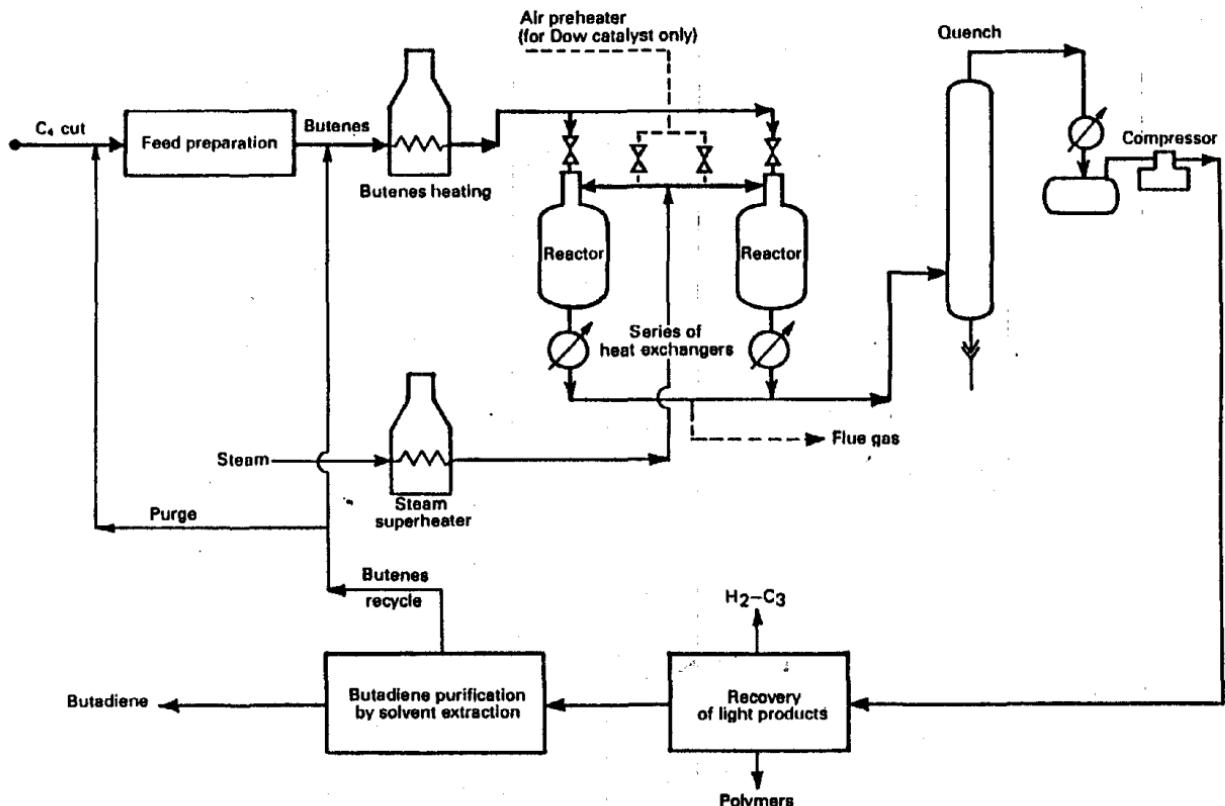
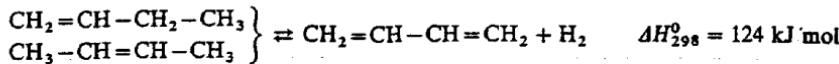


Fig. 6.1. Butadiene manufacture by the dehydrogenation of butenes.

tration of the feedstock C₄ fraction must be at least 70 per cent, and preferably 80 to 95 per cent. This is because, since the conversion of butenes to butadiene is only partial at each passage over the catalyst, the unconverted part must be recycled. Hence the other C₄ hydrocarbons must be eliminated as completely as possible, to avoid losing an excessive amount of unconverted butenes in the purge. The pretreatment of the feedstock to reach these concentrations was discussed above (see Sections 3.1.1 and 3.1.3).

Dehydrogenation takes place according to the following reaction:



These conversions are balanced, endothermic and exentropic. The formation of butadiene is favored at elevated temperature and low pressure.

In practice, industrial processes operate in the presence of catalysts, at above 600°C. with a large adduct of steam, whose effect is to reduce the partial pressure of the hydrocarbons and also to slow down the formation of coke. Depending on the extent of this coking, the process may require operation in cycles, with a frequency proportional to the amount of coke deposited. Table 6.1 gives typical examples of operating conditions and results obtained with several catalysts.

TABLE 6.1

PERFORMANCE ACHIEVED BY DIFFERENT CATALYSTS IN THE DEHYDROGENATION OF BUTENES

Catalyst	Shell 105 Fe ₂ O ₃ /Cr ₂ O ₃	Shell 205 Fe ₂ O ₃ /Cr ₂ O ₃	Dow B Ni and Ca phosphate	Phillips 1490 Fe ₂ O ₃ /bauxite
Temperature (°C).....	620 to 680	620 to 680	600 to 680	620 to 680
Pressure (10 ⁶ Pa absolute).....	—	0.15 to 0.18	0.16 to 0.20	0.15 to 0.18
Steam/butenes (mol/mol)	10 to 18/1	8/1	20/1	9 to 12/1
Space velocity (VHSV)	—	≥ 500	125 to 175	300 to 400
% Conversion per pass	20 to 30	26 to 28	up to 45	27 to 33
% Butadiene selectivity	80 to 70	75 to 73	90	76 to 69
Regeneration time and frequency	1 h to 7 days	1 to 24 h	15 to 30 min	None

B. Processes

The dehydrogenation of butenes in the presence of steam was developed initially by *Esso*, *Shell* and *Phillips*. In accordance with the operating principles of this type of process, the preheated feed is mixed with superheated steam and then sent to adiabatic reactors containing catalyst beds 80 to 90 cm thick. The temperature, initially 620°C, must be raised progressively as catalyst activity decreases. The latter is regenerated by simple steam treatment. The reaction pressure is 0.1 to 0.2 · 10⁶ Pa absolute, and reaches 0.5 · 10⁶ Pa absolute during regeneration.

The reactor effluent is quenched by water injection, and then by passage through a series of heat exchangers in which steam is produced. It is then cooled by a second water quench or by means of a heavy hydrocarbon. The condensates are separated, and the gases are compressed and sent to a train of simple or extractive distillation stages to

remove the light hydrocarbons, hydrogen and carbon dioxide, to extract and purify the butadiene, and to recycle the unconverted butenes.

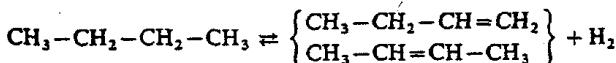
Each cycle lasts 30 min and comprises a 15 min reaction phase, an 11 min regeneration phase with the passage of air diluted with steam over the catalyst, and a 2 min purge before and after regeneration.

6.1.1.2 Catalytic dehydrogenation of *n*-butane

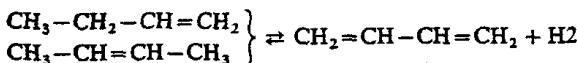
This achieves the conversion of *n*-butane to butadiene in one or two steps, with the intermediate formation of *n*-butenes that may or may not be isolated.

A. Operating conditions

The process takes place according to the following reactions:



$$\Delta H_{298}^{\circ} = 127 \text{ kJ/mol}$$



$$\Delta H_{298}^{\circ} = 124 \text{ kJ/mol}$$

These endothermic and exentropic conversions are balanced. At 600°C and atmospheric pressure, the first achieves a 57.7 per cent conversion, and the second 15.9 per cent. At 10 kPa absolute, and the same temperature, the conversion is 45.4 per cent for the second.

The dehydrogenation catalyst must be sufficiently active to allow for very short contact times and the use of low temperatures, to minimize thermal cracking reactions. Carbon deposits are eliminated by heating in the presence of a gas containing oxygen. This means that the catalyst must be thermally stable to avoid being deactivated during the oxidation of the deposits. The best catalysts contain alumina and chromium oxide, but these cannot be employed in the presence of steam. Operations are conducted at a temperature between 550 and 700°C, and low pressure, less than $0.1 \cdot 10^6$ Pa absolute.

B. Processes

a. UOP process

The first industrial plant for the dehydrogenation of butane to butenes was built by UOP (*Universal Oil Products*) on the ICI (*Imperial Chemical Industries*) complex at Billingham (United Kingdom) in 1939/1940. The UOP process featured a multitube reactor operating with a chromium oxide/alumina catalyst, at 570°C and $0.8 \cdot 10^6$ Pa absolute at the inlet, with a pressure drop of $0.5 \cdot 10^6$ Pa absolute in the tubes (5 m long, 7.5 cm diameter). Once-through conversion was 22.5 per cent with a molar selectivity of 80 to 90 per cent.

A modern version of this technology, called Oleflex, combined with an Olex unit for the separation of olefins on molecular sieves, is used to manufacture cuts rich in *n*-butenes (see Section 2.3.4.3).

b. Phillips process

In its earliest version this process comprises the following steps:

- (a) Dehydrogenation of *n*-butane to butenes.
- (b) Separation of butenes, unconverted butane and other products by fractional and extractive distillations in the presence of an aqueous solution of furfural, and then recycling of *n*-butane.
- (c) Dehydrogenation of butenes to butadiene.
- (d) Separation and purification of butadiene by extractive distillation with furfural, and then recycling of butenes.

Butane is dehydrogenated isothermally in multitube reactors, with tubes 3.5 m long and a diameter of 5 cm. The operating conditions are as follows:

Temperature	565 to 590°C
Pressure	0.1 to 0.2 · 10 ⁶ Pa absolute
Space velocity	700 h ⁻¹
Once-through conversion	30 per cent
Molar selectivity	80 per cent

The feedstock containing 98 per cent *n*-C₄ must first be dried. The process is cyclic, and the reactors operate alternately for one hour in dehydrogenation and one hour in regeneration. Regeneration is carried out at 0.7 · 10⁶ Pa absolute, with a gas containing 2 to 3 per cent oxygen.

From now on, butane can be dehydrogenated by a new technique called the Star process, already mentioned in the case of propane dehydrogenation (see Section 2.3.4.2) and also in that of isobutene manufacture (see Section 6.2).

c. Houdry (Air Products) catadiene process (Fig. 6.2)

This process was formerly the most widely used for the manufacture of butadiene by dehydrogenation. Using a feed containing 95 per cent or more *n*-C₄, it produces a mixture of butenes and butadiene in a single step. The butadiene is separated, and the unconverted butenes and butane are recycled. The catalyst, activated alumina containing 18 to 20 per cent weight of chromium oxide, has a life of more than six months. It is placed in a series of horizontal reactors lined with refractory bricks. The inert alumina is mixed with the catalyst to achieve the uniform distribution of the heat required for the reaction and a high heat capacity of the catalyst bed.

The operating conditions are the following:

Temperature	600 to 675°C
Pressure	15 to 70 kPa absolute
Space velocity	300 h ⁻¹
LHSV	1 to 3 h ⁻¹
Once-through conversion	50 to 60 per cent

The process is cyclic. The feedstock and C₄ recycle are preheated to 600°C and sent to the catalyst bed, forming butadiene, butenes, a number of gaseous by-products and coke. After a reaction period of 5 to 10 min. depending on the number of reactors in the unit, the temperature drops by 15 to 20°C. Regeneration is then carried out, lasting 5 to 10 min. The reactor is first purged with steam, and air at 600°C is then introduced to burn the carbon deposits formed. The heat liberated raises the temperature of the

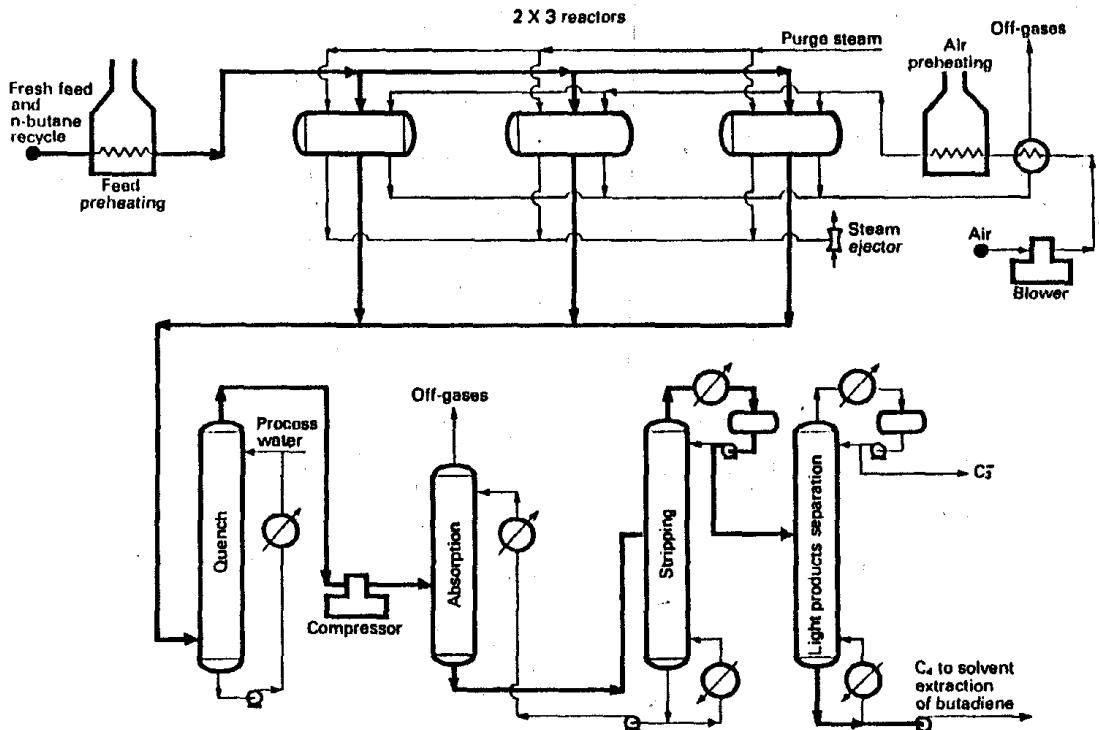


Fig. 6.2. Butadiene manufacture by the dehydrogenation of *n*-butane, Houdry process.

catalyst bed. Following this regeneration at atmospheric pressure and the stoppage of air intake, a combustible gas is introduced to remove excess oxygen and to make the catalyst reducing. The time devoted to these transition periods is at least 3 to 5 min. A complete run therefore lasts a total of 15 to 30 min.

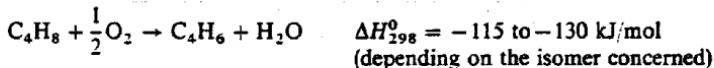
By adjusting the length of the transition periods, continuous operation can be achieved by operating with at least three reactors (reaction, regeneration and purge). As capacity rises, it is more profitable to use five reactors, with only one in purge, followed by seven. Above this number, it is impossible to use a single purge reactor, because the transition period becomes too short.

The application of this technique to light paraffin dehydrogenation is known as the Catofin process (see Sections 2.3.4.2 and 6.2).

6.1.2 Dehydrogenation by the action of an oxidizing agent

This method offers two variants:

- The combination of hydrogen with iodine, which is regenerated by oxygen treatment. This solution, investigated by *Shell* in its Idas process, did not lead to industrialization because of corrosion and, above all, iodine losses.
- Dehydrogenation by oxygen with the formation of water: this process takes place according to the following reaction:



It takes place between 400 and 600°C, at $0.15 \cdot 10^6$ Pa absolute, in the presence of catalysts based on bismuth molybdate and phosphate, doped with various transition metals. Operations are conducted with oxygen to butenes mole ratios of about 1 and steam to butenes ratios of 30 to 50. Once-through conversion is up to 60 per cent and molar butadiene selectivity close to 95 per cent.

If this process is compared with direct dehydrogenation, the addition of 10 to 20 per cent volume of oxygen to the feedstocks serves to boost the production capacity by at least 25 per cent, by raising the once-through yield. The use of oxygen has the following effects:

- Shift of the equilibrium by combustion of the hydrogen produced in the reaction.
- Reduction of the temperature gradient across the catalyst bed, because the reaction becomes exothermic.
- Elimination of coke deposits, thus increasing catalyst life and possibly eliminating cyclic operation.

Various processes have been developed, especially by *BP Chemical*, *Polymer Corporation*, *Shell*, etc., but the main industrial achievements in this area are due to *Phillips* (OXD process, originally used in its Borger, Texas, plant, currently shut down) and *Petrotex* (Oxo-D process employed in the Tenneco facilities at Houston, Texas, and at the Firestone plant at Orange, Texas, etc.). Figure 6.3 gives a flow sheet of the *Petrotex* technology.

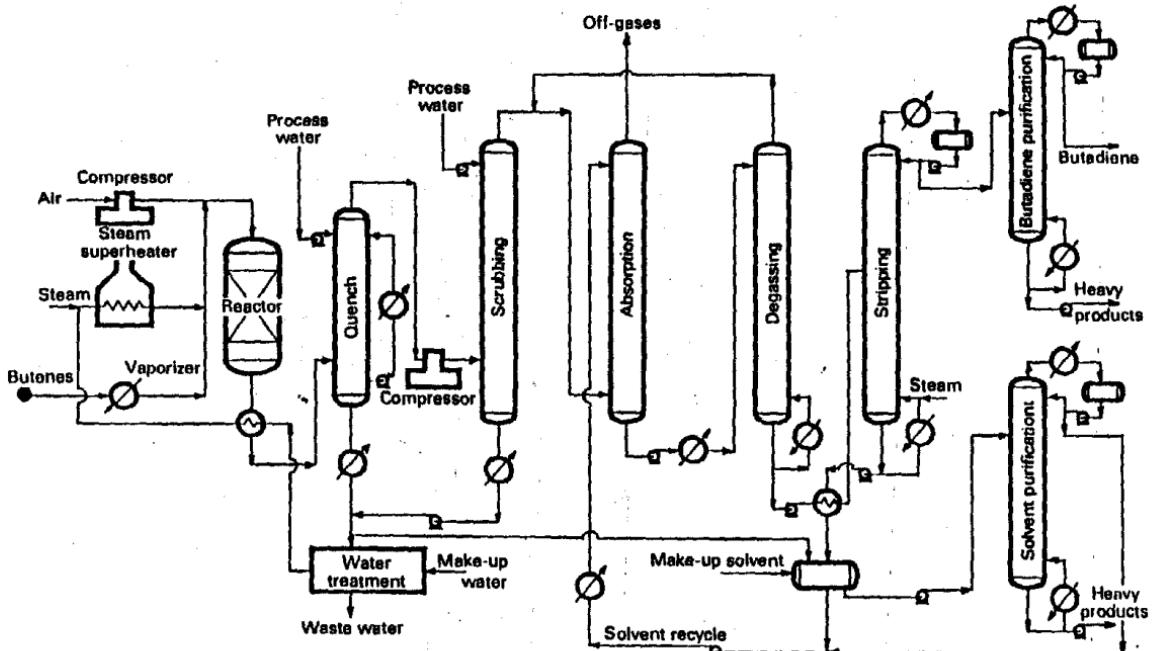


Fig. 6.3. Butadiene manufacture by oxidative dehydrogenation of *n*-butenes. Oxo-D Petrotex process.

6.1.3 Economic data

The main economic data on processes for manufacturing butadiene by dehydrogenation, employed on the industrial scale, are shown in Table 6.2.

TABLE 6.2

BUTADIENE MANUFACTURE BY DEHYDROGENATION. ECONOMIC DATA.
(France conditions, mid-1986)
PRODUCTION CAPACITY 50,000 t/year

Process	Houdry	Petrotex (Oxo-D)
Feedstock	Butane	Butenes
Battery limits investments (10^6 US\$)	61	26
Consumption per ton of butadiene		
Raw materials (t)	1.680	1.115
Chemicals (US\$)	5	2.5
Utilities		
Steam (t)	1.8	6.6
Electricity (kWh)	290	400
Fuel (10^6 kJ)	30	—
Cooling water (m^3)	380	500
Process water (m^3)	5	8
Labor (Operators per shift)	5	4

6.1.4 Uses and producers

The average commercial specifications required for the production of elastomers are summarized in Table 6.3.

Uses and production, manufacturing capacities and consumption figures for butadiene for 1984 in Western Europe, the United States, Japan and the world are summarized in Table 6.4. Some data are given for 1986.

TABLE 6.3
AVERAGE COMMERCIAL SPECIFICATIONS OF BUTADIENE FOR ELASTOMERS

Product		SBR in solution	SBR in emulsion
1,3-butadiene (% Wt) min.	99.0	99.0
C ₅ and C ₆ - Butadiene dimers	(ppm) max.	4,000	4,000
Acetylenics	(ppm) max.	1,000	1,000
Propadiene	(ppm) max.	100	350
1,3-butadiene	(ppm) max.	50	50
Oxygenated compounds	(ppm) max.	150	100
Peroxides (as H ₂ O ₂)	(ppm) max.	3,000	3,000
Methanol	(ppm) max.	5	10
Carbonyl compounds as acetaldehyde	(ppm) max.	15	—
Sulfur (H ₂ S)	(ppm) max.	50	600
Non-volatile residues	(ppm) max.	5	5
Inhibitor (t-butylcatechol)	(ppm) max.	1,000	1,000
		100	100

TABLE 6.4
BUTADIENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan	World
Uses (% product)				
ABS	10	9	12	7
Adiponitrile (nylon 6,6)	8	7	—	4
Chloroprene	7	5	4	7
Nitrile rubber	4	3	7	4
Polybutadiene	21	24	26	22
SB (latices included)	45	50	49	54
Miscellaneous ⁽¹⁾	5	2	2	2
Total	100	100	100	100
Sources (% product)				
Dehydrogenation ⁽²⁾	—	1	—	18
Steam cracking	100	99	100	82
Total	100	100	100	100
Production (10 ⁶ t/year)	1.7	1.1	0.65	5.6
Capacity (10 ⁶ t/year) ⁽³⁾	2.1	1.7	0.75	7.2
Consumption (10 ⁶ t/year)	1.3	1.5	0.70	5.6

(1) 1,5,9-cyclododecatriene, 1,5-cyclooctadiene, ethyldiene-norbornene, 1,4-hexadiene, methylmethacrylate-butadiene-styrene (MBS) resins, nitrile barrier resins, specialty polybutadiene polymers, styrene-butadiene films (K-resins), terephthalic anhydride, thermoplastic elastomers...

(2) Dehydrogenation plants exist in Latin America (110,000 t/year), in Eastern Europe (1,160,000 t/year) and in Asia (3,000 t/year).

(3) In 1986 the worldwide production capacity of butadiene was 7.4 · 10⁶ t/year with the following distribution:

United States	1.7	Western Europe	2.1	Middle East	6
Canada	0.2	Eastern Europe	1.9	Japan	0.8
Latin America	0.3	Africa	—	Asia and Far East	0.4

6.2 ISOBUTENE

Isobutene is used in the field of elastomers, mainly to manufacture a special rubber, butyl rubber, by copolymerization with small amounts of isoprene. It serves essentially for the manufacture of inner tubes, but its production remains modest and accounts for barely 10 per cent of that of SBR (Styrene Butadiene Rubber). Isobutene is also used to produce additives for oils (polyisobutenes), detergents (di- and triisobutylenes) and currently for the manufacture of MTBE.

Isobutene is obtained by:

- (a) The extraction of C₄ cuts from steam cracking or catalytic cracking (Section 3.1.3.2).

TABLE 6.5a
PRODUCTION OF ISOBUTANE AND ISOBUTENE. ECONOMIC DATA
(France conditions, mid-1986)

Reaction	Isomerization		Dehydrogenation		
	No recycle	With recycle	Catofin (Houdry)	Olefplex (UOP)	Star (Phillips)
Production capacity (t/year)	70,000	200,000	200,000 ⁽¹⁾	300,000 ⁽¹⁾	200,000 ⁽¹⁾
Battery limits investments (10 ⁶ US\$) ...	2.5 ⁽²⁾ 0.3 ⁽⁵⁾	11.5 ⁽²⁾ 0.5 ⁽⁶⁾	38 ⁽³⁾ 4	52 ⁽⁴⁾ - 2	48 1
Initial catalyst load (10 ⁶ US\$)					
Consumption per ton of product			(1)	(1)	(1)
Raw materials					
Feed (t)	1.75	1.10	1.25	1.17	1.22
Make-up gas (kg)	22	9.5	-	-	-
By-products					
nC ₄ (t)	0.69	-	-	-	-
Chemicals and catalysts (US\$)	1	1.5	10	3	3
Utilities					
HP steam (t)	-	-	2.0	(-) 2.4	0.8
MP steam (t)	-	0.2	(-) 0.9	-	-
LP steam (t)	1.15	1.6	(-) 2.0	0.4	(-) 0.2
Electricity (kWh)	15	20	20	25	70
Fuel (10 ⁶ kJ) ⁽⁷⁾	-	(-) 3.7	2.7	2.1	1.2
Cooling water (m ³)	65	60	80	5	75
Boiler feedwater (m ³)	-	-	1.5	2.5	-
Labor (Operators per shift)	1	2	5	5	5

(1) Expressed in tons of pure product (100 per cent).

(2) Including de-isobutanizer.

(3) "High conversion" process.

(4) Dehydrogenation (Olefplex) + separation (Olex).

(5) Not including precious metals (platinum) : 25 kg.

(6) Not including precious metals (platinum) : 50 kg.

(7) This item includes fuel use of secondary effluents.

- (b) The dehydrogenation of isobutane by techniques similar to those employed with propylene or *n*-butenes (Section 2.3.4.2) in substantially identical operating conditions, techniques developed in particular by *Air Products* (Houdry Catofin process), *Phillips* (Star process) and *UOP* (Olefex process).

In this context, additional isobutane availabilities could be derived from *n*-butane isomerization, an operation which offers two variants, one of them including the recycling of unconverted *n*-butane after separation. As a rule, isomerization takes place in the gas phase, around 150 to 200°C, under hydrogen pressure (1.5 to 2.5 · 10⁶ Pa absolute), in the presence of a fixed catalyst bed of the reforming type, based on platinum (0.35 per cent weight) deposited on alumina promoted by traces of organic chlorides. Once-through

TABLE 6.5 b
PRODUCTION OF ISOBUTANE AND ISOBUTENE MATERIAL BALANCE
(% Wt)

Reaction	Isomerization		Dehydrogenation		
	No recycle	With recycle	Catofin (Houdry)	Olefex (UOP)	Star (Phillips)
Typical process					
<i>C</i> ₃ - or <i>C</i> ₃ feed	1.4	1.8	1.8	—	2.0
<i>iC</i> ₄	22.0	28.3	93.5	98.0	95.0
<i>nC</i> ₄	75.5	68.8	—	—	—
Other <i>C</i> ₄	—	—	4.2	2.0	3.0
Miscellaneous	2.1	1.1	0.5	—	—
Total	100.0	100.0	100.0	100.0	100.0
Make-up gas H ₂	18.4	16.8	—	—	—
<i>C</i> ₁	11.1	10.9	—	—	—
<i>C</i> ₂	21.1	26.7	—	—	—
<i>C</i> ₃	35.8	24.3	—	—	—
<i>iC</i> ₄	6.8	5.9	—	—	—
<i>nC</i> ₄	6.8	6.4	—	—	—
<i>C</i> ₅ +	—	9.0	—	—	—
Total	100.0	100.0	—	—	—
<i>C</i> ₃ - or <i>C</i> ₃ products	1.3	2.0	0.8	—	0.1
<i>iC</i> ₄	94.2	97.2	41.6	0.8	49.8
<i>nC</i> ₄	4.5	0.8	—	—	—
<i>iC</i> ₄	—	—	53.6	97.0	46.8
Other <i>C</i> ₄	—	—	3.1	2.2	3.2
<i>C</i> ₅ +	—	—	0.9	—	0.1
Total	100.0	100.0	100.0	100.0	100.0
Bv-product <i>iC</i> ₅	5.4	—	—	—	—
<i>nC</i> ₄	88.3	—	—	—	—
<i>C</i> ₅ +	6.3	—	—	—	—
Total	100.0	—	—	—	—

conversion is up to 40 to 50 per cent, and molar selectivity is 95 to 100 per cent for LHSV of 3 to 5 h⁻¹, catalyst life of about three years, and hydrogen to feed molar ratios of 0.1 to 0.5. The main commercial processeses of this type are those developed by BP (British Petroleum), IFP (Institut Français du Pétrole), Union Oil (Butomerate), UOP (Butamer), etc.

Shell has developed a liquid phase technique, operating in the presence of a solution of AlCl₃ (3 to 10 per cent weight) in molten SbCl₃ and hydrochloric acid (5 per cent weight of feed), at 2 · 10⁶ Pa absolute, and between 65 and 100°C. Once-through conversion is up to 60 per cent.

The economic data concerning the production of isobutane by vapor phase *n*-butane isomerization, with and without recycling of unconverted *n*-butane, and concerning the production of isobutene by dehydrogenation, by the three main current industrial processes, are given in Table 6.5a. The corresponding feed and product compositions are given in Table 6.5b.

Uses, production and consumption of isobutene are listed in Table 3.14.

6.3 ISOPRENE

The discovery of stereospecific polymerization methods, which led to the production of practically pure cis-1,4 polyisoprene (natural rubber contains 85 per cent of this isomer), raises the problem of the economic production of isoprene monomer (bp_{1.013} = 34°C, d₄²⁰ = 0.681⁽²⁾).

The extraction of isoprene from the C₅ cut of steam-cracked effluents provides one alternative, and its synthesis by different methods an equal number of other possibilities. However, they are all economically marginal due to the price levels of the natural products.

6.3.1 Synthesis processes

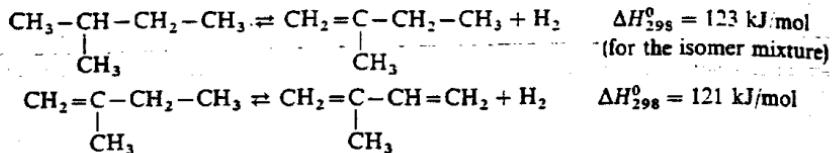
6.3.1.1 Isopentane dehydrogenation. Houdry (Air Products) and UOP processes

Isopentane is available in large amounts in C₅ cuts from catalytic cracking (see Section 2.3.1), and can be produced by *n*-pentane isomerization. However, since it is widely sought after for the manufacture of gasolines due to its high octane number, this raw material is difficult to secure and costly for petrochemicals.

This is why the techniques developed by *Houdry* and *UOP* to manufacture butadiene (see Section 6.1.1.2) and applied in operating conditions similar to isopentane dehydrogenation, have not enjoyed the success in this application that they achieved in others.

(2) Specific gravity, 68.0 39.2.

The following reactions are involved:

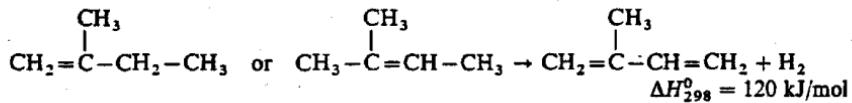


6.3.1.2 Isoamylene dehydrogenation, Shell process

The naphtha fraction from catalytic cracking contains 30 to 40 per cent of the isoamylenes 2-methyl 1-butene and 2-methyl 2-butenes (see Section 2.3.1). They can be obtained in a purity of 95 to 99 per cent by two-step extraction (such as the ARCO technology):

- (a) First with a solution of sulfuric acid.
- (b) Then by means of a hydrocarbon such as *n*-hexane, operating on the aqueous phase formed in the first step, and then recovered by simple distillation.

The double bond is isomerized during this operation, so that the final mixture contains approximately 90 per cent 2-methyl 2-butenes and 10 per cent 2-methyl 1-butene. Either of these two isomers can be dehydrogenated to isoprene by the following reaction:



This conversion, similar to that of butenes to butadiene (see Section 6.1.1.1), is carried out by *Shell* in the presence of steam, on an $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{K}_2\text{CO}_3$ catalyst, at about 600°C. The effluent is cooled by oil which absorbs the polymers formed. The gas is then compressed before separation, which comprises extractive distillation with aqueous acetonitrile, followed by rectification of the isoprene. *Shell* claims the ability to treat butenes and isoamylenes simultaneously to produce butadiene and isoprene. Some idea of the composition of the effluents from sulfuric acid extraction and dehydrogenation is given by Table 6.6.

Most routes to butadiene can be extended to the production of isoprene. These include dehydrogenation in the presence of halogens (*Shell Idas* process) or with oxygen (*Phillips* process, second step).

Another source of isoamylenes is obtained by dismutation of the dedienized C_4 cut using a technique derived from that of *Phillips* (*Triols* process). In the first step, using the C_4 cut, isobutene and 2-butenes react with each other to yield isopentenes and propylene. The propylene reacts in turn with the isobutene to produce an additional quantity of isopentenes and ethylene. The ethylene, by reacting with isohexenes, heavy by-products of the conversion of 1-butene and isobutene, regenerates the initial reactants in a second step.

In these conditions, isoamylenes can yield isoprene by dehydrogenation. The production of 1 t of isoprene requires 1.16 t of isobutene and 1.1 t of *n*-butene. In addition,

0.165 t of ethylene, 0.059 t of propylene and 0.675 t of combustible products are also formed.

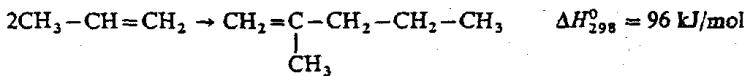
TABLE 6.6
COMPOSITION OF C₅ EFFLUENTS FROM EXTRACTION AND DEHYDROGENATION
(% Wt)

Hydrocarbon	Effluent from extraction with sulfuric acid	Effluent from dehydrogenation
C ₄	Trace	0.9
Isopentane.....	0.3	0.2
n-pentane.....	0.1	0.1
1-pentene.....	0.2	0.1
3-methyl 1-butene	0.1	4.2
2-methyl 1-butene	8.7	23.9
2-methyl 2-butene	87.5	39.4
Isoprene.....	—	29.3
Trans 2-pentene	0.5	{ 0.1
Cis 2-pentene	0.2	
Cis and trans piperylene	—	0.3
C ₆ -.....	2.4	1.5

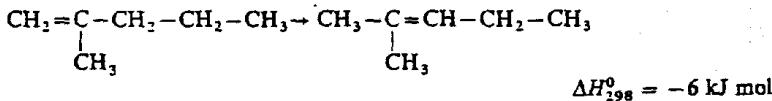
6.3.1.3 Goodyear Scientific Design process (Fig. 6.4)

This process was implemented in a plant in Beaumont, Texas, destroyed accidentally in 1974 and never rebuilt. Starting with propylene, it carries out the following conversion in three steps:

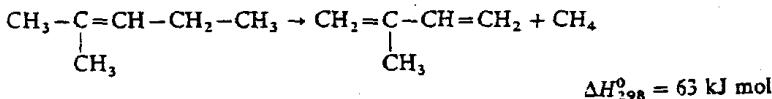
(a) Dimerization:



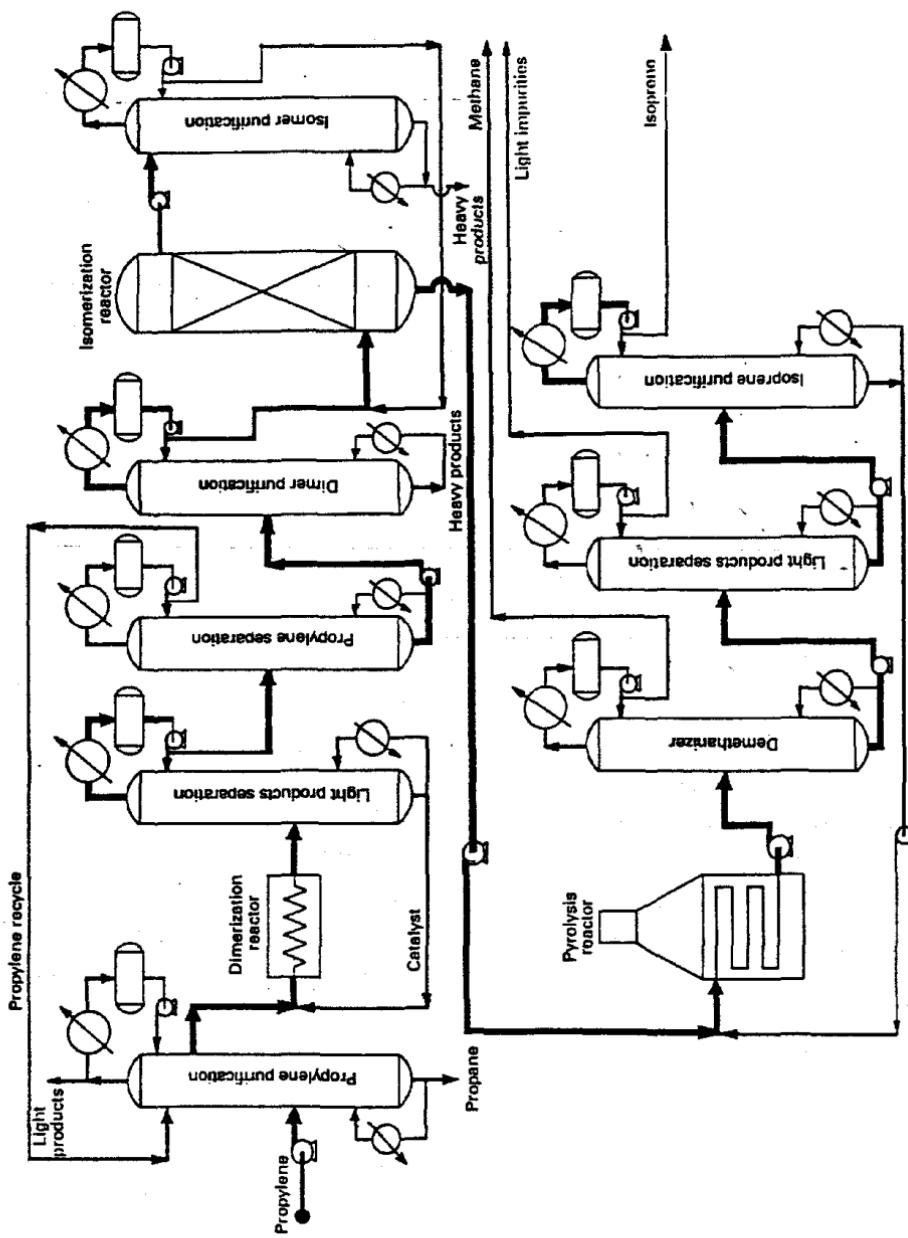
(b) Isomerization:



(c) Cracking:



The propylene (steam-cracked C₃ cut) is dimerized in the presence of tripropylaluminum as catalyst, at 150 to 200°C and 20 · 10⁶ Pa absolute. Residence time is about 15 min. Molar selectivity is as high as 90 to 95 per cent for once-through conversion



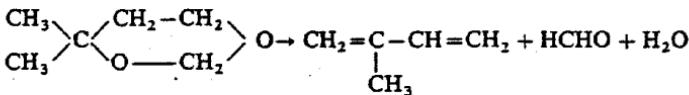
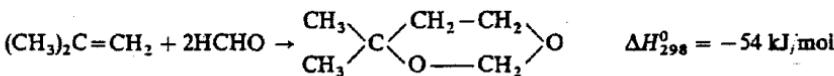
ranging from 60 to 95 per cent. To avoid excessive catalyst consumption, polar compounds and oxygen must be removed. The reactor effluent is flashed to withdraw the catalyst, which is recycled. The overhead products, 2-methyl 1-pentene, propylene and light hydrocarbons, are separated by distillation.

2-methyl 1-pentene is isomerized to 2-methyl 2-pentenes, an isoprene precursor, around 150 to 300°C on an acid catalyst (phosphoric acid), in a fixed bed. Its molar selectivity is high, 98 to 99 per cent. Once-through conversion is 85 per cent. Separation by distillation serves to recycle the unconverted 2-methyl 1-pentene.

Pyrolysis takes place in a furnace at about 650 to 700°C, in the presence of radical initiators (HBr or preferably peroxides) and steam. Residence time is about 1/10 s. The effluent is quenched to recover the catalyst, and then demethanized. The other light hydrocarbons are stripped and the isoprene is separated by simple distillation. A process flow sheet is given in Fig. 6.4.

6.3.1.4 Processes using isobutene and formaldehyde (Fig. 6.5)

The principal developments achieved in this area, some of which have culminated in industrial production, are those of *Bayer*, *Davy Powergas*, *IFP*, *Kuraray* and the Soviet Union. Using a C₄ cut containing isobutene, these processes manufacture isoprene by the addition of formaldehyde in a first step (Prins reaction), followed by catalytic cracking of the dioxane formed in a second step:



Each of these reactions is accompanied by the formation of by-products, which are complex alcohols, sometimes called Residols. These mixtures can be used to prepare phenolic and maleic resins and plasticizers.

In the first step, the C₄ cut is caused to react with an aqueous phase containing a dilute sulfuric acid solution (1 to 10 weight per cent, depending on the process) and formaldehyde. This operation takes place in countercurrent flow in a series of agitated and cooled reactors, or in co-current flow in a sort of extraction column provided with an agitation system, in which the heat of reaction is removed by passing part of the reaction medium through an external heat exchanger. The temperature is about 65 to 70°C, and the pressure about 1 . 10⁶ Pa absolute. Isobutene yields 4,4-dimethyl 1,3-metadioxane (4-4 DMD). It produces *t*-butyl alcohol by a side reaction. The remaining olefins react more slowly to yield other dioxanes. Selectivities in relation to formol and isobutene range up to 95 and 90 mole per cent respectively for once-through conversions greater than 50 and 80 per cent, or even 90 per cent. Decantation of the reactor effluent furnishes two phases, one organic and the second aqueous. The first is neutralized with caustic, washed and then rid of unconverted C₄ and lighter or heavier products than

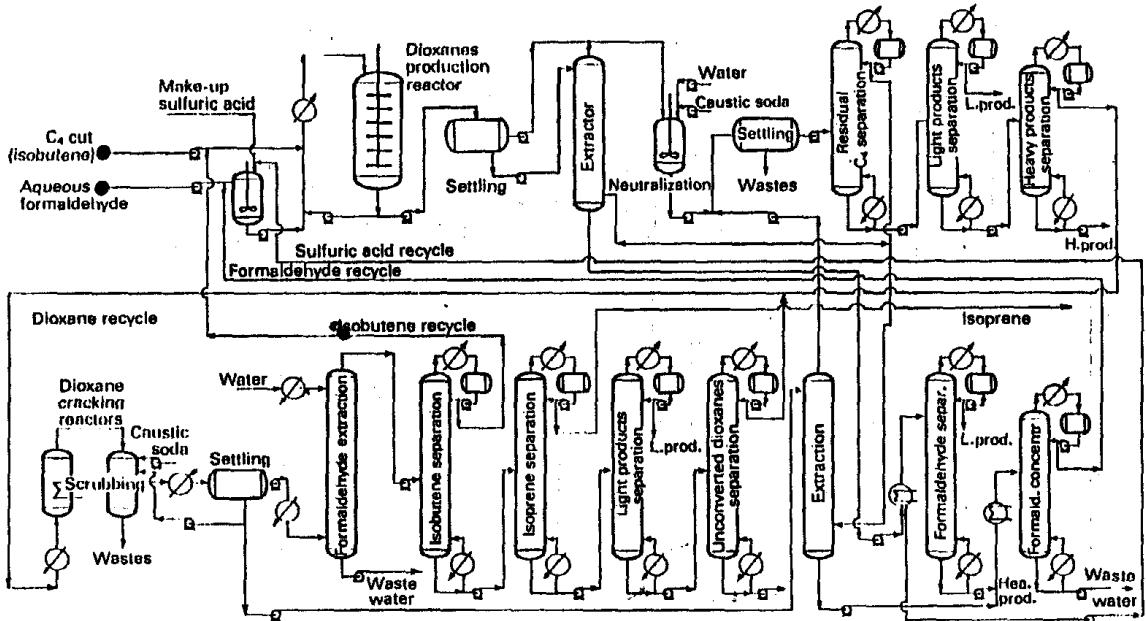


Fig. 6.5. Isoprene manufacture from isobutene and formaldehyde.

4-4 DMD by distillation. Before recycling, the aqueous phase undergoes reconcentration and purification, for example, by passage through an extractor operating in countercurrent flow with the residual C₄ compounds to remove the organic components, and then through an evaporator.

In the second step, the dioxanes are vaporized, superheated, and then cracked on a solid catalyst (supported phosphoric acid) in the presence of steam. The endothermic reaction takes place at about 200 to 250°C and 0.1 to 0.2 · 10⁶ Pa absolute. The heat required is supplied by the introduction of superheated steam, or by heating the support of the catalyst, which operates in a moving, fluidized or fixed bed, and, in this case, implies cyclic operation to remove the coke deposits formed. Isoprene selectivity is about 80 to 90 mole per cent, with once-through conversion of 50 to 60 per cent. The 4-4 DMD produces the isoprene. The other dioxanes present are decomposed into isomers of isoprene (piperylene etc.), while the *t*-butyl alcohol, also present in small amounts, yields isobutene. A separation train, consisting of scrubbers, extractors and distillation columns, serves to recycle the unconverted 4-4 DMD, isobutene and formol, and to produce isoprene to commercial specifications.

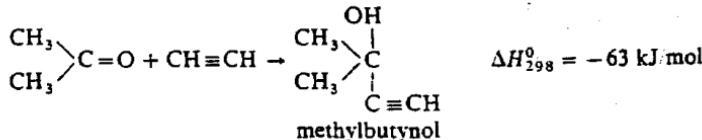
The purity of the isoprene depends on that of the dioxane and hence on the composition of the C₄ cut. The product obtained has a purity of at least 98.5 per cent weight. A simplified flow sheet is shown in Fig. 6.5.

Remark. Several companies have designed techniques derived from the foregoing processes, some of them leading to industrial development. These include isoprene manufacture from isobutene and formaldehyde in a single step (*British Hydrocarbon Chemical, Japan Institute of Physical and Chemical Research, Marathon, Sun Oil, Tokyo Institute of Technology*), and the replacement of formaldehyde by methanol and oxygen or by methylether (*Idemitsu Petrochemical, Sumitomo* etc.).

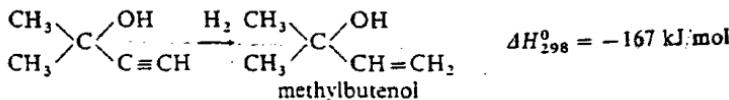
6.3.1.5 SNAM process (Fig. 6.6)

The raw materials used by this process are acetylene and acetone, which present the drawback of being already elaborated products and therefore expensive. However, the chemical operations involved and the equipment required are rather simple, and yields are also high. The main steps in the conversion are the following:

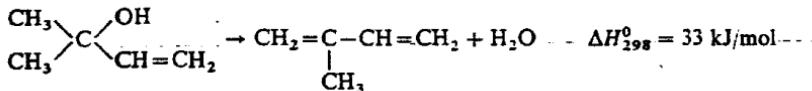
(a) Addition



(b) Selective hydrogenation:



(c) Dehydration



The addition reaction is conducted at a temperature between 10 and 40°C and $2 \cdot 10^6$ Pa absolute, in the presence of a potash solution as catalyst. The operation takes place with liquid ammonia and excess acetylene (2/1) to prevent the formation of by-products from acetone. The reaction yield is as high as 96 molar per cent. 50 to 60 mol of products are obtained per mol of potash. Conversion is stopped by neutralizing the catalyst. Unconverted acetylene and ammonia are recovered by flash and recycled. The methylbutynol is then purified by distillation in two columns. The first removes unconverted acetone at the top, while the second separates the heavy compounds and an azeotrope containing 28 weight per cent water. The yield after distillation is 95 molar per cent.

Hydrogenation is carried out directly on the azeotrope, at 0.5 to $1 \cdot 10^6$ Pa absolute, at a temperature of 30 to 80°C, in the presence of a palladium catalyst. Conversion is total. Less than 1 molar per cent of methylbutanol is formed. Unconverted hydrogen is recycled, similar to the catalyst, which is separated by centrifugation. The remaining product is evaporated to yield a methylbutenol/water azeotrope containing 77 per cent weight of hydrocarbon, which is sent directly to the next section.

Dehydration is carried out at atmospheric pressure and between 250 and 300°C, on alumina. Conversion is virtually total. A number of by-products are retained by water scrubbing. The catalyst is easily regenerated by the combustion of carbon deposits.

The final isoprene product contains 98.5 per cent weight, with a maximum olefins content of 1.5 per cent. Figure 6.6 shows a flow sheet of the SNAM process.

6.3.2 Economic data

The main economic data available on industrial processes for the synthesis of isoprene are summarized in Table 6.7.

6.3.3 Uses and producers

The average specifications of isoprene produced by this type of installation are listed in Table 6.8.

Tables 6.9 a and 6.9 b list the different capacities available worldwide in 1986 to manufacture isoprene, as well as the processes employed. It also points out the uses, capacities, production and consumption figures for Western Europe, the United States and Japan in 1982.

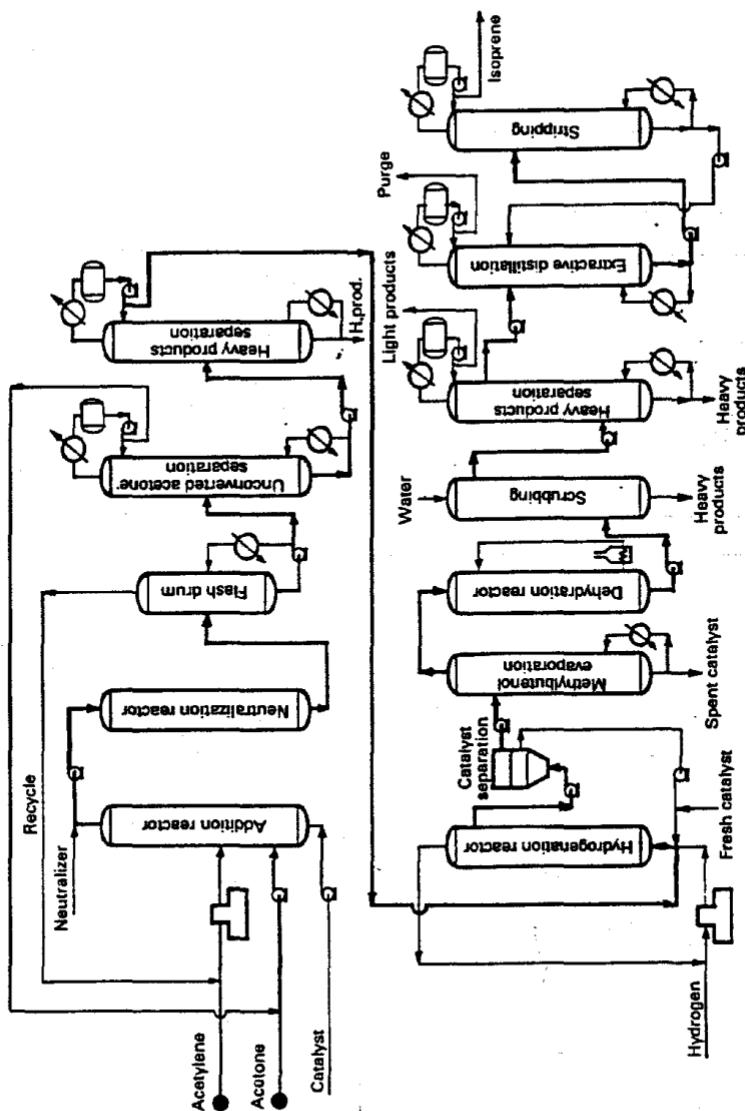


Fig. 6.6. Isoprene manufacture from acetylene and acetone. SNAM Progetti process.

TABLE 6.7
ISOPRENE MANUFACTURE ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 50,000 t/year

Process	Shell	Goodyear	Kuraray	SNAM
Battery limits investments (10 ⁶ US\$)	75	40	45	25
Consumption per ton of product				
Raw materials				
Isoamylenes (C ₅ cut) (t)	3.50	—	—	—
Propylene (t)	—	2.10	—	—
Isobutene (C ₄ cut) (t)	—	—	4.68	—
Formaldehyde (100%) (t)	—	—	0.76	—
Acetylene (t)	—	—	—	0.45
Acetone (t)	—	—	—	1.00
By-products				
C ₃ cut (t)	2.20	—	—	—
C ₄ cut (t)	—	—	3.55	—
Fuel (t)	0.30	—	0.18	—
Catalysts and chemicals				
Miscellaneous (US\$)	22	20	6	11
Hydrogen (kg)	—	—	—	40
Ammonia (kg)	—	—	—	7
Sulfuric acid (kg)	15	—	10	55
Caustic soda (or potash) (kg)	10	—	8	(20)
Ammonium chloride (kg)	—	—	—	40
Solvents (kg)	80	—	—	—
Utilities				
Steam (t)	5	9.5	11.5	12
Electricity (kWh)	500	220	75	890
Fuel (10 ⁶ kJ)	65	13	7	1.5
Cooling water (m ³)	620	450	520	650
Process water (m ³)	10	—	10	1
Labor (Operators per shift)	8	6	7	5

TABLE 6.8
AVERAGE COMMERCIAL SPECIFICATIONS OF SYNTHETIC ISOPRENE

Characteristics	Values
Isoprene (% Wt) min.	99 to 99.5
Olefins (ppm) max.	10,000
Cyclopentadiene (ppm) max.	100 to 150
α -acetylenics (ppm) max.	10 to 50
β -acetylenics (ppm) max.	10
Inhibitor (ppm) max.	200 to 300

TABLE 6.9A
ISOPRENE PRODUCTION CAPACITIES IN 1986

Country	Company	Location	Capacity (10^3 t/year)	Process
United States . . .	Atlantic Richfield Co. (ARCO)	Channelview (Tx)	36	C ₅ -dehydrogenation
	Chevron	Cedar Bayou (Tx)	16	
	Dow Chemical	Freeport (Tx)	18	Extractive distillation of pyrolysis C ₅ -cuts.
		Plaquemine (La)		
	Du Pont de Nemours	Chocolate Bayou (Tx)	21	Extractive distillation of pyrolysis C ₅ -cuts.
	Exxon	Baton Rouge (La)	27	Extractive distillation of pyrolysis C ₅ -cuts.
	Goodyear ⁽¹⁾	Baytown (Tx)	25	Extractive distillation of pyrolysis C ₅ -cuts.
	Shell Chemical	Beaumont (Tx)	84	Extractive distillation of pyrolysis C ₅ -cuts coming from elsewhere.
		Deer Park (Tx)	50	
	Union Carbide	Penuelas (PR)	14	Extractive distillation of pyrolysis C ₅ -cuts.
Total . . .			291	
France . . .	Compagnie Polyisoprène synthétique	Le Havre	40	Extractive distillation of pyrolysis C ₅ -cuts.
Italy . . .	ANIC	Ravenna	(30)	SNAM-acetylene/acetone.
Netherlands . . .	Shell Nederland	Pernis	50	Isononylene dehydrogenation.
Total . . .			115 (145)	Extractive distillation of pyrolysis C ₅ -cuts.
Japan . . .	Geon Isoprene	Mizushima	45	Extractive distillation of pyrolysis C ₅ -cuts.
	Kashima Isoprene Monomer	Kashima	30	Extractive distillation of pyrolysis C ₅ -cuts.
	Kuraray Isoprene Chemical	Kashima	30	Isobutylene/formaldehyde.
Total . . .			105	
USSR ⁽²⁾ . . .	Government	Novokuybychev	60	Isobutylene/formaldehyde.
		Tobolsk	60	Extractive distillation of pyrolysis C ₅ -cuts.
		Others	?	

(1) Goodyear is the only manufacturer of polyisoprène in the United States ($68 \cdot 10^3$ t/year).

(2) The overall production capacity of polyisoprène in centrally planned economy countries is estimated to be $9.35 \cdot 10^3$ t/year (Romania, $85 \cdot 10^3$ t/year and USSR, $850 \cdot 10^3$ t/year). In South Africa the plant capacity of Kurbochem in Newcastle is $45 \cdot 10^3$ t/year.

TABLE 6.9 b
ISOPRENE PRODUCTION AND CONSUMPTION IN 1982

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
Polyisoprene	83	66	96
Butyl rubber	11	8	4
Miscellaneous ⁽¹⁾	6	26	
Total	100	100	100
Production (10^3 t/year)	33	85 ⁽²⁾	72
Capacity (10^3 t/year)	115	290	105
Consumption (10^3 t/year)	48	62	45

(1) Styrene-isoprene thermoplastic elastomers.

(2) In 1984 isoprene production in the United States was $45 \cdot 10^3$ t/year, due to the increasing competition from natural rubber to polyisoprene elastomer.

6.4 STYRENE

All the styrene monomer ($\text{bp}_{1.013} = 145.2^\circ\text{C}$, $d_4^{20} = 0.906^{(3)}$) produced throughout the world is obtained directly or indirectly from ethylbenzene. Most is produced by dehydrogenation, while a certain amount is also obtained as a co-product of the manufacture of propylene oxide. Some attempts have been made to extract styrene from pyrolysis C₅₊ gasolines (Stex process by *Toray*, described in Section 4.2.5), but they have not culminated in commercial plants.

99 per cent of the ethylbenzene is used for the manufacture of styrene. About 95 per cent is obtained by the alkylation of benzene with ethylene, and the remainder by the superfractionation of aromatic C₈ cuts from catalytic reforming.

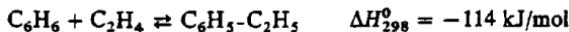
6.4.1 Ethylbenzene manufacture

Techniques for the separation of ethylbenzene in aromatic C₈ cuts, particularly superfractionation and possibly adsorption on molecular sieves, have been covered by specific analyses (see Sections 4.2.3 and 4.3.2.1). Thus, only chemical methods need to be examined, especially synthesis, which is a decisive factor at the industrial level, and which involves the alkylation of benzene with ethylene.

(3) Specific gravity, 68.0/39.2.

6.4.1.1 General characteristics of benzene alkylation with ethylene

The synthesis of ethylbenzene involves the following exothermic reaction:



It is favored by an increase in pressure and a decrease in temperature. However the reaction goes far to the right, below 600°C. It is accompanied by side conversions, especially of consecutive alkylations, leading to the formation of polyethylbenzenes. Dealkylation, dismutation and isomerization reactions also occur.

At atmospheric pressure, benzene alkylation is practically complete around 500°C. However, the extent of side products entails operation at lower temperature, possibly under pressure and, to accelerate the conversion, in the presence of catalyst systems.

Moreover, in order to improve the yields, the formation of polyalkylated derivatives is limited by using excess benzene in the reaction zone, and an attempt is made, after having separated those that have been produced, to achieve their transalkylation. This operation, which is practically athermic, takes place in conditions similar to those required for alkylation and, depending on the catalyst employed, can take place in the same reactor or in a different unit.

At the industrial level, two major synthesis methods employing acid catalysis can be distinguished:

- (a) A liquid or mixed phase process with two methods of using the catalyst system:
 - . In suspension or in a dispersed medium: these employ Lewis acids, such as aluminium chloride.
 - . Supported: the catalysts used in this case are silica aluminas, phosphoric acid deposited on kieselguhr, or boron trifluoride deposited on modified alumina.
- (b) The second method, more recent, is based on the use of molecular sieves in the vapor phase.

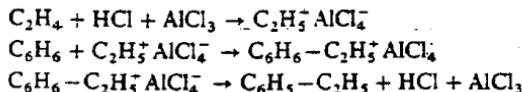
6.4.1.2 Liquid phase alkylation techniques

A. Processes operation in the presence of aluminum chloride

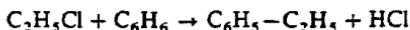
These processes account for over 85 per cent of world ethylbenzene production capacity.

a. Operating conditions

The main Lewis acid employed industrially to synthesize ethylbenzene is formed of the AlCl_3/HCl system. The general mechanism of its action in a Friedel/Crafts type reaction can be illustrated as follows:



In fact, only small amounts of hydrochloric acid are required to activate the aluminum chloride. Hence, to reduce the risks of corrosion, use is made of an initiator, ethyl chloride, whose action mechanism corresponds to the following equation:



In practice, the catalyst system is in the form of a so-called "red" complex, which is not perfectly soluble in aromatic hydrocarbons, and which contains 25 to 30 weight per cent of promoted aluminum chloride, combined with 45 to 50 per cent of benzene/ethylbenzene and about 25 per cent of higher molecular weight hydrocarbon compounds. Because it is heavier the catalyst settles at the bottom of the reactor. Since the complex is also corrosive, the reactor must be provided with a refractory lining or the reactor walls vitrified.

The earliest "first-generation" techniques operate at a pressure of about $0.15 \cdot 10^6$ Pa absolute and a temperature between 80 and 110°C. Certain recent "second-generation" processes operate at higher pressure, about $1 \cdot 10^6$ Pa absolute, and at "high temperature" (160 to 180°C), for better recovery of heat liberated by the reaction, and to reduce catalyst consumption. In the first case, the conditions are such that the upper part of the reaction medium is at the boiling point and the heat generated is removed by vaporization of the benzene. The benzene is then condensed with the production of low-pressure steam. In the second case, this heat exchange takes place directly on the liquid phase of a sidestream passing through a heat exchanger and recycled.

The composition of the reactor effluent depends on the molar ratio of the benzene to the ethyl groups in the feed. It has been demonstrated that the optimal conditions are satisfied with values of this parameter between 2 and 2.5. In this case, the alkylate obtained has the following composition: ethylbenzenes 41 to 43 weight per cent, benzene 38 to 40, diethylbenzenes 12 to 14, triethylbenzenes 2 to 3, heavier polyethylbenzenes 1.5 to 2, miscellaneous 1.5 to 2. Any decrease in the ratio of benzene to ethyl groups has the effect of reducing the formation of the higher molecular weight components.

The polyethylbenzenes can be recycled to the alkylation reactor. Aluminum chloride has the advantage of activating their transalkylation, which can therefore take place at the same time as the main reaction.

The side products formed include chlorinated organic compounds, particularly monochlorobenzene, which is an especially disturbing component, because its boiling point (132°C) is very close to that of ethylbenzene (136°C). The benzene feeds employed must be previously dried because, above 30 ppm water, the catalyst complex is destroyed. In practice, the space velocity of the conversion is defined by the ratio of the hourly benzene throughput to the volume of catalyst complex. This parameter is usually about 2. Benzene once-through conversion is up to 40 to 45 per cent.

b. Processes

Chronologically, several steps can be distinguished in the industrial development of the processes. The earliest, some of which are still used in smaller units, are those of *Dow*, *Hüls*, *IG-Farben*, *Koppers*, *Scientific Design*, *Shell*, *Union Carbide-Cosden-Badger* etc. The latest second-generation processes are those of *BASF* (*Badische Anilin und Soda Fabrik*), *CdF-Chimie-Technip*, *Dow* and *Monsanto-Lummus*.

The differences are primarily associated with the implementation of the catalyst system which, as proposed by Monsanto, may have a sufficiently low concentration to allow for the existence of a single homogeneous reaction phase, while maintaining an acceptable conversion rate by temperature elevation. They are also associated with the treatment of the alkylates, especially the removal of residual aluminum chloride. Successive scrubbings were initially performed with caustic soda, and were highly pollutant and difficult to carry out due to foaming, emulsion problems and fouling. At present, *Monsanto-Lummus* solubilizes the alumina formed in hydrochloric acid medium by hydrolysis and concentration of the liquors, carries out a neutralization with caustic soda, and a final scrubbing with water. *CdF-Chimie-Technip* and *BASF* prefer neutralization with ammonia, dissolution of the salts by washing with water and possibly with caustic soda followed by water to terminate the operation, or a dry operation with flocculation settling and separation of the salts produced by neutralization with ammonia.

As a rule, the installation flow sheet displays four main sections:

- Benzene drying, either by azeotropic or preferably heteroazeotropic distillation, or on molecular sieves. To obtain a residual water content less than 30 ppm, the distillation column must have at least 15 trays.
- Synthesis, which takes place in a reactor with an internal lining of corrosion-resistant bricks, and whose dimensions, for a unit production capacity of 70,000 t/year, are 2.6 to 2.7 m in diameter and 12 m high, for a maximum size of about 150,000 t/year. Hydrochloric acid stripping in the vapor phase requires the use of hastelloy B for the parts of the equipment in contact with this acid.

The ethylene feed, which may first be compressed, depending on the pressure at which it is available and the operating conditions, is sparged at the bottom of the reactor by means of graphite spray bars, a system that serves to maintain effective agitation of the medium, as well as sufficient contact. The initiator is introduced as required, at the same time as the ethylene or the feed benzene. The latter, before reaching the reaction zone and after drying, passes through a packed scrubbing column for the gaseous effluents from the reactor, to rid them of stripped hydrochloric acid.

Variants also exist at two other levels:

- (a) The elimination of heat liberated by the reaction, either by external circulation and cooling of the liquid phase, or by benzene vaporization.
 - (b) The transalkylation of polyethylbenzenes, especially the di- and triethylbenzenes which, after separation, are recycled to a special reactor also operating on the alkylate around 100°C, or to alkylation itself, by introduction at the level of the gas scrubbing column.
- Treatment of the alkylate, which generally exits by overflow from the main reactor and which, depending on each case, after having undergone transalkylation, may be flashed and then cooled to 35 to 40°C. Two phases are then formed by decantation. The heavier, consisting of the soluble catalyst complex at higher temperature, is recycled to the reaction zone. The lighter, which still contains dissolved complex, must be treated by washing with water, caustic soda or ammonia, to ensure that the ethylbenzene produced is free of chlorinated compounds and thus meets the specifications required for dehydrogenation to styrene.

- Separation of the components of the alkylate by distillation in a series of three columns which serve to isolate the following in succession:

- Benzene at $0.4 \cdot 10^6$ Pa absolute and between 138 and 140°C at the top, 210°C at the bottom with 45 trays and a reflux ratio of 1.
- Ethylbenzene at $0.15 \cdot 10^6$ Pa absolute and between 150 and 160°C at the top, $0.2 \cdot 10^6$ Pa absolute and 210°C at the bottom with 40 to 45 trays and a reflux ratio of 1.5.
- Polyethylbenzenes under vacuum: 6.5 kPa absolute and 100°C at the top, 13 kPa absolute and between 210 and 215°C at the bottom: the tars drawn off are burned.

Figure 6.7 shows a typical flow sheet for a plant operating on a second-generation process, like the one developed by *Monsanto-Lummus*.

B. Processes operating on supported catalyst

These processes essentially include the Alkar technology, industrialized in 1958 by *UOP*, which displays the special feature of being able to use cracked gases with a low ethylene content (8 to 10 per cent volume), and another of using boron trifluoride deposited on alumina as the catalyst system, thus minimizing corrosion. It currently accounts for nearly 1 million t/year of capacity.

This type of catalyst does not simultaneously allow alkylation of the benzene and transalkylation of the polyethylbenzenes. Hence distinct units must be employed, operating in different conditions:

- Alkylation takes place in an adiabatic reactor between 120 and 150°C at the inlet, and 170 to 180°C at the outlet, and $3.5 \cdot 10^6$ Pa absolute, in the presence of fixed alumina beds. BF_3 is used as a reactant, added with the benzene feedstock. Its action obeys the following mechanism:



- Transalkylation also takes place adiabatically around 200 to 210°C and $3.5 \cdot 10^6$ Pa absolute, with a benzene to ethylene molar ratio of about 2.

Since no hydrofluoric acid is formed, corrosion problems do not normally arise. On the other hand, traces of water lead to the formation of boron oxyfluorides, such as $(\text{BOF})_x$ with $3 < x < 10$. They accumulate in the benzene recycle, which must therefore be treated before re-use. The make-up benzene must also have a very low water content, about 2 to 3 ppm, as compared with 20 to 30 ppm for processes employing aluminum chloride, thus significantly complicating the initial drying step.

The limitation of conversion rates to between 25 and 30 per cent per pass, by avoiding an excessive temperature rise in the reaction medium, has the effect of preventing the production of heavy products. On the other hand, this entails high benzene recirculation. The following are separated by flash and settling at the reactor exit:

- A light phase rich in benzene and containing most of the boron trifluoride introduced.
- A heavy phase containing the remainder of the benzene and the ethylbenzene: the hydrocarbons are separated by distillation, and the benzene and BF_3 are recycled.

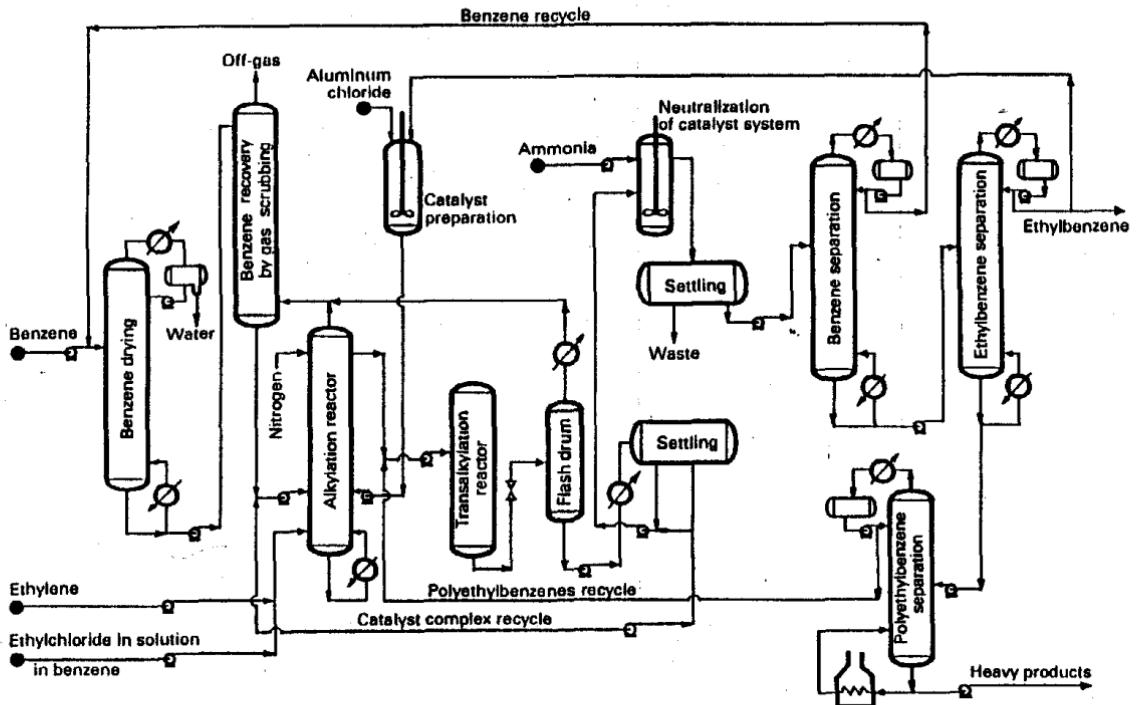


Fig. 6.7. Ethylbenzene manufacture by alkylation of benzene in the liquid phase in the presence of aluminum chloride.

6.4.1.3 Vapor phase alkylation techniques

A. Different types of catalyst employed

The earliest industrial developments of vapor phase alkylation processes involved the use of alumina base catalyst systems. They include the Koppers technique industrialized in the Second World War, which operates around 310°C and between 6 and $6.5 \cdot 10^6$ Pa absolute, but does not allow the transalkylation of polyethylbenzenes.

In the 1960s, *El Paso* employed phosphoric acid deposited on kieselguhr around 325°C and about $6 \cdot 10^6$ Pa absolute. This catalyst is capable of converting the polyethylbenzenes, but their recycle results in a drop in catalyst activity due to the cracking reactions and the formation of coke deposits.

In 1980, investigations conducted on zeolites by *Union Carbide* and *Mobil* in particular found an industrial application with the construction of a first plant with a capacity of 450,000 t/year in Bayport, Texas. This plant uses the Mobil-Badger technology based on the use of ZSM5 type molecular sieves, whose main characteristics are a silica to alumina ratio of about 40, a crystal density greater than 1600 kg/m³, elliptical pores whose minor axis measures about 5 Å and major axis 7 Å. These dimensions enable the ethylbenzene molecules, but not the polyethylbenzene molecules, to diffuse freely, and this, combined with the operating conditions, indirectly favors the transalkylation of the polyethylbenzenes. In this case, these systems operate in the presence of excess benzene, around 400 to 450°C, at moderate pressure. They are also regenerable and serve to overcome the problem of coke deposits. Finally, since only a slight free acidity appears, they are not liable to significant corrosion.

B. Mobil-Badger process

For the production of ethylbenzene, the ZSM5 sieves employed by *Mobil-Badger* are used in the following average operating conditions:

Temperature	420 to 450°C
Pressure	1.5 to $2.5 \cdot 10^6$ Pa absolute
Benzene/ethylene molar ratio at reactor inlet	8 to 16
WHSV in relation to total feedstock	150 to 300
LHSV in relation to ethylene	3 to 5
Benzene once-through conversion	≥ 12 per cent
Ethylbenzene molar selectivity	> 98 per cent

The process flow sheet (Fig. 6.8) comprises the following main steps:

- Synthesis. A mixture of make-up and recycle benzene is introduced into the reactors in a downflow stream, together with polyethylbenzenes, also recycled. This feed is preheated, first by heat exchange with the effluent leaving the reaction system, and then by vaporization in a furnace. Part of the ethylene required is added to it at this point. The reactors contain several beds of molecular sieves, usually four, between which the cold ethylene and benzene are sent to control the temperature rise resulting from the exothermic nature of the alkylation. Their progressive coking entails regeneration every 15 days to one month, by controlled combustion using oxygen-poor air or suitable N₂-O₂ mixtures. The operation

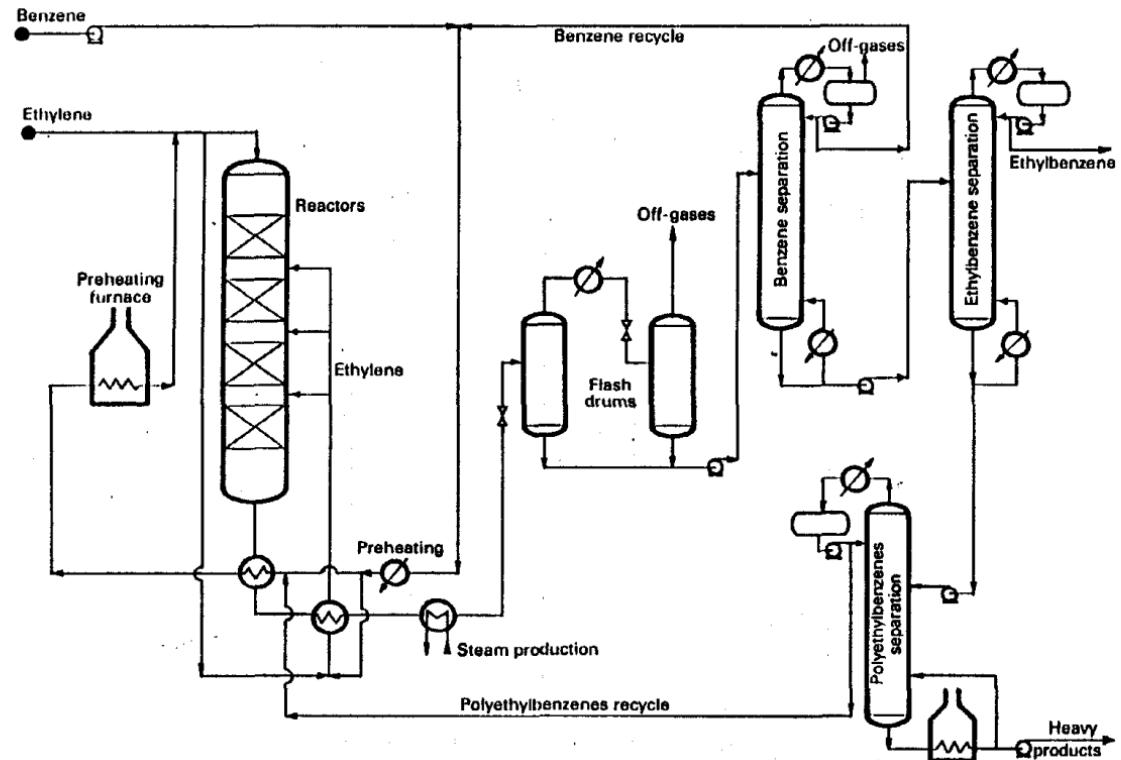


Fig. 6.8. Ethylbenzene manufacture by alkylation of benzene in the vapor phase. Mobil/Badger process.

lasts 24 h. and an additional "swing" reactor is required to ensure continuous operation of the facilities.

- (b) Treatment of the effluent by fractionation in a series of distillation columns. The first separates the benzene and light compounds at the top. Make-up benzene and benzene from subsequent separations are introduced at the reflux level of this distillation column. The heavy ends feed a second column separating the C₇₋ compounds at the top and the C₈₊ compounds at the bottom. The distillate can therefore be added to the by-product consisting of benzene and toluene obtained by the dehydrogenation of ethylbenzene to styrene, so that, after a second distillation, only the C₆ compounds are recycled to alkylation. Two other distillation columns are used to treat the C₈₋ compounds to separate the ethylbenzene and the polyethylbenzenes, which can then be recycled.

6.4.1.4 Economic data

Table 6.10 lists the typical economic data on the main processes used today for the alkylation of benzene with ethylene.

TABLE 6.10
ETHYLBENZENE MANUFACTURE ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 300,000 t/year

Technology	CdF Chimie Technip	Union Carbide Cosden/Badger	Monsanto Lummus	Mobil Badger
Process	Liquid phase	Liquid phase	Liquid phase	Gas phase
Battery limits investments (10 ⁶ US\$)	21	21	20	17
Initial catalyst load (10 ⁶ US\$)	—	—	—	2
Consumption per ton of product				
Raw materials				
Ethylene (t)	0.27	0.27	0.27	0.27
Benzene (t)	0.76	0.75	0.74-0.75	0.74-0.75
Chemicals and catalysts				
Aluminum chloride (kg)	3	3	2	—
Ethyl chloride (kg)	3	3	1	—
Ammoniac (kg)	3	—	—	—
Miscellaneous (US\$)	ε	0.4	0.4	4.0
Utilities				
Steam consumed (t)	—	0.17	0.04	0.15
Steam produced (t)	(—)0.6	(—)1.14	(—)1.00	(—)2.25
Electricity (kWh)	10	15	30	10
Fuel (10 ⁶ kJ)	0.4	1.2	2	3
Cooling water (m ³)	50	20	20	6
Boiler feedwater (m ³)	0.6	0.5	1	0.2
Labor (Operators per shift)	2	2	2	2

6.4.2 Styrene manufacture

Styrene is manufactured nearly entirely by the direct dehydrogenation of ethylbenzene. Smaller amounts are obtained indirectly, as a co-product, from the production of propylene oxide by the Oxirane and Shell technologies, industrialized in the United States, the Netherlands and Spain, and whose essential intermediate step is the formation of ethylbenzene hydroperoxide, or from the production of aniline, by a technique developed in the USSR, which combines the highly exothermic hydrogenation of nitrobenzene with the highly endothermic dehydrogenation of ethylbenzene.

6.4.2.1 Direct dehydrogenation of ethylbenzene

A. General reaction conditions

The conversion of ethylbenzene to styrene is a highly endothermic reaction which obeys the following overall mechanism:



Favored at high temperature and low pressure, it is closely related to the manufacture of butadiene from butenes or the primary dehydrogenation observed in the steam cracking of hydrocarbon feedstocks.

In the absence of catalyst, it occurs around 700 to 800°C with once-through conversions of 20 to 30 per cent and overall yields not exceeding 50 to 60 molar per cent. This low performance can be ascribed to the side reactions, especially hydrodealkylation to benzene and toluene, miscellaneous crackings with the formation of coke or water gas, and the alkylation of the styrene formed to methylstyrene and the conversion of the by-products obtained.

As for steam cracking, dehydrogenation is favored by operating in the presence of steam and by quenching the effluents. It is also facilitated by the use of catalysts.

Steam furnishes the heat required for the reaction, reduces the heat to be supplied per unit volume by dilution, considerably lowers the partial pressure of the hydrocarbons, thus shifting the equilibrium towards styrene production, and slows down coke deposit by maintaining the activity of the catalyst systems employed. These catalysts help to improve once-through conversion and selectivity by lowering the temperature. However, the temperature remains high, at around 550 to 650°C, with a pressure between 0.1 and $0.3 \cdot 10^6 \text{ Pa}$ absolute in older installations, and lower than $0.1 \cdot 10^6 \text{ Pa}$ absolute in more recent plants.

As a rule, present-day catalysts are based on iron oxide Fe_2O_3 , although, at the outset, the pronounced tendency of this compound to lead to elemental iron, which favors dealkylation and coke formation reactions, caused it to be discarded in favor of other systems such as ternary oxide mixes, such as ZnO , Al_2O_3 and CuO (*JG Farben*), or more recently the attempt to employ a combination of V_2O_5 and Al_2O_3 , first alone, and then in the presence of alkali metals (*Dow, CCI: Catalysts and Chemicals Inc., a United Catalysts subsidiary*). Gradually, the good activity of iron oxide was exploited by

first improving its stability, namely its life, by the addition of Cr_2O_3 , and then its selectivity by the addition of alkali metals (potassium or rubidium) in the form of oxides (Shell), and finally by exercising better control of its activity by reducing the specific surface area resulting from calcination at about 900 to 950°C.

Modern catalysts usually contain five elements: a basic active component (Fe_2O_3 etc.), a stabilizer (Cr_2O_3 , Al_2O_3 , MgO etc.) a coke inhibitor (K_2O etc.), an initiator (CuO , V_2O_5 , AgO etc.), and a binder which imparts certain mechanical properties to the system (calcium aluminate etc.).

Performance depends above all on the way in which the catalyst is employed, and this takes place in two different ways, isothermal and adiabatic. Hence the same catalyst formula offers greater abrasion resistance and crushing strength characterized by a lower water to ethylbenzene weight ratio at the reactor inlet and longer life if operation is isothermal. The steam ratio is usually 1 to 1.2 in this case, as compared with 1.6 to 2.5 in adiabatic conditions, and the corresponding lives are 5 to 6 years, against 18 months to 2 years. The essential reason for these differences is the lower feed preheat temperature.

Since adiabatic reactors represent the most widespread industrial choice, catalysts can be classed in three distinct families, as a function of this application:

- (a) Those known to be active (55 to 60 per cent conversion) but slightly selective (89 to 90 per cent molar selectivity) with medium resistance and strength (steam ratio > 2): Shell 105, Girdler G84 etc.
- (b) Those considered highly selective (95 per cent molar selectivity), but less active (40 per cent conversion), operating at a higher temperature, with medium resistance and strength (steam ratio 2 to 2.2): Shell 105, Girdler G64C, Procatalyse DH12 etc.
- (c) Those operating with a moderate steam ratio (> 2), fairly active (50 to 55 per cent conversion) and slightly less selective (90 per cent molar selectivity): BASF, Shell 305, Girdler G641, Procatalyse DH14 and DH16, UOP (Styro-Plus process).

B. Processes

Processes are divided into two major categories, according to whether the reactors are in adiabatic or isothermal (or more precisely pseudo-isothermal) operation.

a. Adiabatic dehydrogenation

In this type of treatment, which demonstrates the most impressive industrial growth, three successive generations of processes can be identified, with differences connected with the design and action of the reaction device, offering the following alternatives:

- (a) A single reactor with once-through conversion of at least 40 per cent and operating between 0.15 and $0.2 \cdot 10^6$ Pa absolute.
- (b) Two reactors in series designed to optimize the selectivity to conversion ratio, at a pressure comparable to that used in the previous generation: in this case once-through conversion is up to 45 to 55 per cent.
- (c) Negative-pressure operation of the reaction system with once-through conversions of more than 60 per cent.

This development is associated with the search for the best possible compromise between once-through conversion, selectivity, and the amount of steam to be introduced.

Within the catalyst bed, in fact, the exothermicity of the reaction results in a temperature drop of 1°C per percent conversion. Hence, to obtain a high conversion rate, substantial steam must be added at a sufficiently high temperature. Above 610°C, however, the ethylbenzene and styrene formed are subject to incipient cracking. One solution thus consists of using several reactors in series with intermediate heating, or operating in negative pressure to shift the reaction in the desired direction. In the latter case, however, the pressure drops due to the thickness of the catalyst beds assume tremendous importance, so that the reactors must feature a special design, for instance with radial instead of axial flow.

In principle, the flow sheet (Fig. 6.9) comprises the evaporation of the make-up and recycle ethylbenzene by means of medium-pressure steam, followed by the heating of this effluent, to which 10 per cent of the total amount of steam required for the conversion has been added, around 530 to 550°C, by passage through a furnace. The temperature of 650°C, at which dehydrogenation begins in practice, is reached by adding the remaining 90 per cent of steam within the reactor itself, at the catalyst level, after first raising it to over 800°C by passing it through the ethylbenzene preheating furnace. In this case, the gases flow radially through the catalyst beds and in a downflow through the annular spaces. The effluent leaving at about 590 to 600°C is rapidly cooled in a quench boiler where medium-pressure steam is produced, and then by passage through an air-cooled exchanger, whose optimal operating conditions are reached by the prior in-line injection of a water spray. Radial gas transfer through the catalyst is indispensable in designing large unit capacities. This is because axial operation does not allow for reactor diameters greater than 6.3 to 6.5 m. The products are cooled and partly condensed, with the formation of three phases:

- (a) A gas phase rich in hydrogen, carbon monoxide, carbon dioxide and light hydrocarbons (methane, ethylene, etc.); after compression and liquefaction of the heavier fractions, this can be used as a fuel.
- (b) An aqueous phase rich in aromatics which are separated by stripping; benzene and toluene serve as reflux during this operation.
- (c) An organic phase mainly consisting of styrene and ethylbenzene, to which the hydrocarbons recovered from the aqueous phase are added.

b. Isothermal dehydrogenation

This process is technologically more difficult to implement, because it requires the use of multtube reaction systems with heat transfer fluid flow outside the tubes. However, it is justified by the energy gains and the better performance achieved by operation at a lower reactor feed inlet temperature, and consequently with a lower steam ratio than with adiabatic operation.

This technique, essentially industrialized by *BASF*, remained economically competitive until the advent of the so-called third-generation adiabatic processes employing highly selective catalysts. The operating conditions and average performance of this type of dehydrogenation are as follows:

Feed reactor inlet temperature	580°C
Heat transfer fluid temperature	
at inlet	750 °C
at outlet	630°C

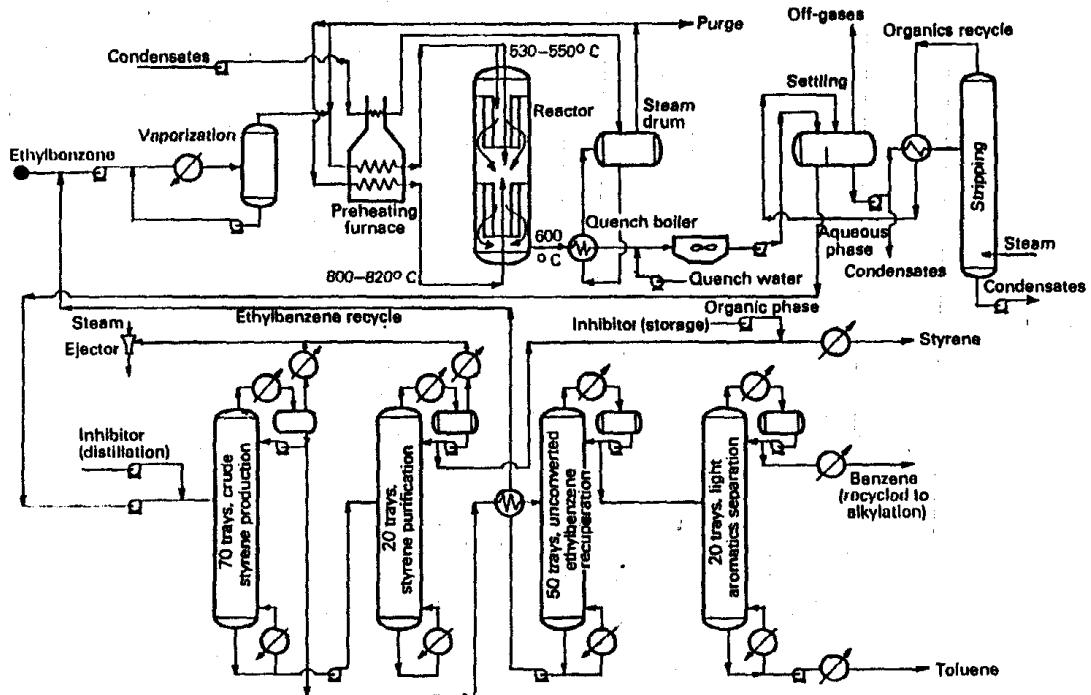


Fig. 6.9. Styrene manufacture by adiabatic dehydrogenation of ethylbenzene.

Steam ratio	1.1 to 1.2
Once-through conversion	60 per cent
Selectivity	92 to 94 mole per cent

The BASF process (Fig. 6.10) proposes the use of a flue gas as the heat transfer fluid. The ethylbenzene and process water are vaporized in this case and superheated by heat exchange with the reactor effluent and with the flue gas. The latter is cooled to 375°C and then heated in a burner.

The reactor has tubes 2.5 to 4 m long and 10 to 20 cm in diameter filled with catalyst. The catalyst, maintained by a grid, overflows at the top and bottom of the actual tubular zone. The operating principle of this type of equipment implies limitations in terms of maximum unit production capacity.

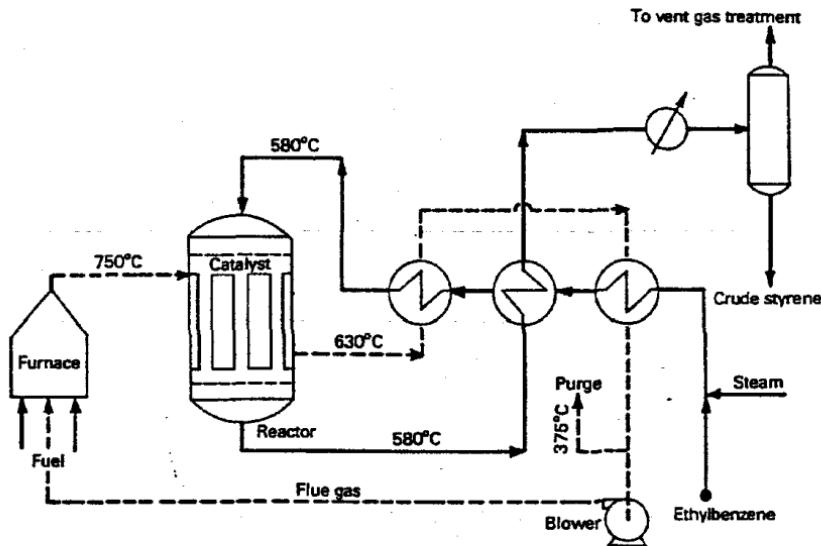


Fig. 6.10. Styrene manufacture by isothermal dehydrogenation of ethylbenzene. BASF process.

C. Treatment of organic effluents produced by dehydrogenation (Fig. 6.9)

This treatment normally includes the following four distillation operations:

- Production of crude styrene at the bottom of the column from a feedstock containing about 50 weight per cent of styrene.
- Purification and adjustment of this styrene to meet commercial specifications.
- Recovery of unconverted ethylbenzene and its recycle to the dehydrogenation stage.
- Treatment of the light fractions recovered, with separation of benzene, which is returned to the alkylation step, and of toluene.

The first operation is by far the most delicate given the small differential between the boiling points of ethylbenzene and styrene (9°C at atmospheric pressure) and the pronounced tendency of styrene to polymerize easily, even under vacuum. Hence it requires special operating conditions including:

- (a) A large number of trays (60 to 70) and high reflux ratios (> 6).
- (b) Partial vacuum (7 to 30 kPa absolute) designed to limit the temperature at the bottom of the column to less than 108°C and to increase the relative volatilities.
- (c) The presence of a polymerization inhibitor, such as sulfur or dinitrophenols.
- (d) Minimization of pressure drops in the condenser and trays.

In practice, a distinction must be made between earlier systems, which performed the separation by means of a set of two columns in series, and current distillation systems using a single high-performance column. Initially, in the techniques like the one commercialized for the first time by *Dow* in 1937, the tray configuration led to a total pressure drop of more than 35 kPa. Given the poor control of inhibition by sulfur, the column bottom temperature could not exceed 98°C, which led to a maximum allowable pressure drop of 20 kPa per unit. In modern technologies, the pressure drop per tray is less than 350 Pa (*Union Carbide*, *Lummus*, *Glitsch* etc.) and sulfur is introduced more regularly, allowing a higher bottom temperature, a larger number of trays per shell, and ultimately the use of a single column.

The separation can also be carried out by using packings such as Intalox by *Norton*, Mellapak by *Sulzer*, etc., offering high efficiency and low pressure drop, although at higher cost, to replace the trays. This technological development has led to substantial energy conservation, at the cost of a loss of flexibility of the installation, because the technical utilization factor must exceed 70 per cent. It should also be noted that the maximum column diameter cannot exceed 12 m, corresponding to the production of 450,000 t/year of styrene.

The purification of crude styrene, which contains 300 to 400 ppm of ethylbenzene and heavy hydrocarbons, requires less severe operating conditions: about 20 trays, top and bottom temperatures of about 50 and 105°C respectively for pressures corresponding to around 10 and 20 kPa absolute. Polymerization inhibitor must also be injected. The styrene product has a minimum purity of 99.7 to 99.8 per cent.

Recovery of the ethylbenzene not converted by dehydrogenation, from an effluent consisting of benzene, toluene and 1.5 to 2 weight per cent of styrene, takes place at the top of an atmospheric column with a bottom temperature of about 140°C. It requires nearly 50 trays. In the earlier techniques with low-selective catalysts, the presence of benzene and toluene in significant amounts raised recovery problems in the condenser, due to the formation of azeotropes with water.

Treatment of the distillate from the previous column consists in separating the benzene at the top at atmospheric pressure, operating around 115°C at the bottom, in a unit containing about 20 trays.

While sulfur and nitrophenols are employed as inhibitors in the distillation of styrene under partial vacuum, other additives, active in the presence of oxygen, are also needed to prevent polymerization in the storage facilities. These are normally ter butyl 4-catechol or hydroquinone, added at the rate of 10 to 100 ppm, depending on the temperature and residence time.

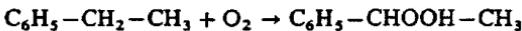
6.4.2.2 Propylene oxide and styrene co-production

This method, initially intended for the more selective production of propylene oxide, is commercialized by *ARCO Chemical* (formerly *Oxirane*), an *Atlantic Richfield Co* subsidiary, and by *Shell*. The first industrial plant was built in 1973 by Montoro, a joint venture of *Oxirane* and *Empetrol*, at Alcudia, Spain. This plant can now manufacture 100,000 t/year of styrene and 40,000 t/year of propylene oxide. Two other facilities based on this technology are also in operation, one at Channelview, Texas, and the second in Japan, owned jointly by *Sumitomo* and *Showa Denka* (*Nippon Oxirane*), capable of producing 455,000 and 225,000 t/year of styrene respectively, as well as about 180,000 and 90,000 t/year of propylene oxide. *Shell* has also built production capacities of 330,000 and 125,000 t/year of these two products at its Moerdijk complex in the Netherlands.

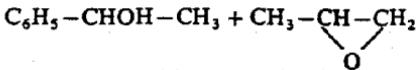
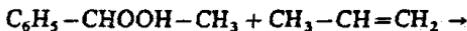
A. General conversion characteristics

This conversion comprises four main steps:

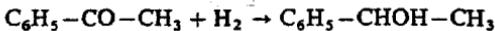
- (a) Liquid phase oxidation of ethylbenzene to hydroperoxide, with acetophenone and phenyl-1 ethanol as by-products:



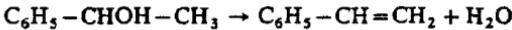
- (b) Liquid phase epoxidation of the propylene in the presence of a homogeneous catalyst (*Oxirane*) or heterogeneous catalyst (*Shell*):



- (c) Hydrogenation of residual hydroperoxide and acetophenone by-product to phenyl-1 ethanol:



- (d) Dehydration of phenyl-1 ethanol to styrene:



- Oxidation.** This highly exothermic reaction takes place in the absence of catalyst. However, it requires the presence of basic compounds (calcium or magnesium carbonate) to neutralize the acids formed and hence to prevent the undesirable decomposition of the hydroperoxide, as well as sodium pyrophosphate or citric acid, designed to counter-balance the destabilization effects exerted by the metallic ions of the walls.

Moreover, to minimize the similar influence of heat and advancement of the reaction, the temperature must be controlled and restricted to between 125 and 155°C, and once-through conversion must not exceed 15 to 17 per cent, or 12 to 13 per cent in practice. In these conditions, hydroperoxide selectivity exceeds 87 weight per cent and that of the styrene precursors 98 weight per cent. The pressure only has the effect of keeping the medium liquid, and is therefore about $1.5 \cdot 10^6$ Pa absolute.

- Epoxidation.** In the *Oxirane* homogeneous phase technique, epoxidation is catalyzed by molybdenum naphthenate, introduced in a solution in phenyl-1 ethanol at the rate of

$1 \text{ to } 5 \cdot 10^{-3}$ mol per mol of hydroperoxide. The presence of sodium naphthenate, by preventing side reaction, helps to reduce the excess propylene required (from 10/1 to 2/1 in moles). In the Shell technology, epoxidation is catalyzed by metallic oxides (molybdenum, vanadium, titanium, etc.) supported on silica. The highly exothermic reaction takes place around 100 to 130°C, at $3.5 \cdot 10^6$ Pa absolute. Hydroperoxide conversion is very high (> 97 per cent). Propylene oxide molar selectivity exceeds 70 per cent and that of the styrene precursors 93 per cent. As for propylene, its once-through conversion is about 15 per cent, for a oxide molar selectivity greater than 90 per cent, and the main by-products are dimers and heavier hydrocarbons.

- **Hydrogenation.** The residual hydroperoxide and acetophenone by-product is hydrogenated to phenyl-1 ethanol at about 120 to 150°C and $1 \cdot 10^6$ Pa absolute, in a heterogeneous phase, in the presence of catalysts based on copper and chromium or nickel oxides on kieselguhr.

- **Dehydration.** This reaction takes place in the vapor phase around 250°C, between 0.2 and $0.3 \cdot 10^6$ Pa absolute, in the presence of aq acid catalyst (10 to 15 weight per cent of TiO₂ on alumina). Once-through conversion is up to 85 per cent and styrene molar selectivity exceeds 95 per cent.

B. Processes

The processes are essentially those developed by *Oxitane* and *Shell*. As a rule, the flow sheet (Fig. 6.11) comprises four sections corresponding to the operations described above:

- **Oxidation.** Ethylbenzene is oxidized to hydroperoxide by air injection in the liquid phase. This takes place simultaneously in several series of reactors in parallel, each containing three elements. These are empty vessels, generally of titanium, in which a residence time of about one hour is maintained. In each series, these units operate at decreasing temperature as the reaction advances. The heat liberated by the reaction is eliminated by the vaporization of a fraction of the liquid phase, which is then recondensed and recycled. The effluent obtained contains about 10 to 12 per cent weight of hydroperoxide. It is sometimes concentrated to 17 per cent weight in an evaporator, and the ethylbenzene recovered is returned to the conversion zone.

- **Epoxidation.** It also takes place in several series of reactors, each with four elements, in the presence of chemical-grade propylene, injected at the inlet to each reactor. Intermediate heat exchangers remove the heat liberated. Residence time is about 1 1/4 hours. Excess propylene is recovered under pressure in a series of two depropanizers. Purge takes place in a third column, separating part of the propane introduced with the propylene feedstock.

Oxygenated compounds and unconverted ethylbenzene, collected at the bottom of the second depropanizer, are first distilled under vacuum to recover the propylene oxide and lighter components at the top. This effluent is rid in succession of the acetaldehyde and propionaldehyde it contains by simple distillation, and then of methyl formate by extractive distillation with ethylbenzene. The latter is then purified and recycled. The operation is terminated by a final column which produces propylene oxide to commercial specifications.

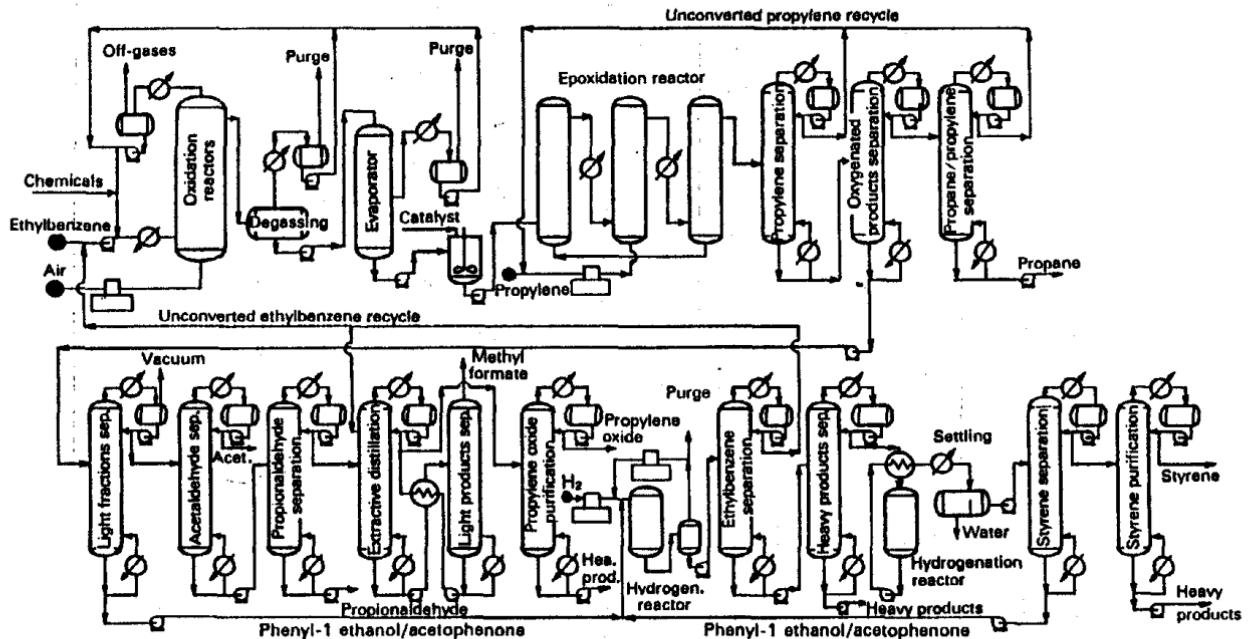


Fig. 6.11. Manufacture of styrene and propylene oxide from ethylbenzene and propylene. ARCO Chemical (Oxirane) process.

- **Hydrogenation.** The withdrawal stream from vacuum distillation is hydrogenated to remove the residual hydroperoxide and to convert the acetophenone. Fractionation removes the ethylbenzene and then the phenyl-1 ethanol from the hydrogenation effluent. The separation of ethylbenzene must be carefully effected to avoid subsequent superfractionation in the presence of styrene.

- **Dehydration.** The alcohol obtained is dehydrated in several tubular reactors laid out in parallel. The water produced is condensed, decanted, and rid of unconverted phenyl-1 ethanol by stripping. The organic phase is distilled in two steps, the first to remove the alcohol and ketone contained and to recycle them to hydrogenation, and the second in order to produce styrene meeting commercial specifications.

6.4.2.3 Other industrial methods for manufacturing styrene

Among the different methods for manufacturing styrene, other than those already examined, and which are likely to lead to industrial production, are the following:

- (a) Dehydrogenation of ethylbenzene by atmospheric oxygen or by oxidants such as SO₂. Already applied by *Phillips* to the manufacture of butadiene from butenes, it is also being considered by *BASF*, *Esso*, *Monsanto*, *Scientific Design*, *Shell*, *SNPA* (*Société Nationale des Pétroles d'Aquitaine*), etc.
- (b) Alkylation of toluene with methanol around 450°C, in the presence of modified molecular sieves. The styrene/ethylbenzene mixture, after separation and recycling of the excess methanol and toluene, is fractionated and dehydrogenated. This method is mainly being investigated by *Monsanto*.
- (c) Dimerization of toluene to stilbene around 600°C, in the presence of a redox catalyst system based on Pb/PbO, and its dismutation in a second step with ethylene, at 500°C, on a catalyst containing tungsten oxide. *Monsanto* is also examining this possibility to produce styrene more cheaply.
- (d) Dimerization of butadiene to vinylcyclohexene in a homogeneous phase around 60°C, in the presence of an organometallic catalyst, by a Diels-Alder reaction, followed by its conversion to ethylbenzene, which is then dehydrogenated at 400°C with a catalyst system based on platinum deposited on alumina. The main license holders concerned by this method are *ARCO*, *CdF-Chimie*, *IFP*, *Maruzen*, *Montedison*, *Phillips* and *SNEA* (*Société Nationale Elf Aquitaine*).

6.4.2.4 Economic data

Table 6.11 lists the typical economic data on the manufacture of styrene by adiabatic dehydrogenation of ethylbenzene, and by the method industrialized by *Oxitane*.

6.4.2.5 Uses and producers

Table 6.12 indicates the average commercial specifications of styrene required for the production of SBR in emulsion.

Table 6.13 lists the main uses of styrene in Western Europe, the United States and Japan in 1984, as well as the production, capacities and consumption in these three geographic areas. Some data are given for 1986.

TABLE 6.11
 STYRENE MANUFACTURE. ECONOMIC DATA
 (France conditions, mid-1986)
 PRODUCTION CAPACITY 300,000 t/year

Process	Dehydrogenation of ethylbenzene		Co-production of styrene and propylene oxide
	Axial reactors	Radial reactors	
Battery limits investments (10^6 US\$)	48	52	175
Initial catalyst load (10^6 US\$)	1.8	2.6	—
Consumption per ton of product			
Raw materials			
Ethylbenzene (t)	1.155	1.107	1.190
Propylene (t)	—	—	0.345
By-products			
Benzene (kg)	30	10	—
Toluene (kg)	50	30	—
Propylene oxide (kg)	—	—	395
Propionaldehyde (kg)	—	—	15
Acetaldehyde (kg)	—	—	5
Miscellaneous fuels (10^6 kJ)	0.8	—	2
Catalysts and chemicals (US\$)	9	9	21
Utilities			
Steam (t)	4.0	2.5	8.0
Electricity (kWh)	110	60	450
Fuel (10^6 kJ)	6	4.5	0.5
Cooling water (m^3)	50	150	250
Boiler feedwater (m^3)	0.5	0.2	0.5
Process water (m^3)	—	—	1.0
Labor (Operators per shift)	3	3	10

TABLE 6.12
 AVERAGE COMMERCIAL SPECIFICATIONS
 OF STYRENE FOR SBR IN EMULSION

Characteristics	Values
Styrene (% Wt) min.	99.9
Polystyrene (ppm) max.	50.0
Benzaldehyde (ppm) max.	300.0
Peroxides (H_2O_2) (ppm) max.	100.0
Sulfur (H_2S) (ppm) max.	50.0
Chlorides (ppm) max.	100.0
Inhibitor (t-butylcatechol) (ppm) max.	10 to 15

TABLE 6.13
STYRENE PRODUCTION AND CONSUMPTION IN 1984

Geographic areas	Western Europe	United States	Japan
Uses (% product)			
ABS	7	8	13
Polystyrene	65 ⁽¹⁾	65	64
SAN	2	1	4
SBR (dry and latex)	14	15	9
Unsaturated polyester resins	7	1	6
Miscellaneous copolymers	5	10	4
Total	100	100	100
Production (10^6 t/year)	3.0	3.4	1.4
Capacity (10^6 t/year) ⁽²⁾	3.4	3.7	1.8
Consumption (10^6 t/year)	3.0	2.9	1.5

(1) Including 14% expanded polystyrene.

(2) In 1984 the worldwide production capacity of styrene was $12.3 \cdot 10^6$ t/year and world demand $9.7 \cdot 10^6$ t/year. In 1986 world capacity was the same with the following distribution:

United States	3.7	Western Europe	3.5	Middle East	0.3
Canada	0.9	Eastern Europe	1.3	Japan	1.3
Latin America	0.7	Africa	—	Asia and Far East	0.6

6.5 *p*-METHYLSTYRENE

p-methylstyrene ($bp_{1,013} = 172.8^\circ\text{C}$, $d_4^{20} = 0.911$ ⁽⁴⁾) has no substantial industrial applications for the time being. For a number of years, however, *Dow* has commercialized it in a mixture with its isomers (*m*- 64 per cent, *p*- 35 per cent and *o*- 2 per cent) under the designation of vinyltoluene, which is employed at the rate of about 25,000 t/year in the coatings sector, as a modifier for siccative and alkyd oils. In the pure state, it gives rise to polymers whose properties and performance are often better than those of styrene derivatives. It is also produced from toluene, a cheaper and more widely available raw material than benzene. In so far as it can be purified easily, these assets offer *p*-methylstyrene the possibility of superseding styrene in the long term.

Of the processes likely to favor its production, only the one proposed by *Mobil* currently appears capable of industrialization. This is because, among the different forms of zeolite developed by this company, the catalyst HZSM5, modified by magnesium and phosphorus, is capable of alkylating toluene by ethylene with a high para isomer selectivity. Thus, a 95/5 blend of *p*- and *m*-methylethylbenzenes can be obtained, which considerably simplifies separation problems and yields *p*-methylstyrene by dehydrogena-

(4) Specific gravity, 68.0/39.2.

tion, at a purity level raised by simple distillation. It is essential, indeed, to avoid producing too much of the ortho derivative, which initiates the formation of indene and indane that are difficult to separate.

Alkylation takes place in the vapor phase, in the presence of a gaseous diluent (nitrogen or hydrogen) around 475°C, at $0.7 \cdot 10^6$ Pa absolute, with excess toluene (5:1 to 10:1 moles) intended to prevent the formation of methyldiethylbenzenes. Dehydrogenation takes place in similar conditions to those applied to produce styrene, namely in adiabatic reactors, with catalyst, around 450 to 500°C, and in the presence of steam. The blend of methylstyrenes currently commercialized by Dow results from the liquid phase alkylation of toluene with aluminum chloride.

6.6 CHLOROPRENE

Chloroprene or 2-chloro 1,3-butadiene ($\text{bp}_{1.013} = 59.4^\circ\text{C}$, $d_4^{20} = 0.9585$ ⁽⁵⁾) is the monomer of polychloroprene, a specialty elastomer better known by its trade name of Neoprene. This polymer, produced since 1930 by *Du Pont de Nemours*, is distinguished by high tensile strength and resistance to oxygen, ozone and solvents, especially hydrocarbons. It is also nonflammable and exhibits excellent adhesivity and vulcanizability. These properties guarantee its superiority over all other elastomers in applications involving contact with solvents (gaskets, manifolds, surface coatings, etc.), severe operating conditions (shoes, transmission belts...), and for the manufacture of adhesives.

Discovered in 1930 by Carothers and Collins during their work on vinylacetylene, chloroprene was also prepared in the same year from butadiene. But although it was developed industrially at the time from the dimer of acetylene, it was only in 1936 that *Distugil* built the first unit employing butadiene, the most widely used industrial method today.

6.6.1 Chloroprene production from acetylene

This transformation is only presented here for information. It involves two main steps:

- Dimerization of acetylene to monovinylacetylene:

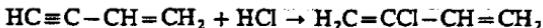


Between 50 and 100°C (preferably between 65 and 70°C), at 0.1 to $0.4 \cdot 10^6$ Pa absolute, in the presence of dry acetylene gas (99+ per cent by volume) introduced in a non-aqueous solvent containing the catalyst (cuprous chloride).

(5) Specific gravity, 68.0/39.2.

In fact, the reaction medium is made of a mixture of solvents, leading to the formation of two phases: a heavier phase containing an amine (dimethylamine or methylamine hydrochloride) and dimethylformamide, both capable of dissolving cuprous chloride, and a lighter phase generally consisting of a hydrocarbon (hexane) allowing the extraction of the reaction products, and thus preventing the formation of divinylacetylene or of tars. In these conditions, the selectivity of the operation is close to 100 per cent, for a once-through conversion exceeding 50 per cent.

- Addition of hydrochloric acid to monovinylacetylene:

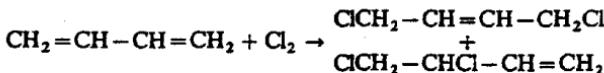


In this second step, gaseous vinylacetylene is introduced around 50°C , at $0.2 \cdot 10^6 \text{ Pa}$ absolute, into an aqueous mixture (70.5 per cent weight) of hydrochloric acid (19.5 per cent weight) and cuprous chloride (10 per cent weight). Selectivity is nearly 90 molar per cent for a once-through conversion of monovinylacetylene of 15 per cent. The main by-products are dichlorobutenes, methylvinylketone etc.

6.6.2 Chloroprene production from butadiene

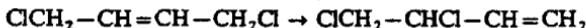
This takes place in three successive steps:

(a) Butadiene chlorination:



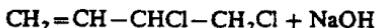
This produces two dichlorinated isomers, 1,4-dichloro 2-butenes and 3,4-dichloro 1-butene.

(b) Isomerization of 1,4-dichloro 2-butene:



This operation is aimed to convert the 1,4-dichloro cis and trans 2-butenes, which are not chloroprene precursors, to the 3,4-isomer.

(c) Dehydrochlorination of 3,4-dichloro 1-butene in the presence of caustic soda:



This leads to chloroprene and sodium chloride.

6.6.2.1 Operating conditions

A. Chlorination

Although this can be carried out in the liquid phase around 60 to 150°C , under 0.1 to $0.5 \cdot 10^6 \text{ Pa}$ absolute, it is preferable in industrial practice to operate in the vapor phase between 250 and 350°C (preferably around 300°C), at atmospheric pressure, to obtain fewer by-products and more reproducible yields. The reaction takes place in the

presence of a large excess of butadiene (3 to 6/1 in moles with respect to chlorine), or hydrochloric acid acting as diluent, to prevent the formation of superchlorinated products, including tetrachlorobutane, to facilitate the removal of the heat generated by the reaction, and thus to help to control the temperature. In addition to the two main dichlorinated isomers (3,4-dichloro 1-butene and 1,4-dichloro 2-butenes), in proportions varying from 1/1 to 2/1, the reaction produces lighter (1-chloro and 2-chloro butadiene) and heavier (trichlorobutenes, tetrachlorobutanes, telomers, tars) products. Selectivity with respect to butadiene exceeds 90 molar per cent, for a once-through conversion close to 15 per cent and a space velocity of 1000 h^{-1} .

B. Isomerization

For the liquid product, the composition at thermodynamic equilibrium of the mixture of dichlorobutenes resulting from the previous step is favorable to the presence of the 1,4-isomers. At 100°C , in fact, and at $0.1 \cdot 10^6\text{ Pa}$ absolute, the following distribution is obtained (molar per cent): 3,4-dichloro 1-butene = 21, cis-1,4-dichloro 2-butenes = 7, and trans-1,4-dichloro 2-butenes = 72. However, these three components have different boiling points, 123, 154 and 158°C respectively at atmospheric pressure. Thus the vapor in equilibrium with the liquid is far richer in 3,4-dichloro 1-butene (52 per cent), a chloroprene precursor. This feature facilitates the shift of the reaction in the desired direction and allows the removal of the more volatile 3,4-isomer by associated distillation.

Moreover, the operation can also be accelerated by employing a catalyst (*cuprous chloride*) in solution in an organic solvent (such as α -picoline), and by raising the temperature. Above 160°C , however, large amounts of by-products are formed: 1-chloro butadiene, hydrochloric acid and especially polymers. Thus, to prevent these side reactions it is preferable to maintain a low thermal level, 105 to 125°C , and distill under partial vacuum (about 20 kPa absolute), in the presence of an inhibitor intended to prevent polymerizations from developing (phenothiazine). For a once-through conversion of 1,4-dichloro 2-butenes of about 80 per cent, molar selectivity of the 3,4-isomer exceeds 75 per cent.

C. Dehydrochlorination

3,4-dichloro 1-butene is usually dehydrochlorinated by simple heating in the liquid phase, around 80 to 110°C , at atmospheric pressure, in the presence of an aqueous solution of dilute caustic soda (5 to 15 per cent) and an inhibitor (such as picric acid). Effective mechanical agitation is necessary to thoroughly mix the aqueous (caustic) and organic (dichlorobutene) phases.

The main by-products are 1-chlorobutadiene, produced from the residual dichloro 2-butenes or formed during the reaction, polymers, sodium chloride and monochlorobutenes (1-chloro 1-butene, 2-chloro 2-butene, 2-chloro 1-butene, etc.). To control the undesirable polymerizations, the reaction takes place in an oxygen-free environment, at the lowest possible temperature, and with an inhibitor. Also effective is the presence of a solvent (methanol, ethanol) or a catalyst. In this case, however, it is necessary to raise the caustic soda concentrations (30 per cent) or to employ other bases (liquid ammonia, ion exchange resins, etc.). In the absence of catalyst, the residence time is 3 to 5 h. and selectivity exceeds 95 molar percent, for a once-through conversion of nearly 95 per cent.

6.6.2.2 The process

The process flow sheet (Fig. 6.12) has three sections.

A. Chlorination

Butadiene is first vaporized and dried in molecular sieves in the first section, to limit the corrosion of the mild steel used in nearly all the equipment of this chlorination section. The dry feed, to which unconverted gas recycle is added, essentially consisting of butadiene and hydrochloric acid, is raised to 150°C, then mixed with the chlorine, itself preheated to this temperature. The mixture is then introduced into the chlorination reactor. At the outlet, the effluents, at a temperature of 340°C, due to the heat generated by the transformation, are first cooled to 105°C, and then stabilized by distillation at atmospheric pressure (10 trays, 5°C, $0.12 \cdot 10^6$ Pa absolute at the top). The recovered gases are recompressed under $0.2 \cdot 10^6$ Pa absolute using a blower, and mostly recycled to the chlorination reactor. The remainder, serving as a purge, is sent to an absorber, operating in the presence of a flux of dichlorobutenes precooled to -50°C and designed to recover the butadiene contained, to return it to the stabilizing column. The hydrochloric acid leaving at the top of the absorber may be concentrated or neutralized after absorption in water. The bottom stream from stabilization is fractionated under vacuum (5 trays, 20 kPa absolute, 95°C at the top) to separate most of the dichlorobutenes produced in the distillate, and the remainder in the bottoms, containing the heavier components in solution. This stream is sent to a falling film evaporator to recover the residual dichlorobutenes, which are recycled to the previous fractionation.

B. Isomerization

The second section carries out the isomerization of the 1,4-dichloro 2-butenes in an exchanger/reactor of the reboiler type, associated with a distillation column operating under vacuum (20 trays, 20 kPa absolute, 75°C at the top) and designed to separate the 3,4-isomer as soon as it is formed, which is then recovered in the distillate. Cuprous chloride in solution in α -picoline is first added to the dichlorobutenes feed from chlorination, and the mixture is raised to nearly 115°C in the reboiler by low-pressure steam. A sidestream, treated in the falling film evaporator of the previous section, prevents the accumulation of heavy products and the fouling of the equipment, and serves to recover the stripped dichlorobutenes. Distillation itself takes place in the presence of phenothiazine injected at the condenser level. The distillate, with a 3,4-dichloro 1-butene recycle from the subsequent separation step, is dehydrochlorinated in a series of agitated reactors operating around 90°C and under low pressure ($0.5 \cdot 10^6$ Pa absolute) to maintain most of the medium in the liquid phase, in the presence of a 10 per cent caustic solution, preheated to 65°C, and of picric acid used as a polymerization inhibitor.

C. Dehydrochlorination

Product separation and purification, which form the final section of the process, take place on the vapor effluent, previously cooled and condensed around 40 to 45°C, from

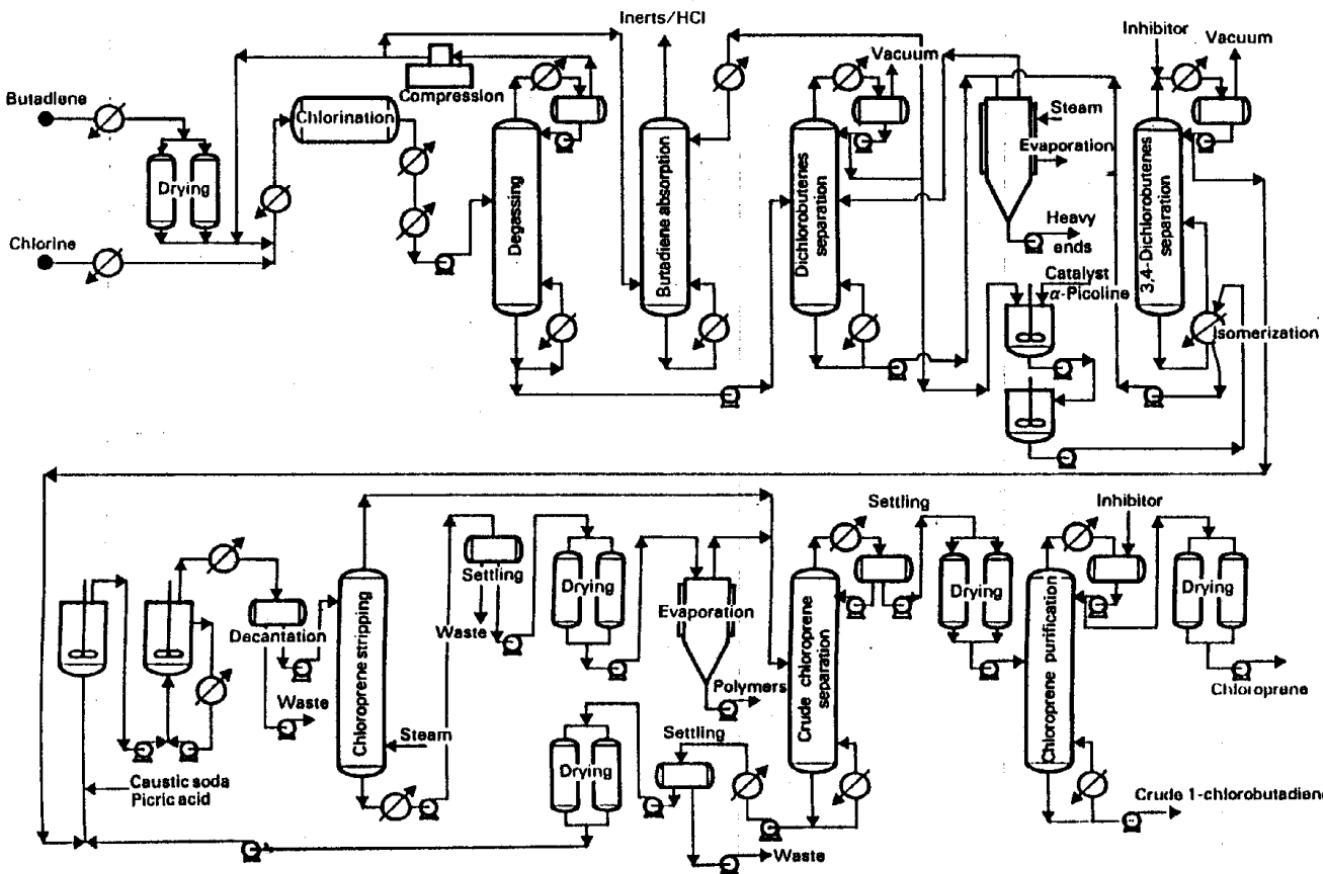


Fig. 6.12. Chloroprene manufacture from butadiene.

the final dehydrochlorination reactor. The treatment first involves settling of the liquid obtained and the removal of the aqueous phase formed. The organic fraction is stripped by steam through a packing designed to separate the raw chloroprene at the top.

Unconverted 3,4-dichloro 1-butene leaving at the bottom is rid of the water it contains by settling and drying, and then purified of its heavy components by evaporation in a falling film evaporator. It is then treated at the same time as the raw chloroprene in a packed column, where it is separated at the bottom. Once again, settled and dried, it is then recycled to dehydrochlorination. After cooling, the water/chloroprene heteroazeotrope leaving at the top gives rise to the formation of two phases: the lower fraction serves as a reflux, while the upper layer is dried. This effluent is sent to a final purification column (65 trays, atmospheric pressure, -60°C at the top), operating in the presence of a polymerization inhibitor (phenothiazine, nitrosodiphenylamine), injected at the condenser level. The 1-chlorobutadiene contained is removed in a withdrawal while the pure chloroprene, separated in the distillate, is dried and stored under nitrogen atmosphere, at less than 0°C using a refrigeration loop.

6.6.3 Other methods for producing chloroprene

Among the solutions that have not yet reached the industrial stage, but have been proposed to improve the economics of chloroprene production, various attempts have

TABLE 6.14
CHLOROPRENE PRODUCTION. ECONOMIC DATA
(France conditions, mid-1986)
PRODUCTION CAPACITY 30,000 t/year

Typical technology	Du Pont	BP Distillers
Feed	Acetylene	Butadiene
Battery limits investments (10 ⁶ US\$)	11	8
Consumption per ton of chloroprene		
Raw materials		
Acetylene (t)	0.70	—
Butadiene (t)	—	0.75
Chlorine (t)	—	0.90
Hydrochloric acid (t)	0.50	—
Catalysts and chemicals		
Caustic (t)	—	0.70
Miscellaneous (US\$)	20	100
Utilities		
Steam (t)	4.0	2.7
Electricity (kWh)	95	70
Cooling water (m ³)	220	180
Refrigeration (-15 to -20°C) (10 ⁶ kJ)	1.3	0.15
Labor (Operators per shift)	6	6

TABLE 6.15
AVERAGE COMMERCIAL SPECIFICATIONS OF CHLOROPRENE FROM BUTADIENE

Characteristics	Values
2-chlorobutadiene (% Wt) min.	98.5
1-chlorobutadiene (% Wt) max.	1.0
3,4-dichloro 1-butene (ppm) max.	100
Dimers (ppm) max.	100
Aldehydes (expressed as acetaldehyde) (ppm) max.	1000
Peroxides (ppm) max.	1

TABLE 6.16
CHLOROPRENE PRODUCTION AND CONSUMPTION IN 1984⁽¹⁾

Geographic areas	Western Europe	United States	Japan
Production (10 ³ t/year).....	104	130	83
Capacity (10 ³ t/year).....	133	163	85
Consumption (10 ³ t/year).....	87	90	40

(1) Chloroprene is used to produce neoprene (polychloroprene rubber). In 1986 worldwide production capacities of neoprene were the following:

(a) Western Europe: 10^3 t/year

France : <i>Distugil, Champagnier</i>	40
West Germany : <i>Bayer, Dormagen</i>	60
United Kingdom: <i>Du Pont de Nemours, Maydown</i>	33
Total	<u>133</u>

(b) United States:

<i>Denka Chemical, Houston (Tx)</i>	27
<i>Du Pont de Nemours, Laplace (La)</i>	34
<i>Du Pont de Nemours, Louisville (Tx)</i>	90
Total	<u>151</u>

(c) Japan:

<i>Denki Kagaku, Omi</i>	45
<i>Showa Neoprene, Kawasaki</i>	20
<i>Toyo Soda, Shin Naya</i>	20
Total	<u>85</u>

(d) Centrally planned economy countries:

<i>China, Changshoo</i>	10
<i>China, Daiton</i>	5
<i>China, Qindao</i>	5
<i>Poland, Oswiecim</i>	50
<i>USSR, Raznoimport, Erevan</i>	120
Total	<u>190</u>

been made to reduce the number of steps. One alternative calls for the chlorination of the butadiene directly producing the desired monomer.

Others, such as the one developed by *Distillers*, attempted to change the starting raw material by using butenes (preferably 2-butenes) alone and mixed with butadiene, whose chlorination leads to chlorobutenes and chlorobutanes, which can then be converted to chloroprene. Yet others attempted to replace chlorine by hydrochloric acid (*Monsanto*, *Shell*, *ICI*) and to oxychlorinate the butadiene, at around 260 to 290°C and atmospheric pressure, in the presence of cupric chloride deposited on a support based on alumina or pumice stone, and operating in a fluidized bed.

6.6.4 Economic data

Table 6.14 gives the main economic data concerning the production of chloroprene from acetylene and butadiene.

6.6.5 Uses and producers

Table 6.15 summarizes the average commercial specifications of chloroprene produced from butadiene. Table 6.16 lists the main uses of chloroprene in Western Europe, the United States and Japan in 1984, and gives the production, production capacities and consumption of this monomer for these three geographic areas.

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Chapter 1

HYDROGEN, SYNTHESIS GASES AND THEIR DERIVATIVES

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Chapter 2

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