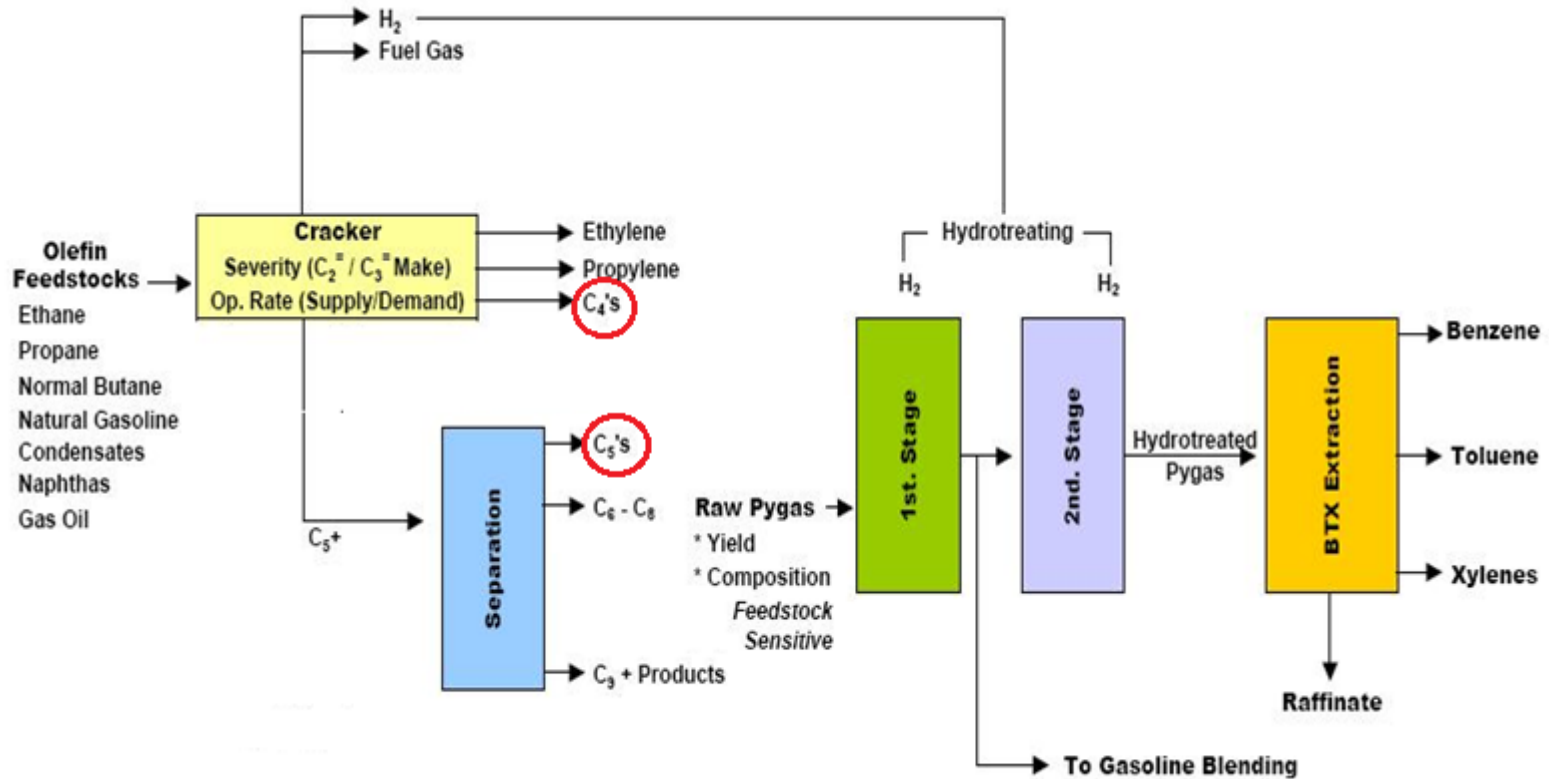


Petrochemical Technology

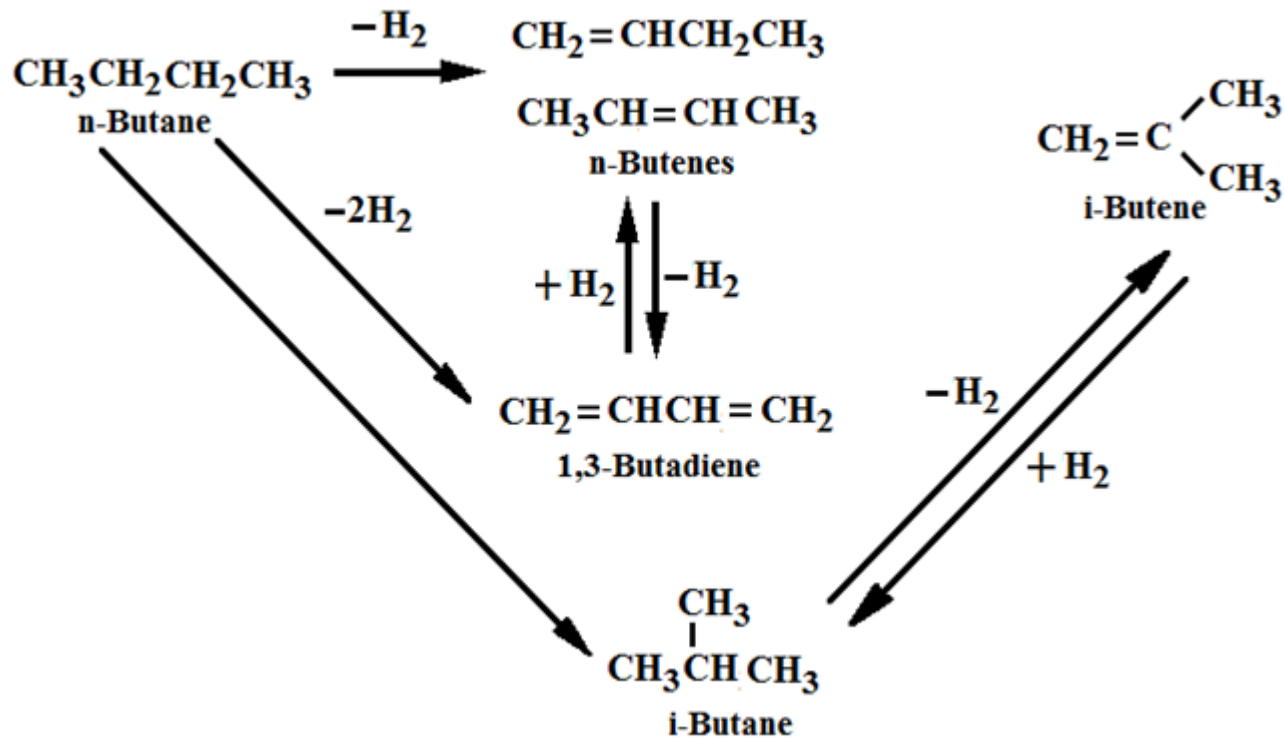
Chemicals from C₄ Hydrocarbons



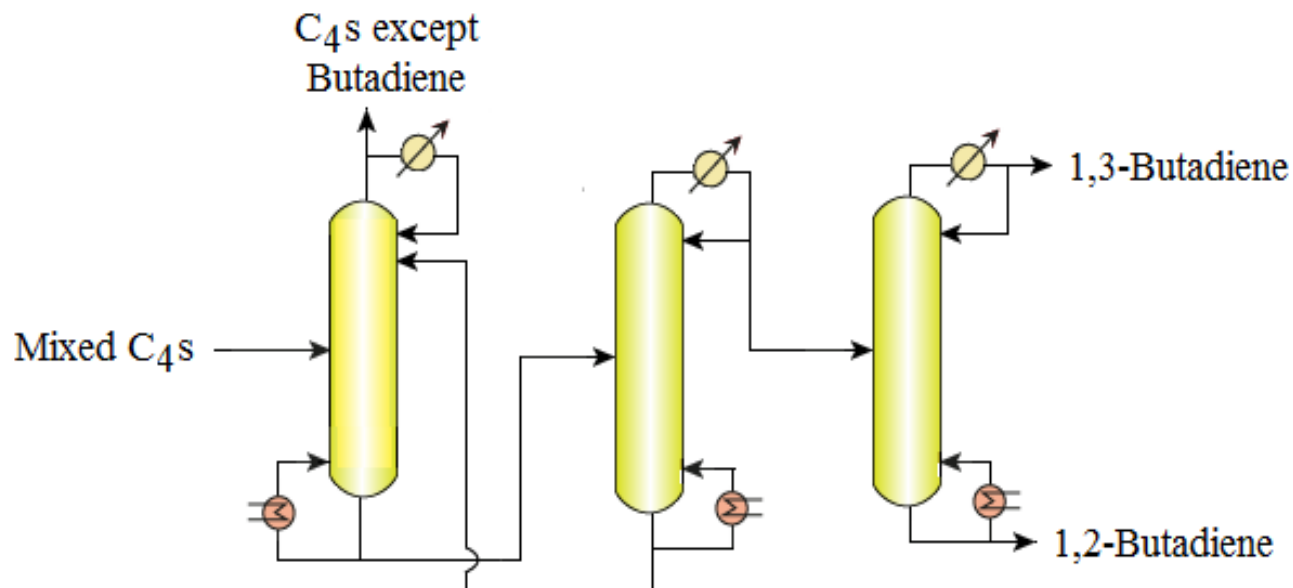
Production of Olefins by Steam Cracking

Processing of 'Mix C₄s'

Component	C ₃	n-C ₄	i-C ₄	i-C ₄ ⁼	1- C ₄ ⁼	2- C ₄ ⁼	Butadiene	C ₅ ⁺
Percentage	0.5	3.0	1.0	23.0	14.0	11.0	47.0	0.5



The first step is the removal of 1,3-butadiene by extractive distillation with an aprotic solvent, usually acetonitrile, N-methyl pyrrolidone (NMP), or N,N-dimethyl formamide (DMF). Each of these solvents is effective in depressing the volatility of components other than butadiene. However, use of acetonitrile (ACN) is advantageous to other solvent systems for a number of reasons. ACN's lower boiling point results in lower operating temperatures resulting in low fouling rates and long run lengths. Only low pressure steam is required for reboilers. The low molecular weight and low molar volume of ACN combined with its high selectivity to butadiene results in low solvent circulation rates and smaller equipment sizes. The low viscosity of ACN increases tower efficiencies and reduces column size and cost. ACN is also very stable, noncorrosive and biodegradable.



A small amount of butadiene is left in the raffinate, which must be removed by after treatment (selective hydrogenation), if pure 1-butene is desired later in the process. The butadiene-free raffinate contains the two *n*-butenes and isobutene. The isobutene is reactive and may be separated by hydration to *tert*-butanol in the presence of sulphuric acid or, in more modern plants, by use of a fixed bed catalyst. *tert*-Butanol may be used as such or it may be dehydrated to pure isobutene.

In an alternative process, raffinate reacts with MeOH to give MTBE. This usually is used as such but, like *tert*-butanol, it may be cracked to give pure isobutene. The etherification process to MTBE is highly selective. It goes to about 97% conversion and if all the isobutene must be removed, a second step is necessary in which the raffinate is reacted with a large excess of methanol.

The mixture of 1- and 2-butenes that remains is called and traded as Raffinate II. It may be hydrated to *sec*-butanol or oxidized to maleic anhydride. In the process, 1-butene isomerizes to more stable 2-butene.

The two butenes in Raffinate II may also be separated to yield pure 1-butene for linear low density polyethylene (LLDPE) production.

There are three procedures to separate the isomers:

Fractionation requires a high, multiplate, low-temperature column because the boiling points are - 6.47 °C (1-butene) and 3.73 °C (*cis*-2-butene).

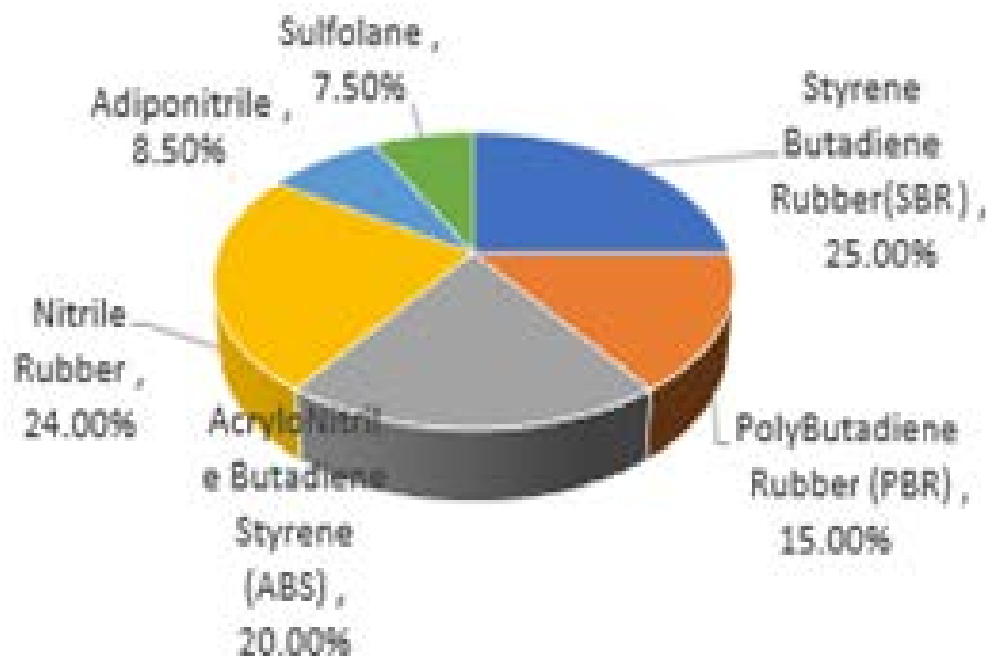
Extractive distillation and molecular sieve adsorption (UOP's Sorbutene process) are also possible.

The advantage of the UOP process is that pure 1-butene results even if appreciable isobutene remains in the Raffinate II. The other two processes are useful only if the butadiene and isobutene contents of Raffinate II are low. The *cis*- and *trans*-2-butene stream that results is called Raffinate III. The pure isomers do not have many uses and the material is not usually purified but sent to the alkylation unit.

Chemicals from Butadiene

Global production capacity of butadiene is expected to increase from 21.91 million metric tons in 2024 to 26.95 million metric tons in 2028.

Global Butadiene Market size was valued at around USD 11.7 Billion in 2023 and is estimated to grow at a CAGR of approximately 9.3% between 2024 and 2033.

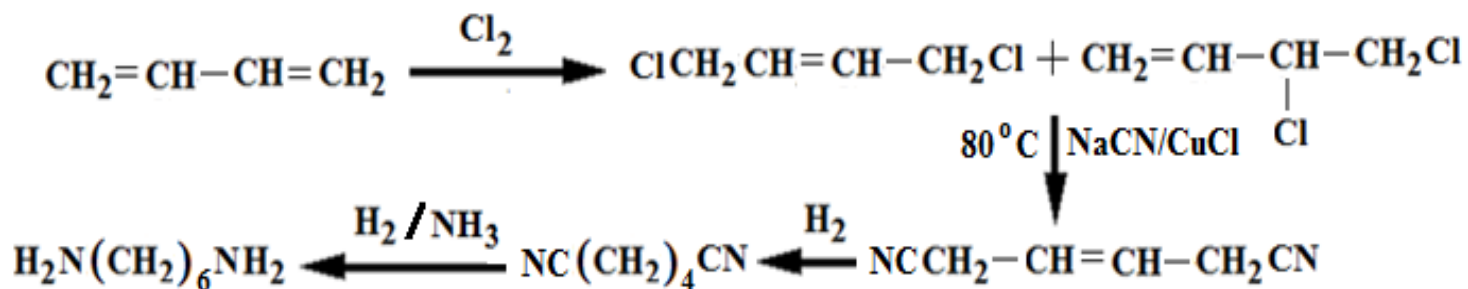


Butadiene Market share (vol%) by End-use

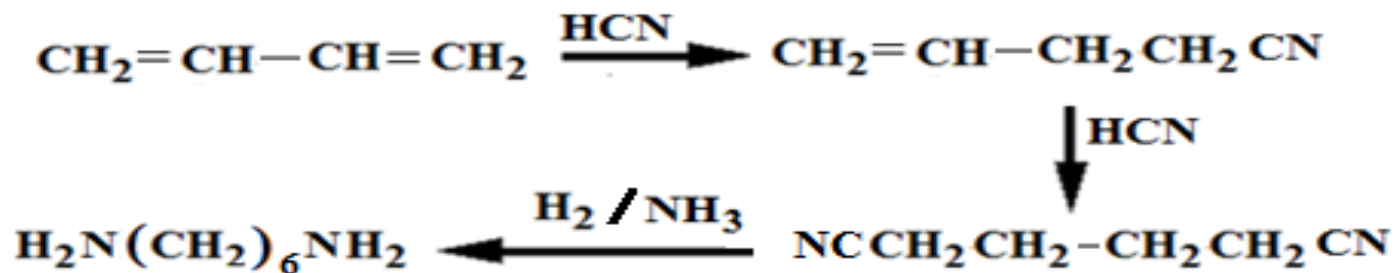
Hexamethylene Diamine (HMDA)

Only two of the various routes to HMDA start with butadiene, but they include the most economic synthesis and HMDA is butadiene's most important non-polymer use.

(1) Butadiene is first chlorinated to give a mixture of *cis*- and *trans*-1,4-dichloro-2-butenes and 3,4-dichloro-1-butene. This mixture was treated with sodium cyanide to give 1,4-dicyano-2-butene. The reaction takes place at about 80°C in the presence of CuCl. The 1,4-dichloro compound yields the desired dicyano compound. The 3,4-dicyano-1-butene, which is formed from the corresponding dichloro compound, undergoes an allylic rearrangement to give more of the desired 1,4-dicyano-2-butene, in both *cis* and *trans* forms at high selectivity. In the final stage, the hydrogenation of adiponitrile to HMDA is carried out in the presence of excess ammonia to depress the formation of a triamine, which nonetheless is formed in small quantities.



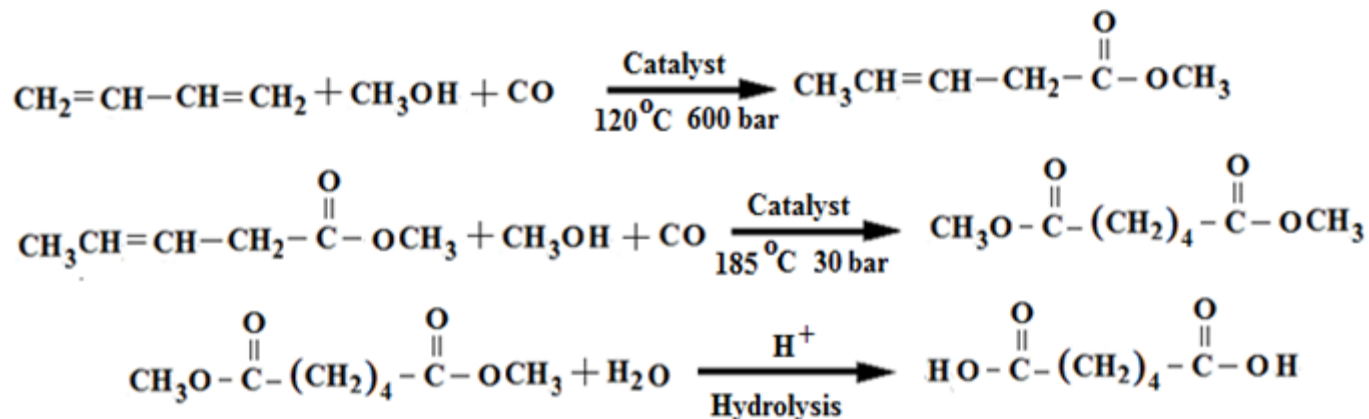
(2) Another process, turns out to be the most economic, starts with the 1,4-addition of hydrogen cyanide to butadiene. The catalyst, nickel with triaryl phosphate ligands, $\text{Ni}[\text{P}(\text{OAr})_3]_4$ is remarkable. It not only effects the 1,4-addition but it also isomerizes the byproduct 2-methyl-3-butene nitrile, which is produced in appreciable quantities, to the desired isomer. In addition, it shifts the double bond to a terminal position and then makes possible the addition of another mole of hydrogen cyanide anti-Markovnikov to the terminal bond. If it were not possible to use the same catalyst for both reactions, the double bond shift could not be carried out in high yield because of an equilibrium. The resulting adiponitrile may be hydrogenated to hexamethylene diamine.



This synthesis as opposed to the one starting with the chlorination of butadiene, eliminates the need for costly chlorine, use hydrogen cyanide, which is now cheaper than sodium cyanide (but not when the synthesis based on 1,4-dichloro-2-butene was devised), eliminates the handling of carcinogenic 1,4-dichloro-2-butene, and solves the problem of disposing ecologically unacceptable copper contaminated sodium chloride.

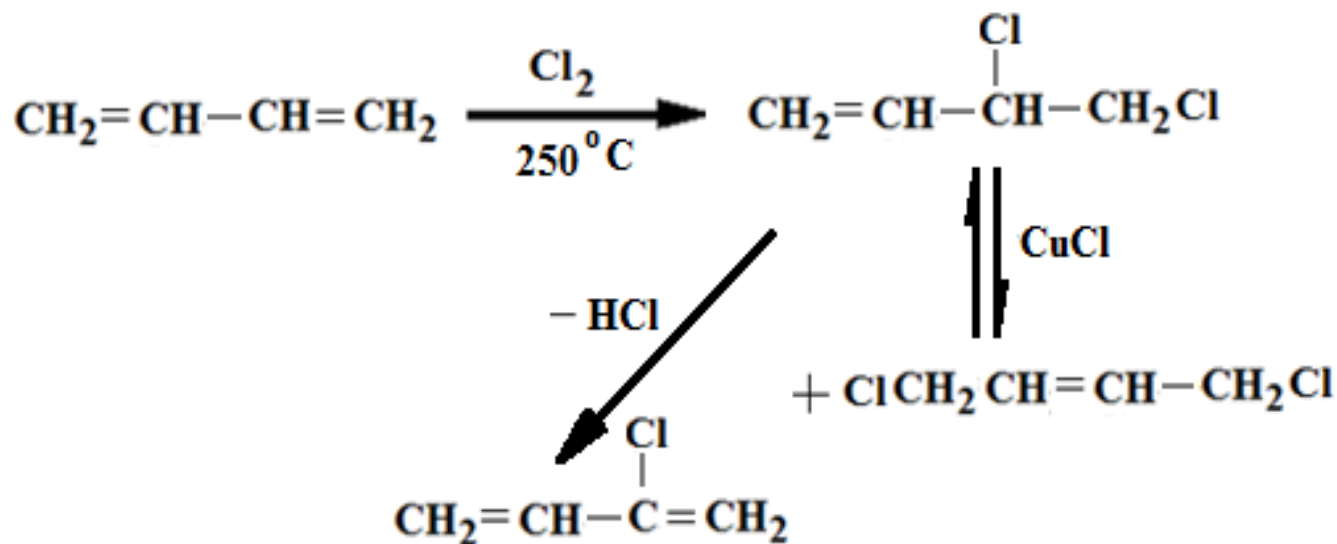
Adipic Acid

Adipic acid is produced in large quantities by the classical synthesis based on cyclohexane. BASF (Badische Anilin und Soda Fabrik) has developed a process based on dicarbonylation of butadiene. This technology appears competitive with the classical route. The reaction proceeds in two stages since the carbonylation is difficult. Carbon monoxide and methanol react with butadiene in the presence of dicobalt octacarbonyl $[\text{Co}_2(\text{CO})_8]$ in quinoline or a related base at 600 bar and 120°C to give **methyl-3-pentenoate** at 98% selectivity. The second step takes place at a higher temperature of 185°C but at a lower pressure of 30 bar in the presence of additional CO and methanol. Selectivity at this point is about 86% to the desired **dimethyl adipate**. The migration of the double bond in the second step makes possible linearity. Other catalyst systems include platinum and palladium halides, phosphine promoted cobalt complexes and rhodium complexes. Byproducts include methyl-3-pentenoate, methyl glutarate, methyl ethyl succinate, dimethyl and diethyl succinate and methyl pentenoates. The first two materials are obtained in largest amounts.



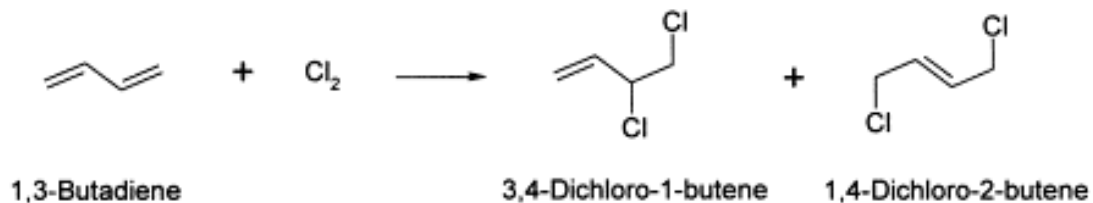
Chloroprene

The chlorination of butadiene in vapour phase at 250°C gives a mixture of 3,4-dichloro-1-butene and 1,4-dichloro-2-butene. The latter may be isomerized to the former in the presence of cuprous chloride. Dehydrochlorination of 3,4-dichloro-1-butene leads to chloroprene, the monomer for **Neoprene** or **Polychloroprene** rubbers.

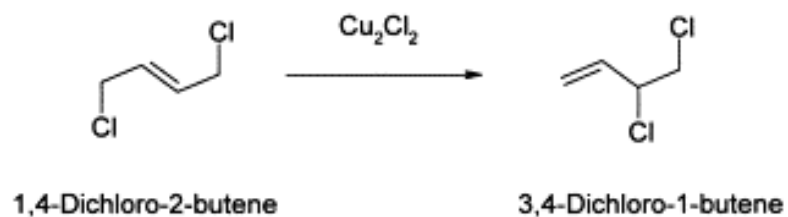


Chloroprene Synthesis

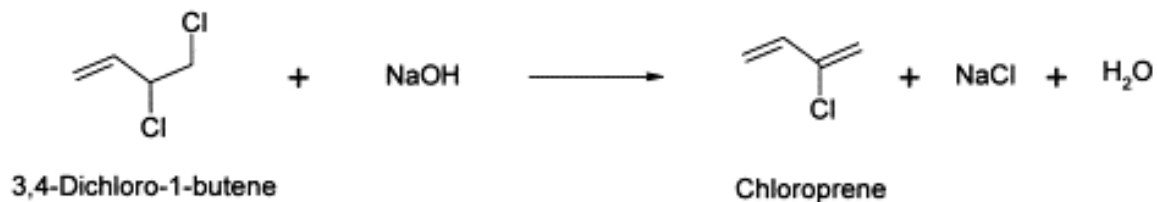
Dichlorobutene Synthesis



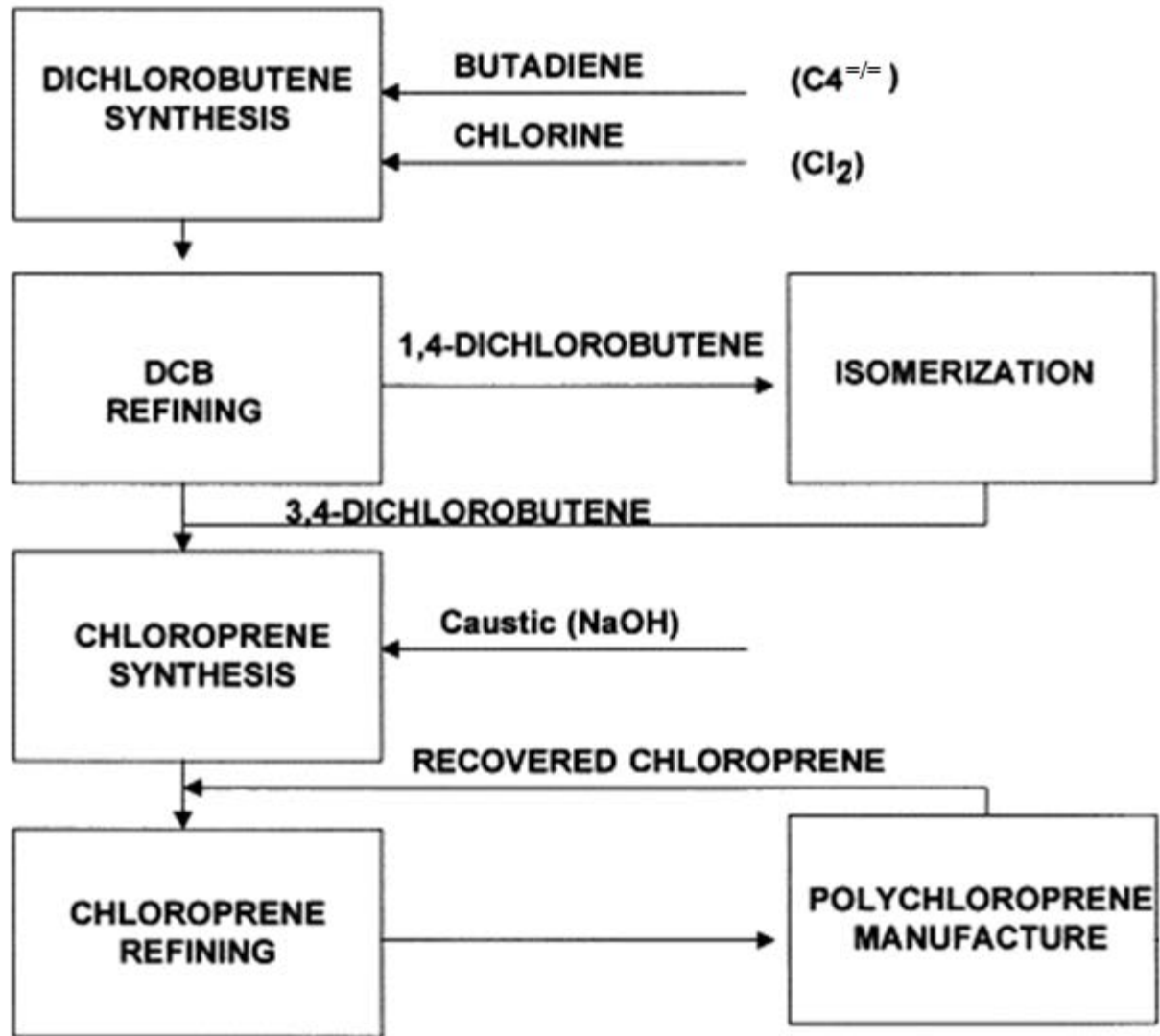
Dichlorobutene Isomerization



Chloroprene Synthesis



BUTADIENE POLYCHLOROPRENE PROCESS



Neoprene was an early synthetic rubber. It lacks the resilience necessary for use in tires, the major consumer of rubber, but it has good resistance to oil and ozone, which suits it for many specialized uses such as roofing and flexible hose.

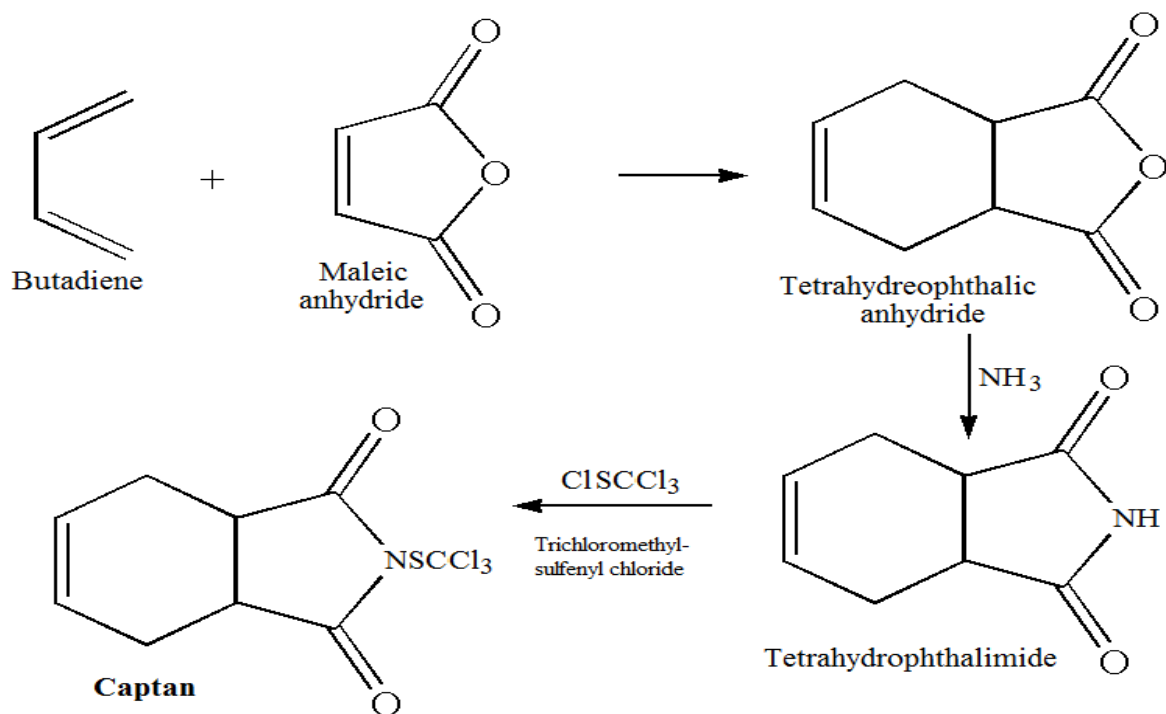
In the early days, it was made by reacting dimerized acetylene (i.e., vinyl acetylene) with hydrogen chloride. Here is another example of petrochemicals replacing acetylene, for Du Pont phased out the last acetylene-based polychloroprene plant in the United States in 1974 and in Northern Ireland in 1977.

The major uses of polychloroprene are the adhesives, gaskets, conveyor belts, and cables. Because of its tensile, abrasive and impact strengths and non-inflammable nature, it has much demand in industry.

Nitrile rubber is a copolymer of acrylonitrile and butadiene, a typical ratio being 1:2. It is characterized by outstanding oil and abrasion resistance, which makes it suitable for oil seals, fuel tank fabrication, oil resistant hoses and ink rollers for printing presses.

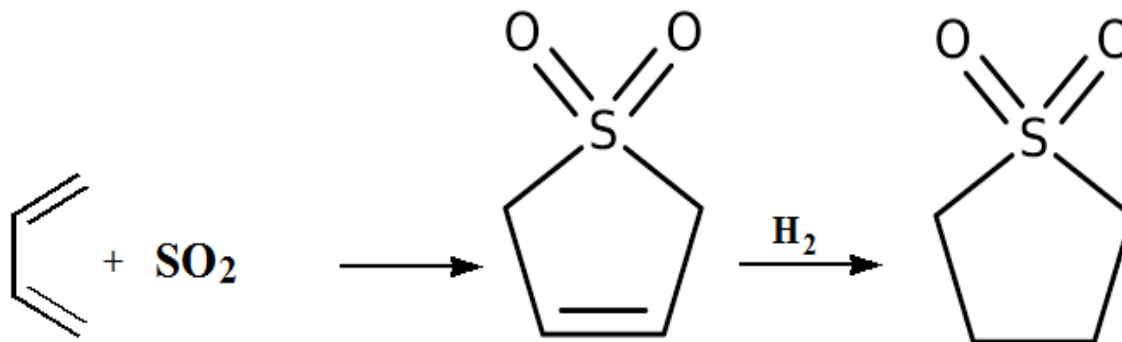
Other Chemicals from Butadiene

Butadiene reacts with maleic anhydride to give tetrahydrophthalic anhydride, used in polyester and alkyd resins and as an ingredient in the fungicide, Captan.

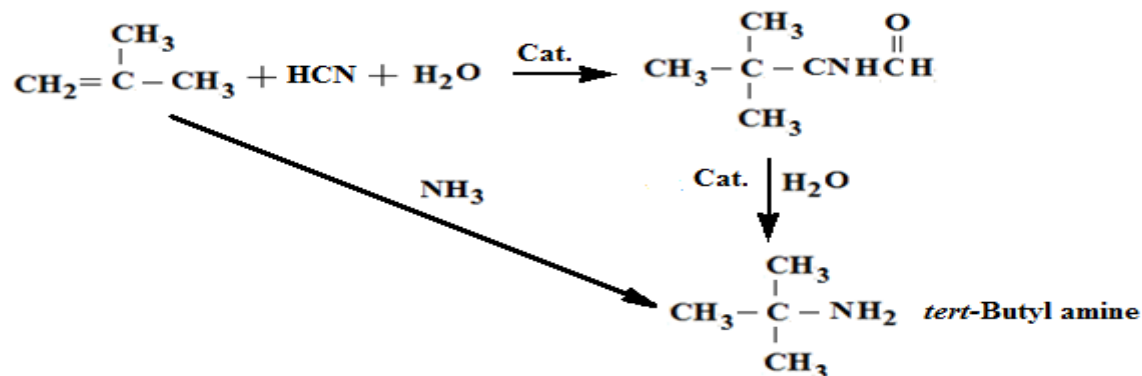
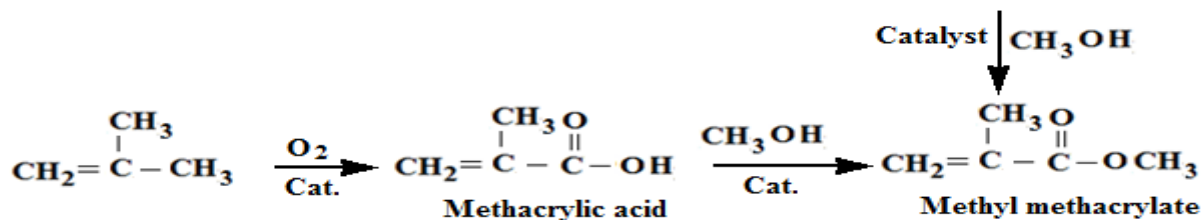
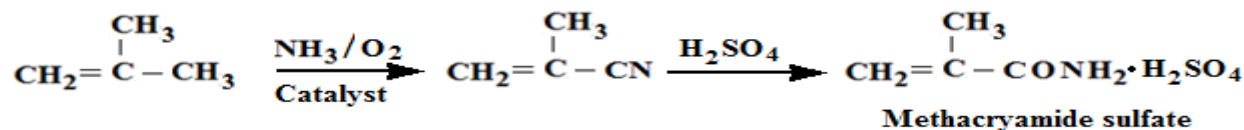
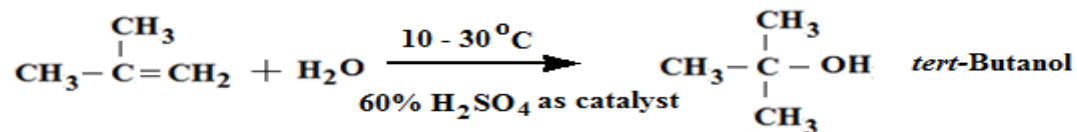
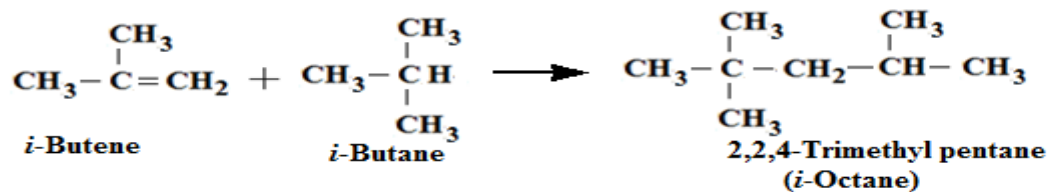


Sulfolane

Diels-Alder addition of sulfur dioxide to butadiene at room temperature followed by hydrogenation yields tetramethylene sulfone (sulfolane), which is used to extract aromatic compounds from catalytic reformat in petroleum refineries. It is also mixed with diisopropanolamine and water in the so called Sulfinol process for the removal of hydrogen sulfide, carbon dioxide, carbonyl sulfide and other acid components from so-called sour gas. The acid components are absorbed chemically by the amine and physically by the sulfolane. Being aprotic, sulfolane is also useful in extractive distillations.



Chemicals from Isobutene



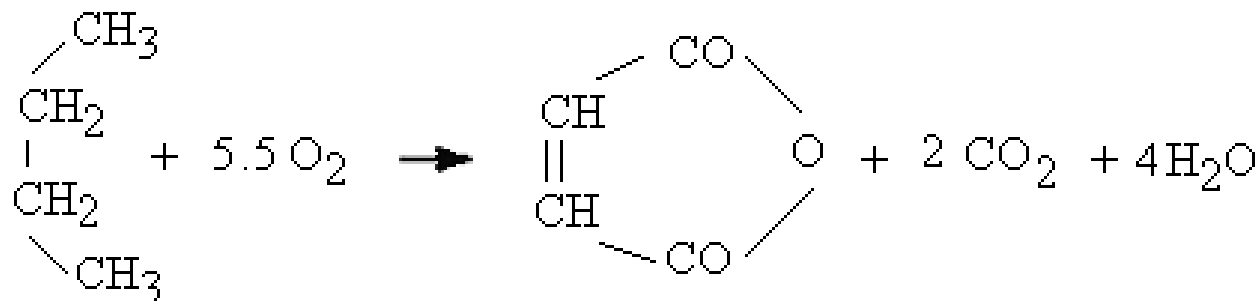
Polymeric use of *i*-Butene

Butyl rubber: The second largest outlet for isobutene, after MTBE, is in butyl rubber, a copolymer of isobutene with 2-5% isoprene. Butyl rubber was used for inner tubes before the advent of the tubeless tire because of its impermeability to air. It is still used as an inner liner for tubeless tires, for truck inner tubes, for tire sidewall components, and for air cushions and bellows. Without the isoprene, the polymer would contain no double bonds and would not vulcanize with sulfur. The isoprene comonomer leaves only a small number of double bonds to be cross-linked and the resulting polymer contains little if any unsaturation. For this reason, it resists aging and is, therefore, useful in constructions such as convertible tops.

Polyisobutenes: Isobutene can be polymerized to polyisobutene under the influence of Friedel-Crafts catalysts such as boron trifluoride or aluminum chloride. The low molecular weight liquid products are adhesives and tackifiers. The higher molecular weight products are used in caulking compounds and as a chewing gum base.

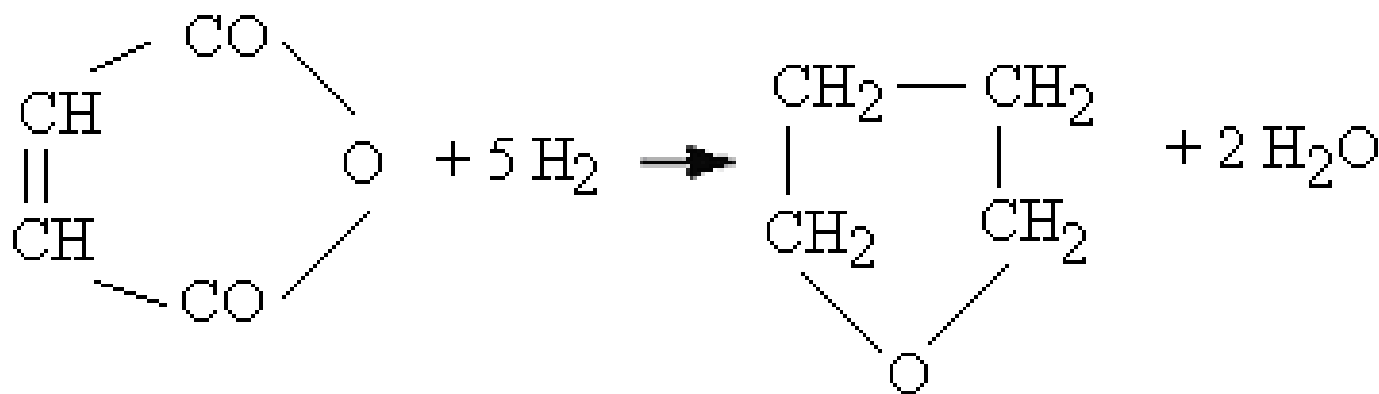
Maleic Anhydride from n-Butane

Most maleic anhydride is made by oxidation of n-butane or, less frequently, 1- and 2-butenes. The vapour phase oxidation is carried out at 400°C with a supported vanadium pentoxide catalyst. A mixture of maleic acid and maleic anhydride results, and the acid may be dehydrated to anhydride directly without separation.



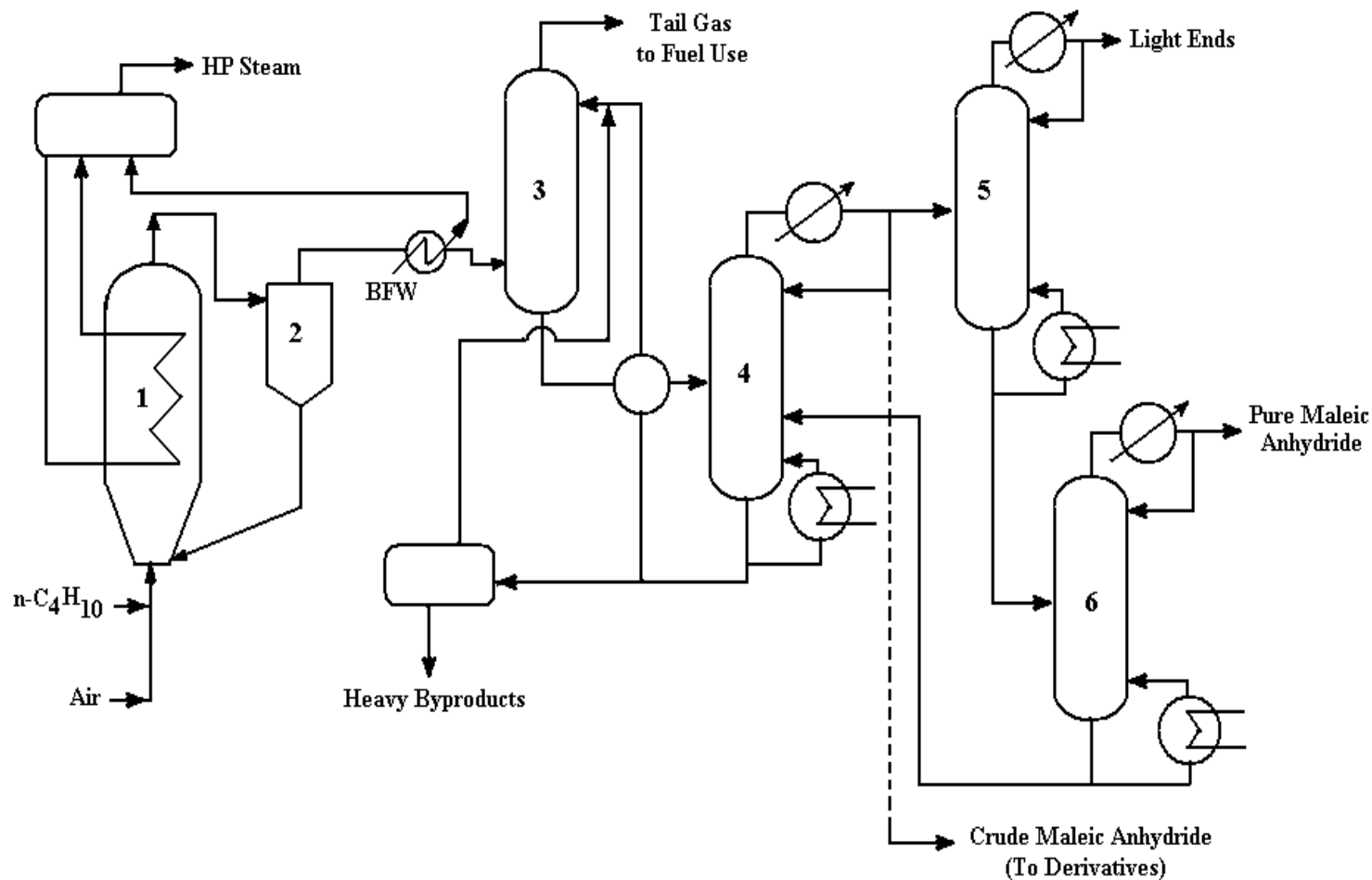
Du Pont developed a catalyst containing mixed oxides of vanadium and phosphorus with promoters, primarily silicon and one other element such as indium, antimony, and tantalum. It is formulated to be highly attrition-resistant. The unique aspect, however, which increases the yield from the conventional 50-52% to 72%, is that no oxygen is used in the oxidation other than that which is part of the catalyst. The catalyst is thus a reactant and its double role is recognized by the term '**Cataloreactant**.' In this way, the side reactions in which the n-butane is oxidized to water and carbon dioxide are limited. The conversion is, of course, determined by the amount of oxygen available from the catalyst and is about 8.5%. The catalyst is inactivated in each run and must be removed for reactivation and replaced with fresh catalyst. This is accomplished by a so-called transport bed process, which requires the catalyst to be attrition-resistant. Its economics are comparable to those of the fluid bed process, when solvent is used in both processes for the extraction of the products.

Water may be used for the extraction, but its evaporation increases operating costs. However, Du Pont intends to use water, since the aqueous solution without isolation of maleic acid can be subjected to hydrogenation, hydrogenolysis to yield tetrahydrofuran with a newly developed catalyst that makes possible the use of milder temperatures and pressures than are commonly required for hydrogenolysis.



Du Pont requires tetrahydrofuran for oligomerization to a polybutene ether for use in their **Spandex** polymer. Spandex is a block copolymer comprising hard urethane blocks and flexible polyether blocks, useful for swimsuits, sports cloths and elastic in undergarments. Although it is an old polymer, its use increased rapidly in the late 1980s and early 1990s when tights became fashionable.

The dominant end use of maleic anhydride (MA) is in the production of unsaturated polyester resins. These laminating resins, which have high structural strength and good dielectric properties, have a variety of applications in automobile bodies, building panels, molded boats, chemical storage tanks, lightweight pipe, machinery housings, furniture, radar domes, luggage, and bathtubs.



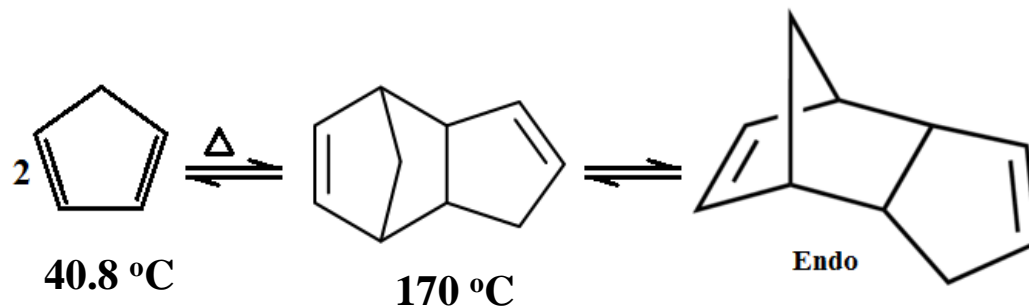
1: Reactor; 2: Cyclone separator; 3: Absorber; 4: Stripper; 5: Light ends stripper; 6: Maleic anhydride column

Flow sheet for the production of maleic anhydride from n-butane

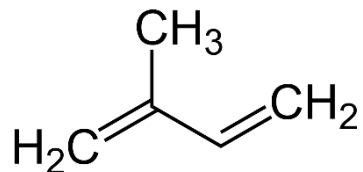
Separation of C₅ Hydrocarbons

Separation of the many C₅ components is difficult and is done differently around the world. Following figure provides a conceptual scheme that combines processes used in several refineries. It comprises four major steps: cyclopentadiene removal, extractive distillation, solvent regeneration and product distillation. Cyclopentadiene amounts for 15-25% of the C₅ olefin fraction from the high severity steam cracking of naphtha. If gas oil is cracked, it is the predominant olefin.

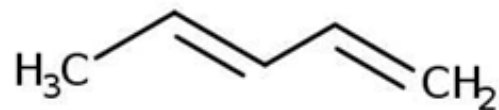
Cyclopentadiene must be removed first because it polymerizes and can foul the reboilers of the downstream distillation columns. Its isolation depends on facile and reversible dimerization that takes place when the C₅ fraction is heated at 100 °C for 2-3 h or at 150 °C under pressure for a shorter period. The dimer, dicyclopentadiene, forms by a Diels-Alder reaction and normally has the endo form. Since it boils 130 °C higher than the monomer, it is readily separated from the other components by vacuum distillation. At 350 °C in a tubular reactor the monomer is rapidly regenerated.



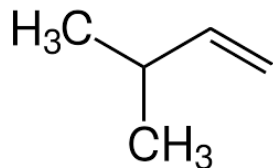
Dimerization of Cyclopentadiene



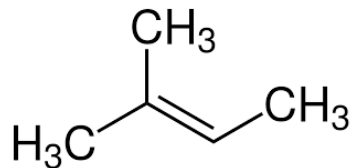
Isoprene (34 °C)



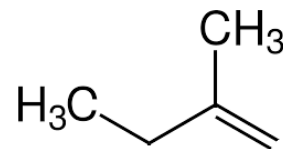
Piperylene (42 °C)



3-Methyl-1-butene (20 °C)



2-Methyl-2-butene (38.5 °C)



2-Methyl-1-butene (31 °C)

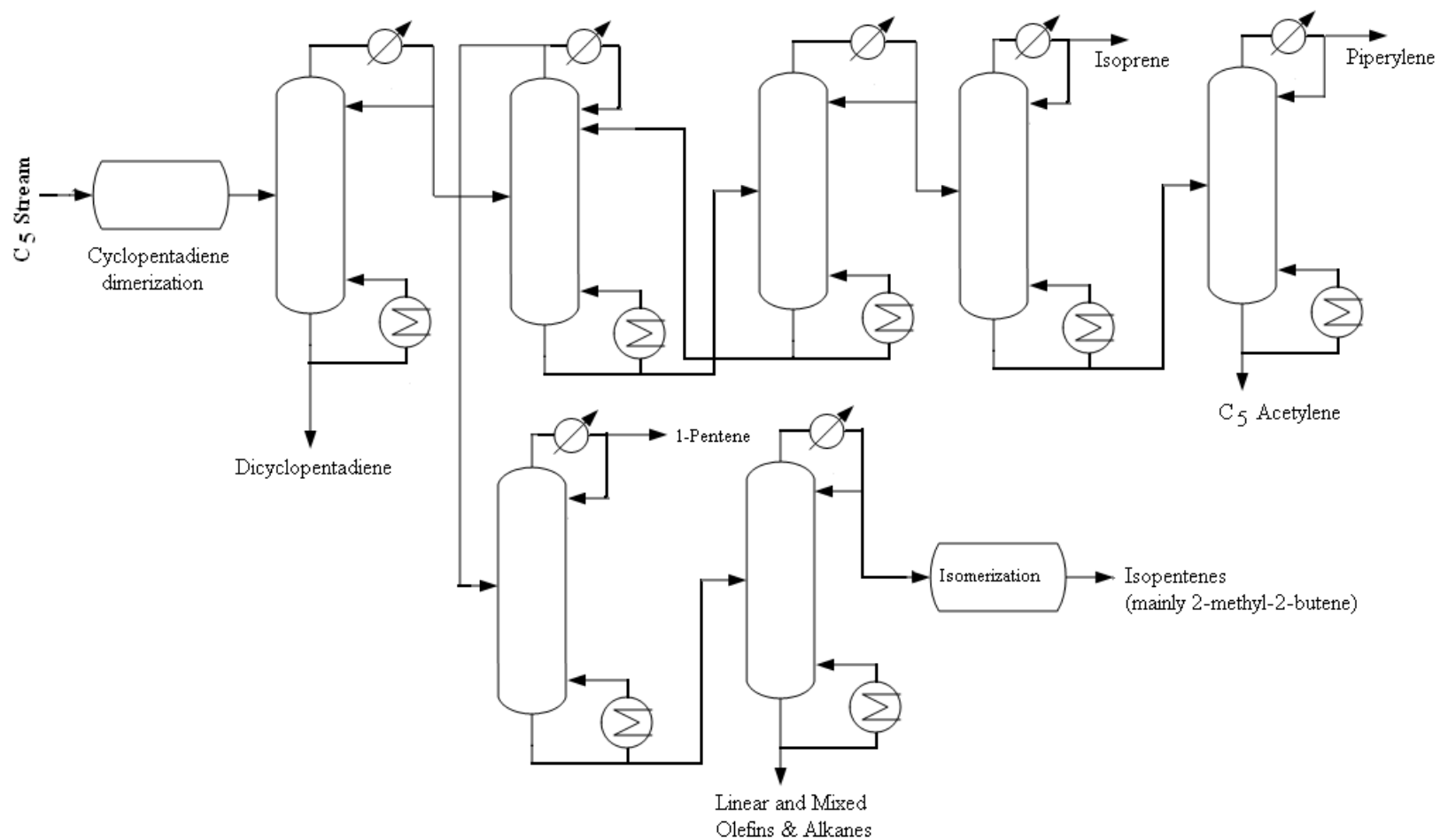
Isopentenenes

Isoprene is removed next by extractive distillation with the aprotic solvents acetonitrile or N-methyl pyrrolidone. Almost all the alkanes and most of the olefins distil overhead, while the solvent, the diolefins and C₅ acetylenes appear at the bottom of the tower. Successive distillations of this bottom stream regenerate the solvent for recycle. The hydrocarbon stream is split into acetylenes and diolefins and diolefins are split into isoprene and piperylene (1,3-pentadiene). Polymerization grade isoprene requires a further distillation for adequate purification.

The overhead stream from the extractive distillation can be further distilled to give 1-pentene, isopentenes (methyl butanes), and a mixture of the remaining C₅ alkanes and olefins. The isopentenes, mainly 3-methyl-1-butene, are isomerized by 65% H₂SO₄ primarily, to 2-methyl-2-butene, (CH₃)₂C = CHCH₃ and to a lesser extent to 2-methyl-1-butene, CH₂ = C(CH₃)-CH₂-CH₃. These readily react with water in the presence of H₂SO₄ at 0-10°C to yield a tertiary alcohol, just as isobutene does in the process for separating the C₄ olefins. The 2-methyl-2-butanol is separated and heated to 350 °C to regenerate the alkene. The methylbutanol can be dehydrogenated to isoprene with a catalyst based on iron, chromium oxides and potassium carbonate at 600 °C. Selectivity is 85% at 35% conversion. Just as with isobutene, methanol may be used instead of water. With 2-methyl-2-butene, TAME results.

The residual C₅ stream contains linear and mixed olefins. They can be separated without difficulty but there is little demand for them. The mixture can be polymerized to give an inexpensive hydrocarbon resin useful in coatings and adhesives.

Cyclopentadiene and piperylene are used for the production of hydrocarbon resins. These resins are used in thermoplastic and contact adhesives and in printing inks. In rubber formulations, they increase hardness and flex life (ability of a cable to bend many times before breaking). The second important use of cyclopentadiene is in unsaturated polyester resins instead of styrene. The products are said to be more brittle but have a smoother surface.



Flow sheet for separation of C₅ hydrocarbons

The liquid phase chlorination of cyclopentadiene provides hexachlorocyclopentadiene, which undergoes a Diels-Alder reaction with maleic anhydride to form so-called chlorendic anhydride, used as a flame retardant in unsaturated polyester resins.

