

PETROCHEMICAL FEEDSTOCKS

The preparation of hydrocarbon feed stocks for petrochemical manufacture can be a significant operation in today's petroleum refineries. There are three major classes of these feedstocks according to use and method of preparation. These are aromatics, unsaturates (olefins and diolefins), and saturates (paraffins and cycloparaffins). Aromatics are produced using the same catalytic reforming units used to upgrade the octanes of heavy straight-run naphtha gasoline blending stocks. For petrochemical use the aromatic fraction is concentrated by solvent extraction techniques. Some of the unsaturates are produced by the fluid catalytic cracking unit, but most have to be produced from refinery feedstocks by steam-cracking or low molecular polymerization of low molecular weight components.

To provide better continuity from regular refinery operations, the petro-chemical feedstock preparation will be covered in the order (1) aromatics, (2) unsaturates, and (3) saturates.

AROMATICS PRODUCTION

For aromatics production for petrochemical use, the catalytic reformer can be operated at higher severity levels than for motor gasoline production. Highly naphthenic feedstocks also aid in high aromatics yields because the dehydration of naphthenes is the most efficient reaction taking place and provides the highest yield of aromatics. Table illustrates the increase in aromatics yields as the reformer operating severity is increased [the clear research octane number (RON) is the measure of operating severity].

Product RON	Percent aromatics
90	54
95	60
100	67
103	74

The C_6 – C_8 aromatics (benzene, toluene, xylene, and ethylbenzene) are the large volume aromatics used by the petrochemical industry with benzene having the greatest demand. The product from the catalytic reformer contains all of these aromatics and it is separated into its pure components by a combination of solvent extraction, distillation, and crystallization. In addition, because of the much greater demand for benzene, the excess of the toluene and xylenes over market needs can be converted to benzene by hydrodealkylation.

Solvent Extraction of Aromatics

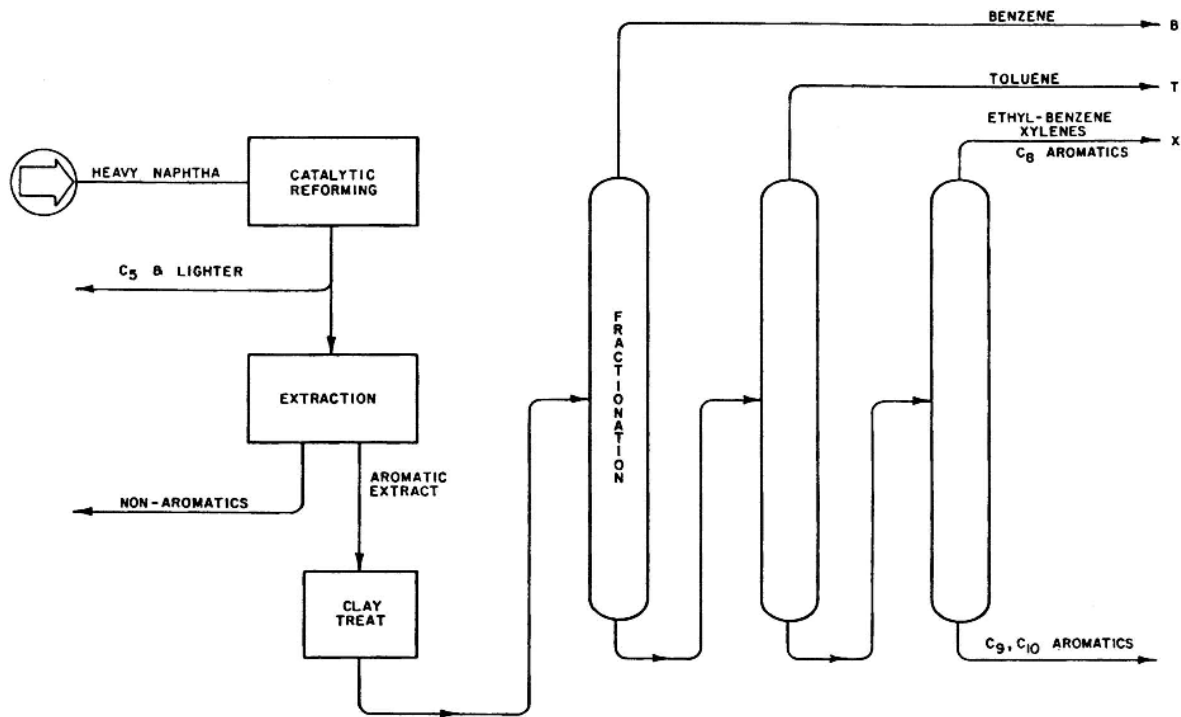
Present separation methods for recovery of aromatics from hydrocarbon streams use liquid–liquid solvent extraction to separate the aromatic fraction from the other hydrocarbons. Most of the processes used by U.S. refineries use either polyglycols or sulfolane as the extracting solvent. The polyglycol processes are the Udex process developed by Dow Chemical Company and licensed by UOP

and the Tetra process licensed by the Linde Division of Union Carbide. The solvents used are tetraethylene glycol for the Tetra process and usually diethylene glycol for the Udex process, although dipropylene glycol and triethylene glycol can also be used. It uses sulfolane (tetrahydrothio- phene 1-1 dioxide) as the solvent and a simplified process flow diagram is shown in Figure 15.1a.

The important requirements for a solvent are :

1. High selectivity for aromatics versus nonaromatics
2. High capacity (solubility of aromatics)
3. Capability to form two phases at reasonable temperatures
4. Capability of rapid phase separation
5. Good thermal stability
6. Noncorrosivity and nonreactivity

Sequence of aromatics recovery operations:



EXTRACTION PROCESS:

At a given selectivity, the solubility of aromatics in sulfolane is about double that in triethylene glycol. The higher solubility permits lower solvent circulation rates and lower operating costs.

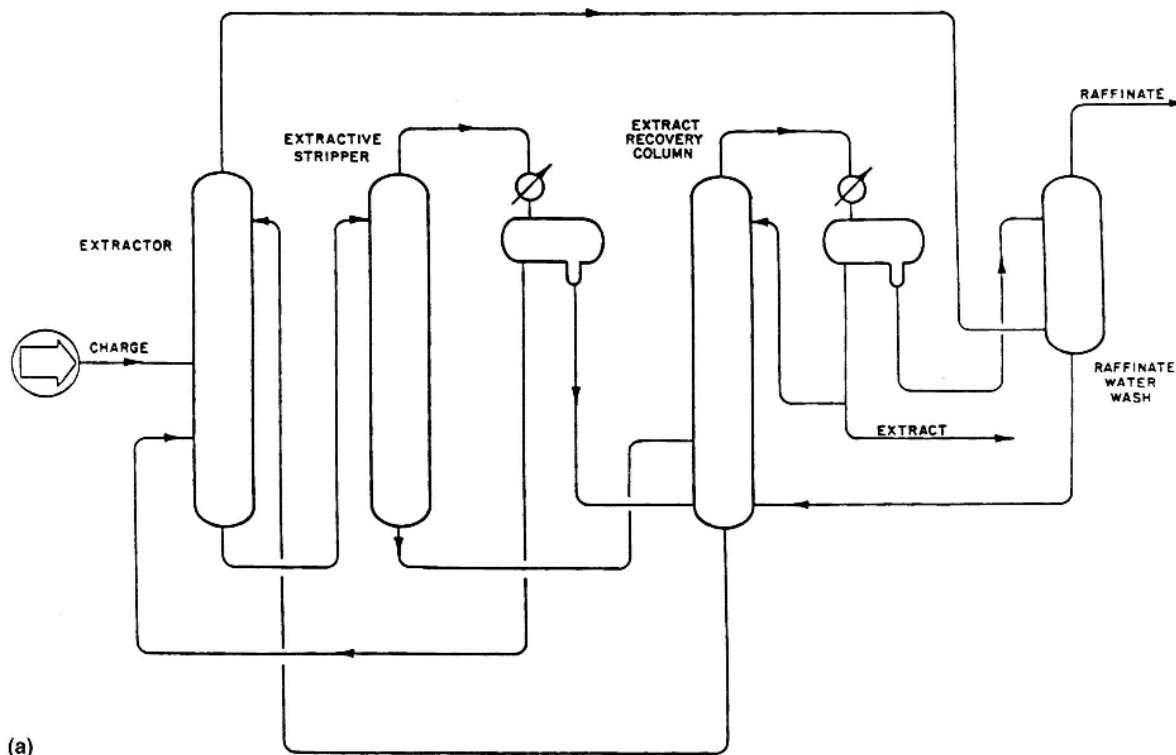


Figure 15.1a Sulfolane aromatics extraction unit.

Both the polyglycol and sulfolane solvent processes use a combination of liquid–liquid extraction and extractive stripping to separate the aromatics from the other hydrocarbons because of the characteristics of polar solvents. As the concentration of aromatics in the solvent increases, the solubility of the nonaromatic hydrocarbons in the extract phase also increases. This results in a decrease in the selectivity of the solvent and a carryover of some of the nonaromatic hydrocarbons with the extract phase to an extractive stripper. In the extractive stripper an extractive distillation occurs and the nonaromatic hydrocarbons are stripped from the aromatic–solvent mixture and returned as reflux to the extraction column. The solvent is then recovered from the nonaromatic hydrocarbon-free extract stream leaving an extract which contains less than 1000 ppm (0.1%) aliphatics.

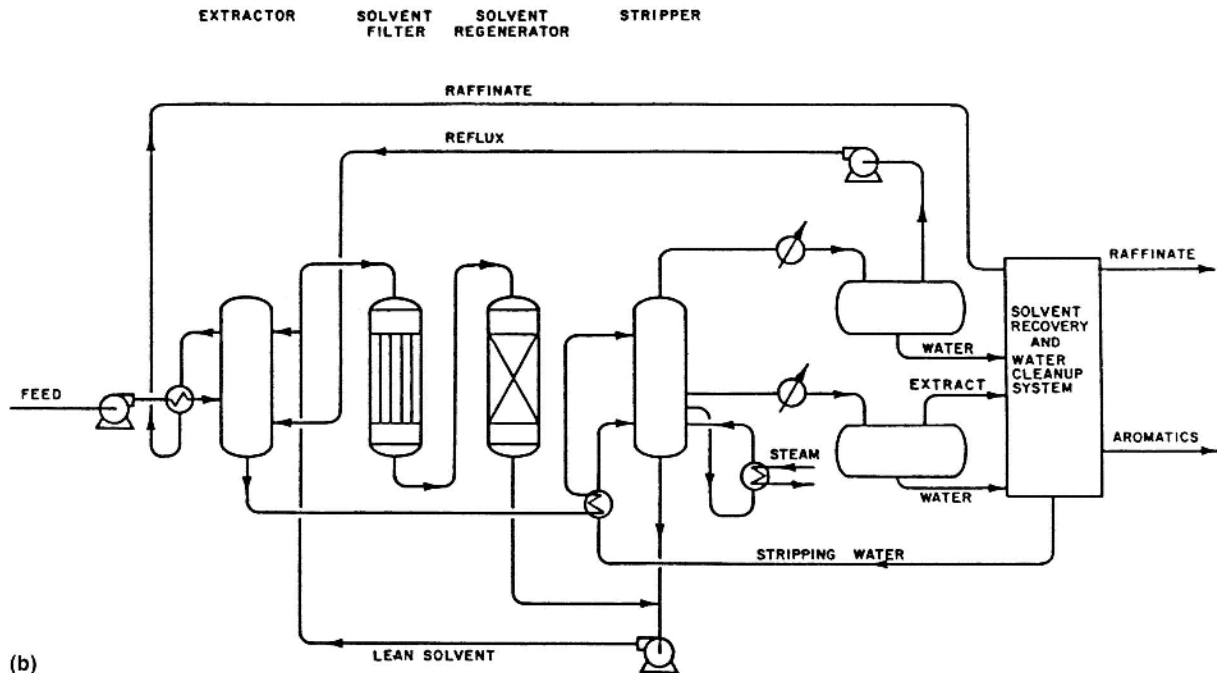
Aromatics recoveries are typically equal to or better than 99.9, 99.0, and 97.0% for benzene, toluene, and xylenes, respectively.

Because of the high affinity of the polar solvents for water and the low solubilities in the nonaromatic hydrocarbon raffinate phase, the solvent is recovered from the raffinate phase by washing with water. The water is returned to either the extractive stripper (Tetra) or extract recovery column (Sulfolane) for recovery of the solvent.

The water content of the solvents is carefully controlled and used to increase the selectivity of the solvents. The water content of the polyglycols is kept in the range of 2 to 10 wt% and that of sulfolane is maintained at about 1.5 wt%.

The solvent quality is maintained in the Sulfolane process by withdrawing a slip stream from the main solvent recirculation stream and processing it in a solvent reclaiming tower to remove any high-boiling contaminants that accumulated.

The Tetra process solvent quality is maintained by using a combination of filtration and adsorption to remove accumulated impurities.



Tetra aromatic extraction unit

Sulfolane and the polyglycols have thermal stability problems, and the skin temperatures of heat exchange equipment must be limited. For sulfolane, skin temperatures must be kept below 450°F (232°C).

Aromatics Separation

Benzene and toluene can be recovered from the extract product stream of the extraction unit by distillation. The boiling points of the C8 aromatics are so close together that separation by distillation becomes more difficult and a combination of distillation and crystallization or adsorption is used. The ethyl- benzene is first separated from the mixed xylenes in a three-unit fractionation tower with 120 trays per unit for a total of 360 trays. Each unit is about 200 feet in height, and the units are connected so they operate as a single fractionation tower of 360 trays. High reflux ratios are needed to provide the desired separation efficiency because the difference between the boiling points of ethylbenzene and p-xylene is only about 3.9°F (2°C). This is a very energy-intensive operation and, with today's energy costs, it is usually less costly to make ethylbenzene by alkylating benzene with ethylene.

A typical processing sequence for the separation of C₈ aromatics is shown in Figure 15.3. After removal of the ethylbenzene by super-fractionation, the o-xylene along with the higher boiling C₉ aromatics is separated from the p- and m-xylenes by fractionation. The boiling point of o-xylene is more than 9.6°F (5°C) greater than that of its closest boiling isomer, m-xylene, and it can be separated economically in a 160-plate distillation column. The overhead stream from this column is a mixture of m- and p-xylenes and the bottoms stream contains o-xylene and the C₉ aromatics. The bottoms stream is processed further in a 50-tray rerun column to separate 99% purity o-xylene from the C₉ aromatics.

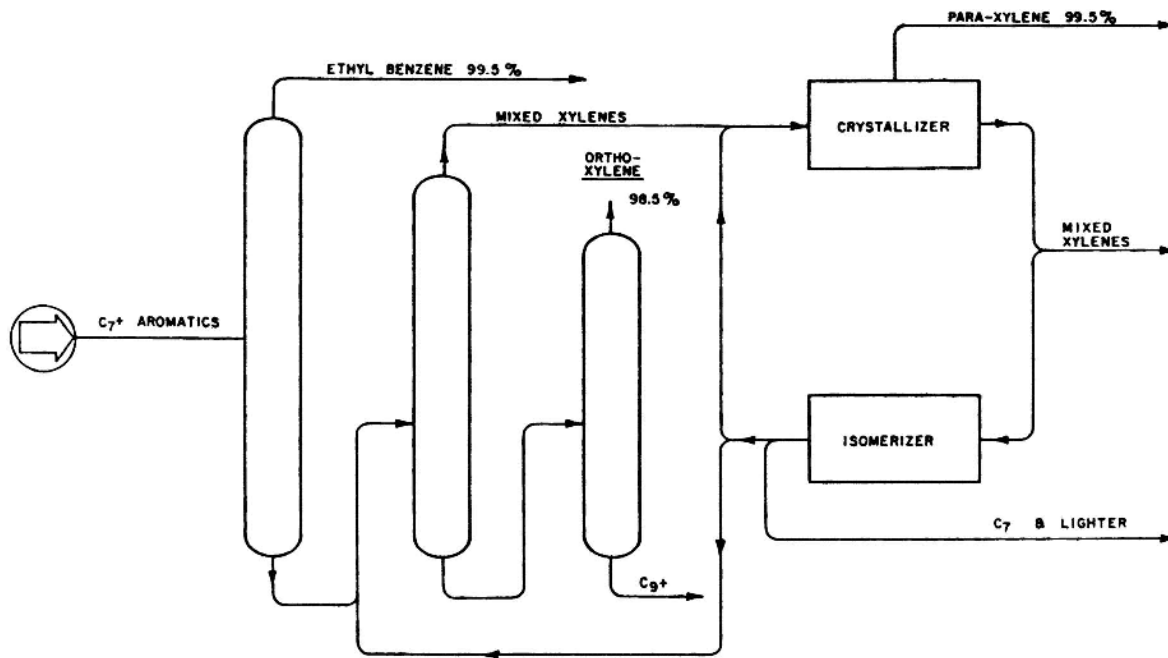


Figure 15.3 Processing sequence to produce C₈ aromatics

The mixed m- and p-xylene overhead stream from the fractionator is sent to either the Parex unit or the crystallization unit to separate the m- and p-xylenes. The UOP Parex process uses adsorption of p-xylene on a molecular sieve adsorbent to separate the m- and p-xylenes. The adsorbent is selected such that p-xylene molecules will be adsorbed and the m-xylene molecules will pass through the adsorbent bed. Recoveries of 96% per pass of pure p-xylene can be achieved as compared with 60–65% recovery of p-xylenes by the freeze-crystallization process.

The p-xylene usually is stripped from the adsorbent with p-diethylbenzene or a mixture of diethylbenzene isomers. The UOP process uses a simulated moving-adsorbent-bed design.

If fractional crystallization is used for separation, the mixed m- and p-xylene overhead stream from the fractionator is fed to the crystallization unit to separate the m- and p-xylenes. The solidification point of p-xylene is 55.9°F (13.3°C), while that of m-xylene is -54.2°F (-47.9°C). The xylenes feed is dried, chilled to about -40°F (-40°C) and charged to staged crystallizers. Ethylene is used as the refrigerant in indirect chilled surface scraped heat exchangers, and the mixture is chilled to 60°F (50°C) in the first crystallizer stage and to -90°F (-68°C) in the second stage crystallizer.

effluent is charged to a combination solid and screen bowl centrifuge to separate the p-xylene crystals from the mother liquor. The operation of this centrifuge is critical to the cost effectiveness of this process because it controls the subsequent purification costs and the overall refrigeration requirements of this separation [8].

The p-xylene crystals from the centrifuge are purified in a series of partial remelting, recrystallization, and centrifugation stages. The temperatures are increased for each remelting and recrystallization stage and the filtrate from each stage is recycled to the preceding stage. This counter-current operation gives a high-purity p-xylene product from the last stage. The m-xylene rich filtrate stream is used as feedstock for a xylene isomerization unit or sent to gasoline blending.

The m-xylene-rich stream from the crystallizer and the o-xylene stream from the rerun column can be converted to p-xylene by a xylene isomerization process if demand for p-xylene warrants it. The process flow diagram for this process is similar to the isomerization process in Chapter 10. The catalyst used is a zeolite-non-noble metal catalyst developed by Mobil. The aromatic-rich feedstock is mixed with hydrogen, heated to 700–800°F (375–425°C), and charged to a fixed-bed reactor containing a non-noble metal catalyst at a pressure of about 150 psig (1034 kPa). The mixture is isomerized to a near-equilibrium mixture of o-, m-, and p-xylenes [6,8]. After cooling, the xylenes are separated from the hydrogen-rich gas in a flash separator and from other hydrocarbons in distillation columns. The xylene-rich stream is returned to the p-xylene crystallization unit or the Parex unit as feed.

Other isomerization processes are used to maximize p-xylene production by both isomerizing o- and m-xylenes and by converting ethylbenzene into xylenes [8]. A two-stage process is generally used for conversion of aromatic hydrocarbons with two or more carbons in the side chains, with the first stage for partial hydrogenation and the second for dehydrogenation. A single-stage process can also be used. The catalysts are either silica-alumina containing a small amount of platinum or molecular sieve silica-alumina catalysts containing about 1% platinum. The equilibrium concentration of p-xylene obtained in the effluent is about 24%.