4

The BTX Chain: Benzene, Toluene, Xylene

4.1 Overview of the BTX Chain

Benzene, Toluene, and Xylene Are Co-Products

Benzene, toluene, and xylene are all aromatic compounds[1] important to the production of polymers, other chemicals, and numerous consumer products (solvents, paints, polishes, pharmaceuticals) (see Figure 4-1). These three aromatics are often co-produced by catalytic reforming of naphtha, although other methods are also employed in their manufacture. Toluene, for example, can be hydroalkylated to form benzene.
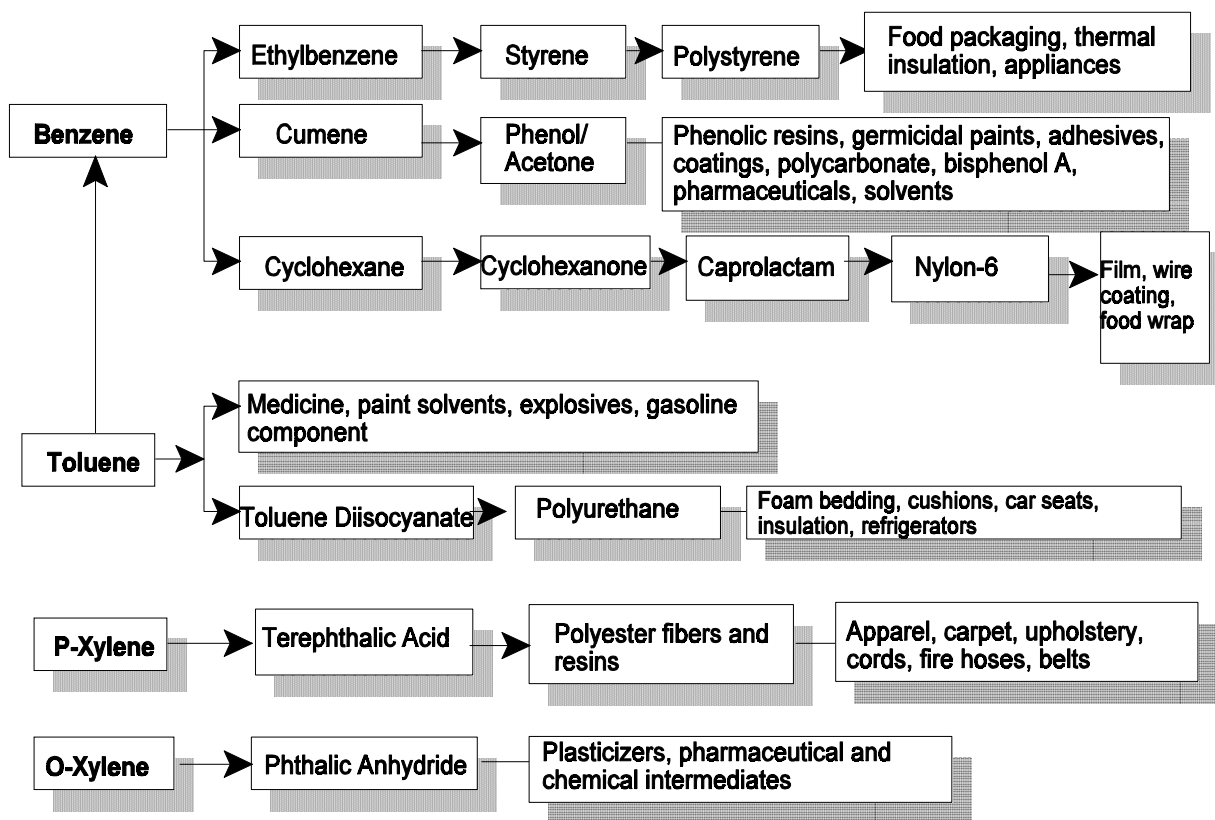
Benzene ranks fifteenth on the list of top fifty chemicals produced in the United States, with about 15 billion pounds produced in 1997. Most of the benzene produced is used in the manufacture of **ethylbenzene**, which is used solely to produce **styrene** and subsequently

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Production of Benzene, Toluene, and Xylene and Their Derivatives (1997)

Benzene (14.9 billion lbs)
Ethylbenzene (13.9 billion lbs)
Styrene (11.4 billion lbs)
Polystyrene (6.4 billion lbs)
Cumene (5.8 billion lbs)
Phenol (4.4 billion lbs)
Acetone (2.9 billion lbs)
Cyclohexane (2.2 billion lbs)
Caprolactam (1.7 billion lbs)
Nylon (1.2 billion lbs)
Toluene (8.3 billion lbs)
Toluene-diisocyanate (0.9 billion lbs)
p-Xylene (7.9 billion lbs)
o-Xylene (1.1 billion lbs)
Terephthalic Acid (10 billion lbs)
Phthalic Anhydride (1.0 billion lbs)
Adipic Acid (2.0 billion lbs)

Sources: CMA 1998, SPI 1998.

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[1]   *In the late nineteenth century "aromatic" referred to compounds that had low hydrogen-to-carbon ratios and were fragrant, as most were made from balsams, resins, or essential oils (e.g., bitter almond oil). Today, aromatics are characterized as compounds having fully conjugated (hybridized unsaturated orbital) ring structures, which may have 6 carbons, or 10 carbons, or many more carbons, and may also contain heteroatoms. Ring structures with 6 carbons like cyclohexane are called naphthenes, and are not aromatics.*

Ethylbenzene → Styrene → Polystyrene → Food packaging, thermal insulation, appliances

Benzene →
- Ethylbenzene
- Cumene → Phenol/Acetone → Phenolic resins, germicidal paints, adhesives, coatings, polycarbonate, bisphenol A, pharmaceuticals, solvents
- Cyclohexane → Cyclohexanone → Caprolactam → Nylon-6 → Film, wire coating, food wrap

Toluene →
- Medicine, paint solvents, explosives, gasoline component
- Toluene Diisocyanate → Polyurethane → Foam bedding, cushions, car seats, insulation, refrigerators

P-Xylene → Terephthalic Acid → Polyester fibers and resins → Apparel, carpet, upholstery, cords, fire hoses, belts

O-Xylene → Phthalic Anhydride → Plasticizers, pharmaceutical and chemical intermediates

Figure 4-1. The BTX Chain (CMA 1998)

polystyrene, an important polymer. Small amounts of styrene are also used in the manufacture of ABS resins (acrylonitrile-butadiene-styrene).   Ethylbenzene ranked sixteenth on the top fifty list in 1997, with nearly 14 billion pounds produced. Styrene followed closely, with about 11.4 billion pounds produced. Polystyrene is the fourth largest thermoplastic produced, with over 6 billion pounds in 1997. Its primary uses include food packaging, appliances, and thermal insulation.

About 22 percent of the benzene produced is used to manufacture **cumene,** which is used solely to produce phenol and acetone. Phenol is an intermediate in the production of phenolic resins, pharmaceuticals, and various plastics. Benzene, along with xylene and toluene, is also used as a component of gasoline. Its use for this purpose is declining, however, as different regions of the country impose limits on benzene because of its known carcinogenicity.

Toluene ranked twenty-fifth on the list of the top fifty chemicals in 1997, with 8.3 billion pounds produced. More than half of the toluene produced is used to manufacture benzene by hydroalkylation. Other important uses are the production of **toluene-diisocyanate** (TDI), a monomer for polyurethanes, and the manufacture of explosives (TNT).

The most widely used isomers of xylene include **ortho-xylene** and **para-xylene**, named for the relative position of methyl (CH_3) groups on the six-carbon ring. *Ortho* indicates the groups are substituted on adjacent carbons; *para* indicates the groups are substituted on the first and fourth carbons. Demand is much greater for **p-xylene**, which ranked twenty-sixth on the list of the top fifty chemicals in 1997 with about 7.9 billion pounds of production. It is used primarily to manufacture terephathalic acid, an important intermediate in the production of polyester fibers and resins (see Section 2 for more information on polyester). Production of **o-xylene** was about

1 billion pounds in 1997, and this compound is used almost entirely to make **phthalic anhydride**, an intermediate in the synthesis of plasticizers, pharmaceuticals, and other chemicals (CMA 1998, CHEMX 1999, Orica 1999.

Demand for BTX and Their Derivatives Is Closely Linked to the Plastics Market

Like most petrochemicals, the **demand for benzene, toluene, and xylenes** is strongly linked with consumer demand for plastics, their primary end-use. Currently, the demand for certain plastics is relatively high demand (e.g., polyethylene, polypropylene) but is weakening for others (e.g., polystyrene, polyvinyl chloride). Over-capacity, lower demand for exports from Asia, and declining prices and margins will continue to be near-term problems for the BTX chemicals as well as for some of their end-products.

The demand for **cumene**, which is produced from benzene, remains strong, however, and is being driven by steadily increasing consumption of bisphenol A, an intermediate in polycarbonate manufacture, and steady growth in the use of phenolic resins. Markets for both of these derivatives are linked to a strong demand in the downstream consuming industries of transportation and construction.

The strong underlying global demand for polyester fibers, film, and bottle resins is keeping the demand for **p-xylene** strong. Good margins have stimulated projects to construct additional capacity for p-xylene production, which may lead to overcapacity in the future.

The capacity for **o-xylene** production is in close agreement with the demand for this product. Exports to South American markets have been increasing, and have helped to offset falling shipments to the Asia Pacific region. In the future, some expansion is expected in the use of o-xylene for herbicides, lubricant additives, and specialty chemicals manufacture (CHEMX 1999, CHEMWK 1999).

4.1.1 BTX Manufacture

The Same Process Can Be Used To Produce Benzene, Toluene, and Xylenes

Benzene was originally made solely from coal tar, until new processes began to emerge in the 1950s. The new production methods were based on the catalytic reforming of naphtha, and by 1980 they had gradually eliminated the use of coal tar. **Toluene and xylenes** are also produced during the production of benzene using the newer process. The amounts of each aromatic produced may vary depending on current market demand, but typically, production of benzene is favored. Benzene produced from reformate accounts for about 40 percent of petrochemical-based benzene. Another 40 percent is produced by extracting benzene from pyrolysis gas. About 20 percent is produced by catalytic hydrodealkylation of toluene or other methods.

A typical flow diagram for production of benzene, toluene, and xylene from naphtha is shown in Figure 4-2. Naphtha feed enters a reactor or series of reactors containing platinum catalysts in a gas atmosphere (typically hydrogen to suppress coke formation). Coke is usually removed from the catalyst and the catalyst is regenerated and recycled to the reactor. Hydrogen is also recycled.

The reformate is then subjected to further processing by various methods, depending on the desired product slate: (1) solvent extraction of mixed aromatics, (2) the separation of each aromatic by distillation, or (3) the hydro-dealkylation of toluene.

Solvent extraction processes use solvents such as diethylene glycol, tetraethylene glycol, or sulfolane to extract the aromatic from non-aromatic compounds. These solvents also have high boiling points to make later fractionation of individual products easier. A typical product slate for deriving aromatics from naphtha reformate (which is also subjected to solvent extraction and fractionation) is shown in Table 4-1. Fractionation is used to separate and recover the solvent, which is then returned to the process.
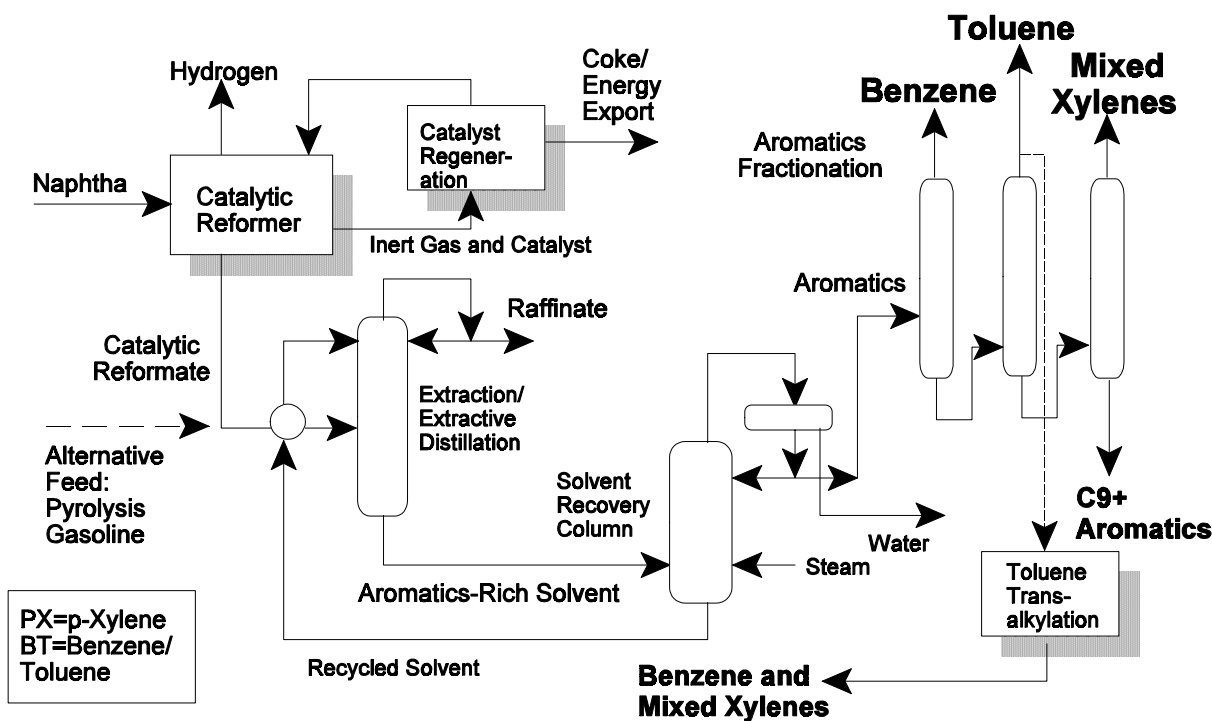
Figure 4-2. Possible Configuration for Reforming of Naphtha To Produce Benzene, Toluene, and Xylene (Chenier 1992, HP 1999, Orica 1999)
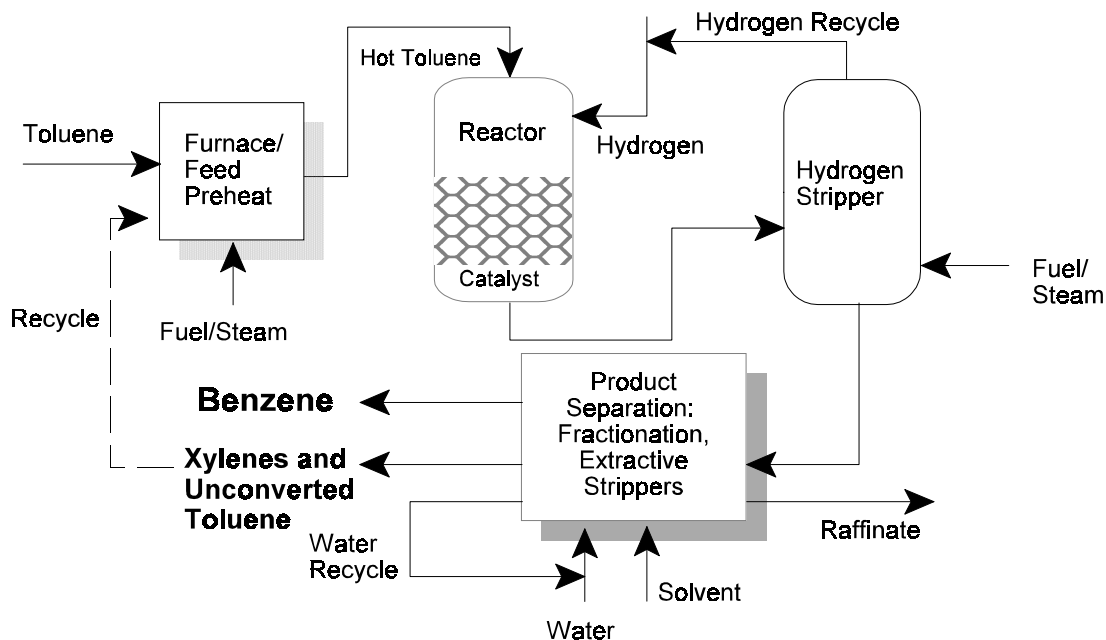
Key Energy and Environmental Facts - Naphtha Reforming to Produce BTX			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 1,025 Btu/lb* *Feedstock: 299 Btu/lb (based on refinery stock)*	*Largest source - fugitive emissions (benzene, toluene, xylenes, solvents)*	*Largest source - process water*	*Raffinate, coke, spent catalyst*

Table 4-1. Product Slate: BTX from Naphtha Reformate (% Yield)	
Benzene	8.5
Toluene	26.3
Xylenes	26.1
TOTAL AROMATICS	74.3

When distillation is used, as shown in Figure 4-2, three columns are used to separate benzene first, then toluene, and then mixed xylenes. The toluene stream can be sold or rerouted to the toluene trans-alkylation unit. The mixed xylene stream also contains ethylbenzene compounds, and can be routed to a number of process units, depending on the desired products. The bottoms column from the xylene column contains C9 or higher aromatics and can be blended into distillates or sold.

Additional processes may be used to optimize yields of benzene or p-xylene. These processes may combine special units to produce ultra-high-purity p-xylene with toluene dealkylation units, which produce benzene from the toluene product

Figure 4-3. Toluene Hydrodealkylation to Produce Benzene (HP 1999, Orica 1999)

Key Energy and Environmental Facts - Toluene Hydrodealkylation			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: Process Energy: 1,117 Btu/lb Feedstock ΔHc: 23,330 Btu/lb	Largest source - fugitive emissions (benzene, xylenes, toluene, solvents)	Largest source - process water	Nonaromatic byproducts

stream. The mixed xylene and toluene cuts from naphtha reformate are the typical feedstocks to these units.

There are a variety of technologies available for production of high-purity p-xylenes from mixed C8 isomer streams. Some are based on simulated countercurrent adsorption, selective catalytic isomerization, or a combination of these with fractionation (xylene splitter). The C8 feed stream may contain up to 40 percent ethylbenzene, which is converted to xylenes or benzene during the process. Typical yields from such processes are shown in Table 4-2. Toluene hydrodealkylation (HDA) is also used to produce benzene, although it is more costly than the reforming route (depending on the cost and availability of hydrogen). A flow diagram for

HDA is shown in Figure 4-3. In this process toluene is combined with a stream of hydrogen

Table 4-2. Product Yields from Mixed C8 Aromatic Streams Downstream Processing		
	Feed (wt %)	Products(wt%)
p-Xylene	14.0	71.1
m-Xylene	41.0	–
o-Xylene	19.5	19.6
Ethylbenzene	25.5	--

Source: HP 1999.
Note: Based on UOP's Isomar and Parex processes for selective production of p-xylene.

and enters a vessel packed with catalyst. Current catalysts include chromium or molybdenum oxides, and platinum or platinum oxides, supported on silica or alumina.

Operating temperatures are relatively high: 900ºF–100ºF (480ºC–590ºC), with pressures ranging from 40 atmospheres–60 atmospheres. The catalytic reaction can proceed at lower temperatures and with higher selectivity, but requires frequent catalyst regeneration under these conditions. The reaction is very exothermic (heat releasing), requiring temperature control, which is accomplished by injection of quenching hydrogen at appropriate places during the reaction. The conversion rate per pass is as high as 90 percent, and it is common to obtain cumulative conversions of greater than 95 percent.

The products pass through a separator to remove hydrogen, which is recycled. Fractionation is then used to separate other aromatics and non-aromatics from the benzene product. HDA units can usually be operated with feeds of differing aromatic content, and can be used to produce primarily benzene or a mix of benzene and xylenes, depending on the desired product slate. A typical feed containing about 47 percent toluene and 50 percent C8 aromatics yields about 76 percent of benzene by weight (Process Description: Orica 1999, HP 1999)**.**

4.1.2 Ethylbenzene Production

Ethylbenzene Is Produced through Friedel-Crafts Alkylation

Early methods for producing **ethylbenzene** from benzene and ethylene were based on an **electrophilic aromatic substitution reaction** (Friedel-Krafts alkylation), conducted in the vapor phase using boron trifluoride, phosphoric acid, or alumina-silica as catalysts. Since 1980, ethylbenzene has been produced using zeolite catalysts in a liquid phase operation.

The flow diagram for producing ethylbenzene using zeolite catalysts is shown in Figure 4-4. Ethylene and benzene enter a liquid-filled

alkylation reactor that contains fixed beds of zeolite catalyst. The reaction is very exothermic (heat-producing), and heat is recovered as low-pressure steam. The process is generally a net energy producer, with some of the energy used to supply heat for the distillation of products. Since nearly all the ethylbenzene produced (99 percent) is used to produce styrene, this process is usually integrated with styrene production, which is very energy-intensive.

The product, mostly ethylbenzene and small amounts of polyethylbenzene, then enters a transalkylation reactor containing additional catalyst, which converts the polyethylbenzene to ethylbenzene. Effluents from both reactors pass through a benzene column to remove and recover unreacted benzene. The reaction requires excess benzene, in ratios of about 1:0.6 benzene to ethylene. The unreacted benzene is fed to a vent-gas column to remove impurities. The ethylbenzene-rich bottoms from the benzene column are sent to an ethylbenzene column to remove recyclable alkylbenzenes and other byproducts.

A product with a purity as high as 99.95 to 99.99 percent can be achieved with a benzene feedstock of only moderate to high purity. The catalysts are highly selective and their expected lifetime is two to four years before they need to be regenerated. Regeneration is performed at an outside facility (Process Description: ANL 1980, Chenier 1992, HP 1999)**.**

4.1.3 Styrene Manufacture

Nearly All Styrene Is Made from Ethylbenzene by Dehydrogenation

Most of the styrene produced in the United States is made by **dehydrogenation of ethylbenzene**. Technology is also emerging to recover styrene from raw pyrolysis gasoline produced during steam cracking of naphtha, gas oils, or natural gas liquids. About 25 percent of worldwide styrene production comes from propylene oxide production, where it is produced as a byproduct.
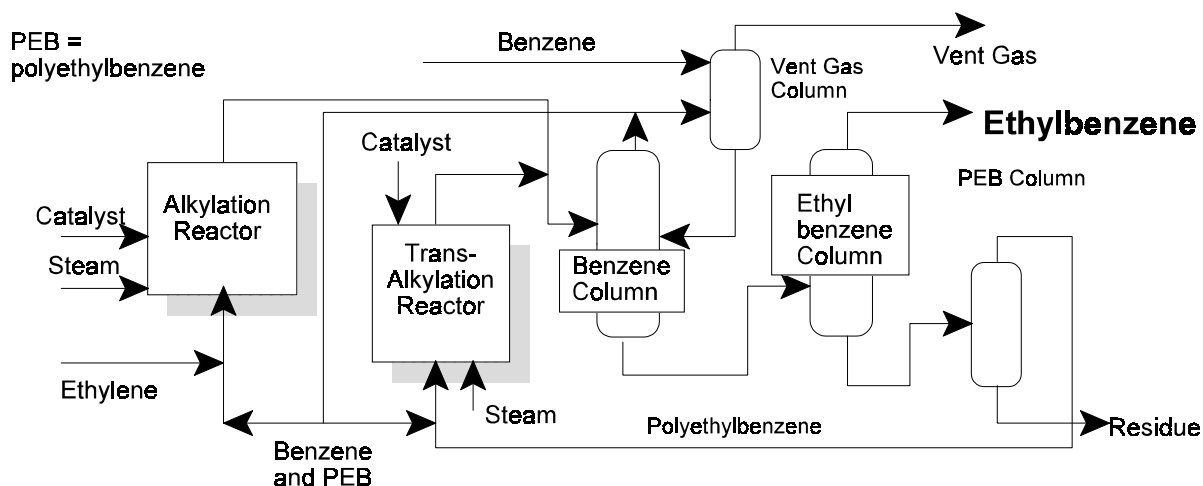
Figure 4-4. Ethylbenzene Manufacture (HP 1999)

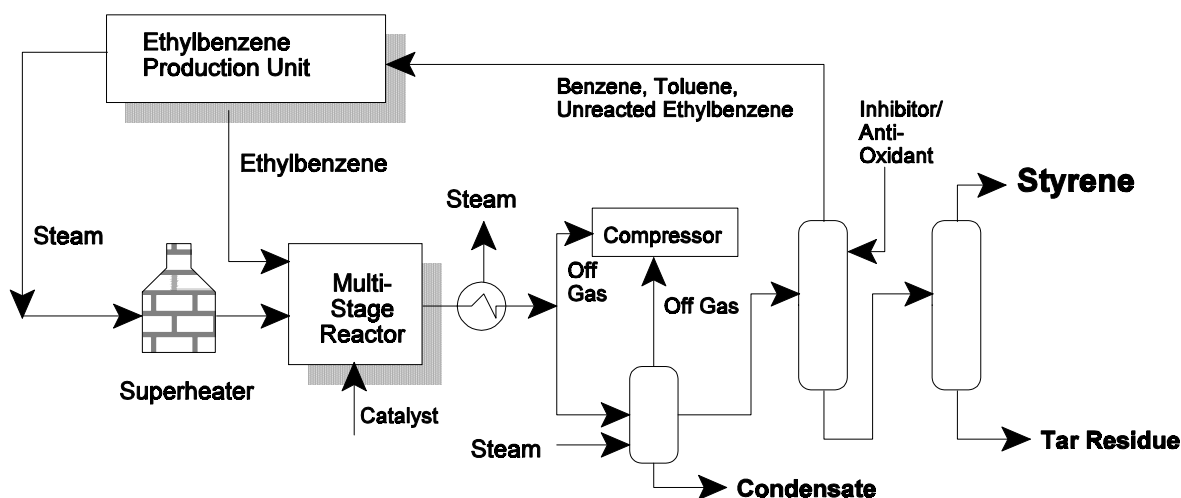| Key Energy and Environmental Facts - Ethylbenzene Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 1,174 Btu/lb* *Feedstock ΔHc: 19,044 Btu/lb*	*Largest source - fugitive emissions (benzene, ethylene, ethylbenzene)*	*Largest source - process water*	*Residues, vent gas*

Yields of styrene by this process are considerably higher by a ratio of about 2:1 than by dehydrogenation of ethylbenzene (DOW 1999). Many plants integrate production of ethylbenzene with styrene to make use of the energy exported during ethylbenzene production. A typical configuration is shown in Figure 4-5. In this process, the ethylbenzene is catalytically dehydrogenated to styrene in the presence of steam. The process is conducted at high temperatures of 1200°F (2100°C) and greater, and under vacuum.

The ethylbenzene feed and primary steam are mixed with superheated steam and dehydrogenated in a multi-stage reactor. One or two plants in the United States are injecting air or oxygen between stages to oxidize the hydrogen produced, reheat process gas, and lower equilibrium limits for the dehydrogenation reaction. However, no air or

oxygen is injected in the majority of styrene plants based on ethylbenzene dehydrogenation.

Effluents from the reactor are cooled, which permits recovery of waste heat and condenses hydrocarbons and steam. Off-gases are compressed and later utilized as fuel. Condensed hydrocarbons are sent to a fractionation train, where high-purity styrene, unreacted ethylbenzene, and byproducts (minor amounts of tar, toluene, and benzene) are separated and recovered. Benzene, toluene, and unreacted ethylbenzene are recycled; tar residues are used as fuel. Conversion of ethylbenzene can be as high as 80–90 percent.

Various metal oxides can be used as catalysts, including zinc, chromium, iron, or magnesium oxides coated on activated carbon, alumina, or

Figure 4-5. Styrene Manufacture (ANL 1980, HP 1999)

Key Energy and Environmental Facts - Styrene Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 16,891 Btu/lb* *Feedstock ΔHc: 20,058 Btu/lb*	*Largest source - fugitive emissions (benzene, toluene, styrene, ethylbenzene)*	*Largest source - process water*	*Tar residues, benzene, toluene*

bauxite. Iron oxide or potassium carbonate are also sometimes used. Styrene readily polymerizes to polystyrene, so sulfur or an anti-oxidant (p-t-butylcatechol) is usually added to inhibit polymerization (Process Description: ANL 1980, Chenier 1992, HP 1999).

4.1.4 Polystyrene Manufacture

***Polystyrene Is Usually Made by Bulk Polymerization***

Continuous **bulk polymerization** processes are among the least costly and least energy-intensive methods for producing polystyrene from styrene monomers, and are therefore used most frequently. Most bulk processes can make a range of products, including high-impact polystyrene, styrene acrylonitrile resins, general purpose (crystal) grade polystyrene, and certain

specialty grades such as high-gloss, high-strength polystyrene.

Polymerization of styrene can occur very easily at room temperatures, without a catalyst or an initiator, but it can take months to accomplish. If heated to 300ºF (149ºC), polymerization occurs within hours. If an initiator is added along with heat, the reaction can be completed in less than an hour. Most processes use initiators at moderate temperatures to ensure the high molecular weight and strength of the product and prevent the possibility of a runaway reaction.

Polymerization can be accomplished in either batch or continuous processes. Various configurations are possible for continuous styrene polymerization, but most have a similar process flow. In a typical process, styrene
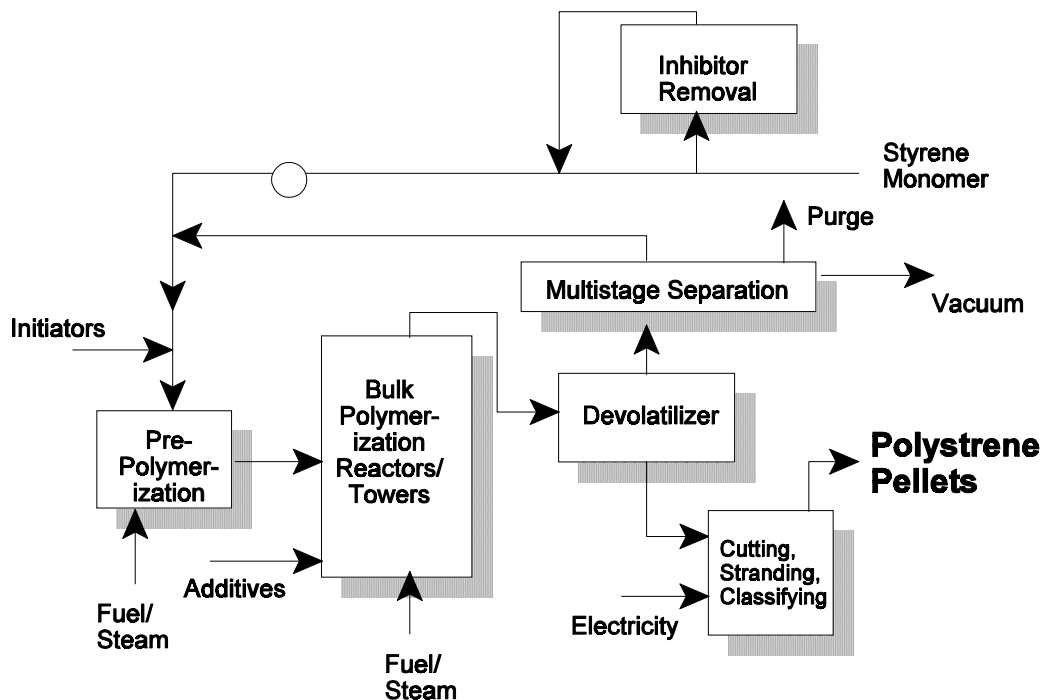
Figure 4-6. Polystyrene Manufacture (ANL 1980, HP 1999)

Key Energy and Environmental Facts - Polystyrene Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 2,264 Btu/lb* *Feedstock ΔHc: 20,058 Btu/lb*	*Largest source - fugitive emissions (volatile hydrocarbons, styrene)*	*Largest source - process water*	*Off-grade polymer*

is sent to a prepolymerizing reactor where it is heated (see Figure 4-6). Partial polymerization occurs to various degrees upon heating, depending on the specific operating parameters of the process. The viscous, partially polymerized solution is then fed to a continuously stirred reactor, plug-flow reactor, or tower, along with initiators.

Temperatures in the reactors or towers are carefully varied from 230ºF to 350ºF (110ºC to 177ºC) to achieve the desired polymerization rates. The desired molecular weight and molecular weight distribution of the products can be controlled by adjusting process conditions and additives.

After heating to more than 500ºF (260ºC), the viscous molten polymer is pumped out of the tower through small die holes to form strands. These strands are then cooled and cut into pieces for bulk storage and shipment. They may be used in this form or blended later with additives and extruded again.

Unreacted styrene monomer is flashed into a vacuum, and then recovered for separation and recycling. Styrene can also be removed from the polystyrene product by vacuum rolling, in which mechanical work raises the temperature and volatilizes light components, or by screw devolatilization, a rapid process that minimizes degradation of the polymer.

During batch polymerization, the styrene feed is sent to a prepolymerization reactor, typically an autoclave, to increase its molecular weight. During prepolymerization, small amounts of lubricant, plasticizer, polymerization regulator, and anti-oxidant may be added to the feed. The blended feed is pumped from the prepolymerization reactor into a batch reactor, where some styrene vaporizes and is vented through an overflow drum. The mixture is heated and an initiator may be added to drive the polymerization.

After polymerization is complete, the molten polymer is pumped to a devolatilizer to remove residual styrene monomer, ethylbenzene, and polymers of low molecular weight. The molten polystyrene is heated, extruded through dies, and immersed in a cold water bath. It is then pelletized and sent to bulk storage. Conversion of styrene is usually higher in batch processes.

Although bulk polymerization is the most commonly used method, polystyrene can also be produced using suspension polymerization. In this process, batches of styrene, initiators, and water (for heat removal) are added to stirred kettle reactors or jacketed cylinders, achieving a conversion rate of 90-93 percent. The small polymer beads that result are centrifuged, dried, and stored.

Polystyrene foam can be made by the absorption of a volatile hydrocarbon (e.g., pentane, propylene, methylene chloride) during polymerization. Upon heating with steam or boiling water, the volatilized beads expand to produce a foam product (Process Description: ANL 1980, EPA 1991b, HP 1999).

4.1.5 Cumene Manufacture

Cumene Is Made from Propylene and Benzene Using Friedel-Crafts Alkylation

Cumene is produced by the Friedal-Crafts alkylation of benzene and propylene over a catalyst. Catalysts may include solid acid phosphoric acid, or one of the new generation of zeolite catalysts. A new process for producing cumene uses catalytic distillation based on zeolite catalysts, which has undergone demonstration trials. A large commercial plant was scheduled for start-up in Taiwan in 1999.[2] Most new plants for cumene production use processes based on the less corrosive zeolite catalyst.

In a typical alkylation process, refinery- or chemical-grade liquid propylene and benzene are introduced to a fixed-bed alkylation reactor, where the propylene is consumed completely by the benzene (see Figure 4-7). The effluent from the alkylation reactor is sent to a column to remove propane, which enters in small quantities with the propylene. The bottoms from this column are sent to a benzene column where unreacted benzene is distilled and recycled. Effluent from this column proceeds to a cumene separation column to recover the cumene product as an overhead stream.

The byproduct from the cumene column is diisopropylbenzene (DIPB). The DIPB is separated from a small quantity of heavy hydrocarbon byproduct and recycled along with benzene to a transalkylation reactor, where the DIPB reacts with benzene to produce additional cumene. With the reaction of DIPB, nearly stoichiometric amounts of cumene are produced (a yield of nearly 100 percent).

The zeolite catalyst is regenerated (life cycles are two years or more, with total life of six years or better), and is non-corrosive. Yields of cumene of up to 99.97 percent by weight and better are routinely achieved with this process. Catalysts are highly selective, environmentally benign, and generally do not produce oligomers or coke as byproducts. Zeolite-based processes are also much more cost-effective and provide better yields than older processes based on solid acid catalysts.

The process produces liquified petroleum gases that can be combusted to produce steam, and

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[2] Formosa Chemicals & Fibre Corporation

DIPB = Diisopropylbenzene
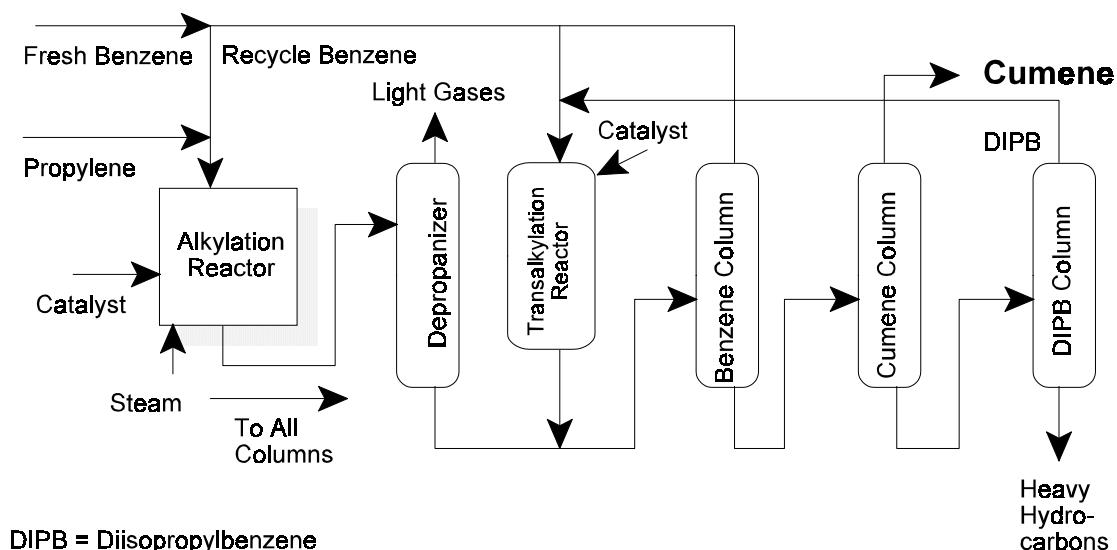
Figure 4-7. Cumene Manufacture (ANL 1980, HP 1999)

Key Energy and Environmental Facts - Cumene Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Exporter: *Net Export Steam: 392 Btu/lb* *Feedstock: 19,032 Btu/lb*	*Largest source - fugitive emissions (volatile hydrocarbons)*	*Largest source - process water*	*Heavy hydrocarbons, light gases*

the process is a net energy exporter. Since nearly all the cumene produced is used to make phenol and acetone (these are co-produced by the same process), the exported steam is often utilized in a phenol/acetone manufacturing unit that is located nearby (Process Description: Chenier 1992, HP 1999).
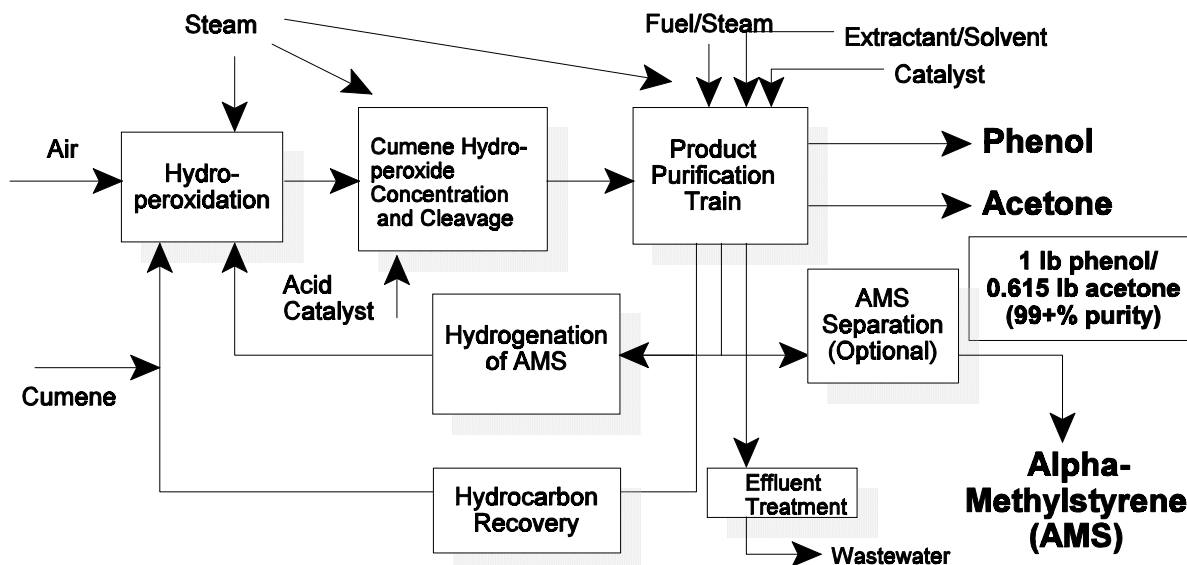
4.1.6 Phenol/Acetone Manufacture

Phenol and Acetone Are Co-produced from Cumene by Hydroperoxidation

The formation of **phenol and acetone** from **cumene hydroperoxide** was first discovered by German chemists Hock and Lang in 1944 and was commercialized in the United States and Europe by 1953. It remains the process of choice for making over 90 percent of acetone and phenol produced today (Chenier 1992).

In the first stage of the process (see Figure 4-8), cumene is oxidized with air to form cumene hydroperoxide. The reaction proceeds at about 230ºF (110ºC). The hydroperoxide is then concentrated and decomposed (cleaved) by acid-catalyzed rearrangement into acetone and phenol. The catalyst is removed and the

Figure 4-8. Phenol/Acetone Manufacture (Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Phenol/Acetone Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 7,850 Btu/lb* *Feedstock ΔHc: 15,112 Btu/lb*	*Largest source - fugitive emissions (cumene, phenol, acetone, AMS)*	*Largest source - caustic and other wastewaters*	*Spent catalyst, acetophenone, 2-phenylpropan-2-ol, and alpha-methylstyrene*

effluent neutralized before being sent to a fractionator for separation into high purity products. Byproducts may include acetophenone, 2-phenylpropan-2-ol, and alpha-methylstyrene. The alpha-methylstyrene and acetophenone are sometimes recovered as useful products, or may be recycled back to the hydroperoxidation unit.

After initial fractionation, a series of steps may be required in order to purify the acetone and the phenol. These may include hydroextractive distillation, catalytic treatment, and extraction with caustics. The purity of products is greater than 99.99 percent by weight (Process Description: Chenier 1992, HP 1999).
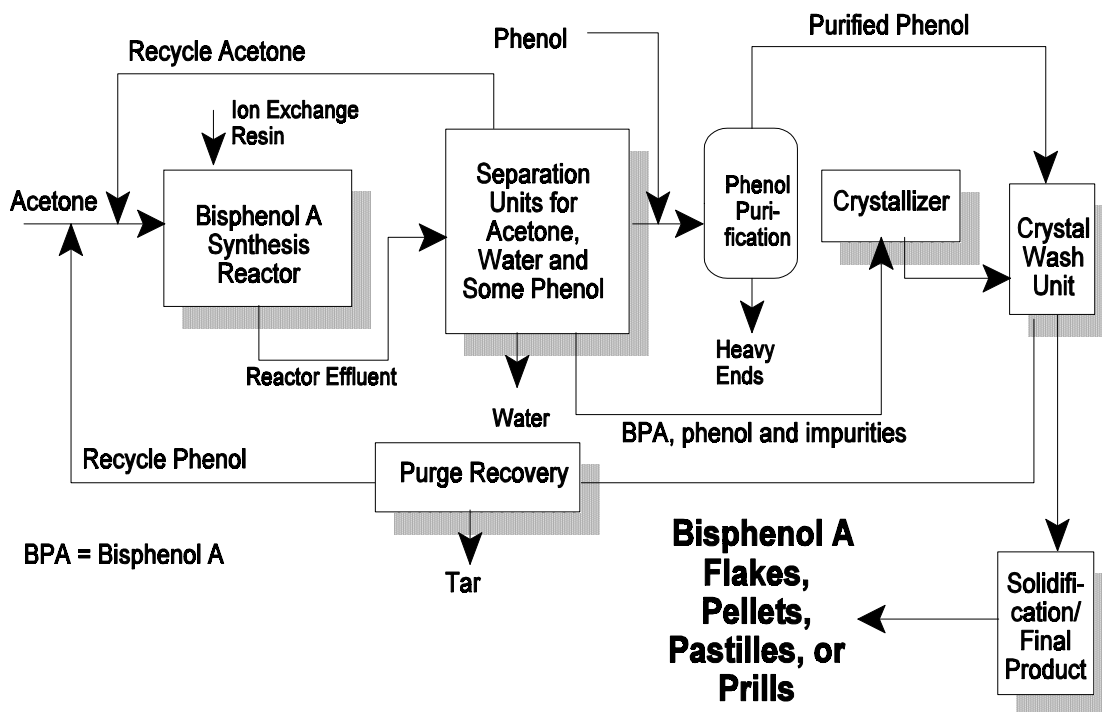
Figure 4-9. Bisphenol A Manufacture (Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Bisphenol A Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Not available	*Largest source - fugitive emissions*	*Largest source - wastewater, produced waters*	*Tars and heavy ends (can be used as fuel)*

4.1.7 Bisphenol A Manufacture

Acetone and Phenol Are Used To Make Bisphenol A, a Building Block for Polycarbonates, Plastics, and Resins

Acetone and phenol can be used to manufacture **bisphenol A,** an important intermediate in the production of polycarbonates, epoxy resins, and engineered plastics. A typical process configuration based on ion-exchange resin catalyst is shown in Figure 4-9.

Acetone and excess phenol are first reacted in a catalytic reactor packed with ion exchange resin.

The water produced in the reaction is separated and unreacted acetone and a portion of the phenol are separated from the reaction mixture by a series of distillations. Acetone is recycled to the reactor, and the phenol is mixed with fresh phenol and purified before recycling.

The remaining effluent containing bisphenol A, phenol, and impurities is crystallized and washed to remove impurities. The crystals are then melted and vacuum distilled and subjected to evaporation to remove residual phenol and raw bisphenol A. The molten bisphenol A is solidified to form flakes, pastilles, or prilles (Process Description: HP 1999).

4.1.8 Derivatives of Xylene

Xylenes Are Used To Produce Three Major Chemicals: Terephthalic Acid, Dimethyl Terephthalate, and Phthalic Anhydride

Terephthalic acid (TPA) and **dimethyl terephthalate (DMT),** which are primarily used in the production of polyester fibers, films, and resins, can both be produced from p-xylene through different routes. High purity TPA is produced through oxidation of p-xylene (see Figure 4-10). In this process, p-xylene and a solvent (acetic acid) are oxidized with air over heavy metal catalysts (cobalt, manganese salts of heavy metal bromides). Terephthalic acid is

formed, with a purity of about 99.6 percent and a yield of about 90 percent. The crude TPA is cooled and crystallized, and the acetic acid and unreacted xylene are evaporated away. The crystals are then washed with hot water to remove traces of the catalyst and acetic acid. Incomplete oxidation usually results in the formation of small amounts of a byproduct, p-formylbenzoic acid, which can be removed by hydrogenation. Recrystallization of the TPA provides polyester-grade product with a purity of 99.9 percent.

DMT can be made from crude TPA, or directly from p-xylene. If DMT is made from TPA, a series of steps involving oxidation to produce TPA (as above), esterification, distillation, and
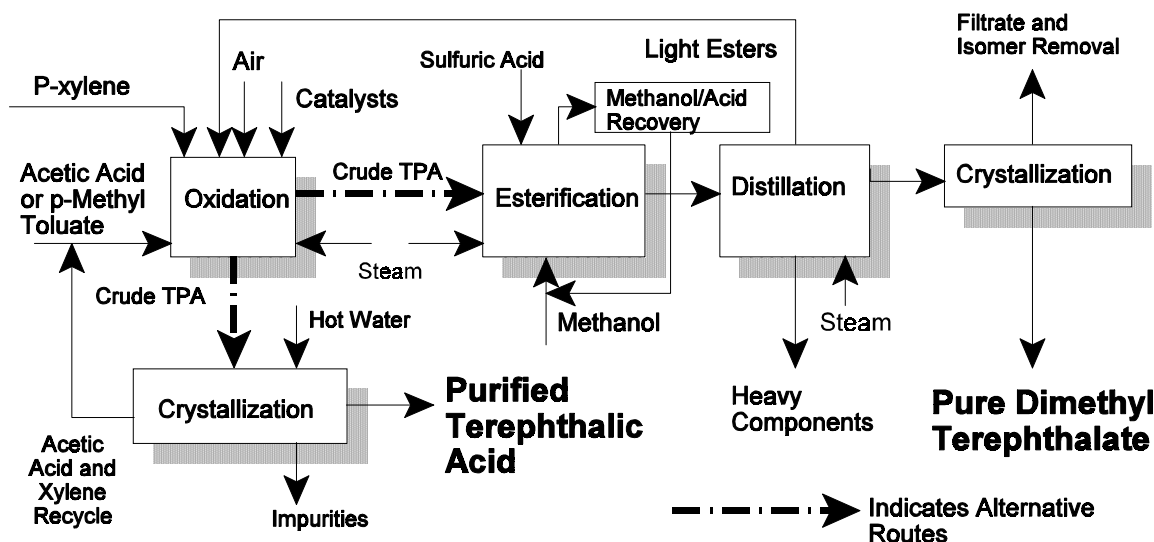
Figure 4-10. Manufacture of Terephthalic Acid and Dimethyl Terephthalate
(Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Terephthalic Acid and Dimethyl Terephthalate Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 1,779 Btu/lb* *Feedstock ΔHc: 18,843 Btu/lb*	*Largest source - fugitive emissions (xylenes, TPA, DMT)*	*Largest source - wastewater*	*Heavy residues, aldehydes, methanol, p-formylbenzoic acid*
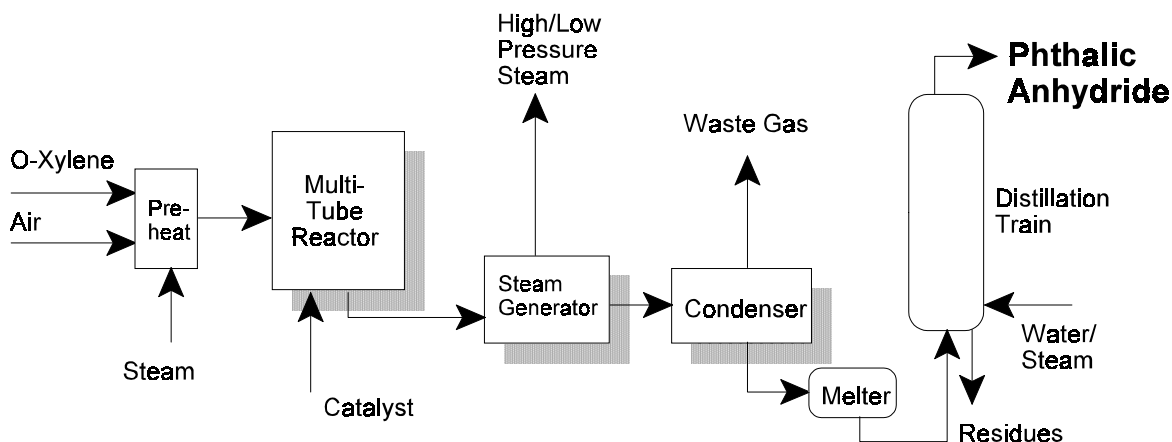
Figure 4-11. Manufacture of Phthalic Anhydride (Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Phthalic Anhydride Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Exporter: *Steam Export: 1,920 Btu/lb*	*Largest source - fugitive emissions (xylene)*	*Largest source - wastewater*	*Heavy residues, waste gases, spent catalyst*

crystallization are employed (see Figure 4-10). This processing method can produce both TPA and DMT if desired. During esterification, the crude TPA mixture from oxidation is esterified with methanol and produces a mixture of esters, usually in the presence of sulfuric acid catalyst. The ester mixture is distilled (often using a series of distillation towers) to remove heavy components and residues. Lighter esters are recycled. Crude DMT from distillation is sent to a crystallization section where DMT isomers and aromatic aldehyde byproducts are removed, and pure DMT is produced.

DMT can also be made directly from p-xylene and p-methyl toluate by oxidation over heavy metal catalysts, followed by esterification, in a process similar to that just described (Process Description: HP 1999).

Phthalic anhydride is not a "top-fifty" chemical, but is an important chemical intermediate used as a plasticizer and in resins manufacturing. Phthalic anhydride reacts with

some alcohols to form liquids called plasticizers, which, when mixed with plastics, give them a greater flexibility without affecting their strength.

Phthalic anhydride is the primary chemical made from o-xylene, normally by way of the von Heyden process (see Figure 4-11). In this process, the o-xylene is charged with air to a catalytic multi-tube reactor. An agitated molten salt removes the heat of reaction to maintain the proper temperature. The heat of reaction is used to generate process steam. Effluent from the reactor is condensed as a solid sublimate, then melted to produce liquid product. Effluent gases are vented to the atmosphere after water scrubbing or incineration. Further purification is carried out through distillation. The purified product can be stored in the molten state or flaked for bulk storage (Process Description: Chenier 1992, HP 1999).

4.1.9 Cyclohexane, Caprolactam, and Nylons

Both Nylon 6 and Nylon 6,6 Have Their Origin in Cyclohexane

Cyclohexane, which is derived by the hydrogenation of benzene over a nickel or platinum catalyst, is used to manufacture adipic acid and caprolactam. **Adipic acid** is the starting material for **Nylon 6,6**, one of the first synthetic polyamides (proteins) ever developed. Work on nylons originated with researchers at

Du Pont interested in finding a cheap replacement for silk in stockings. Commercial production of hexamethyleneadipamide (Nylon 6,6) began in 1940.

The name **caprolactam** is derived from the original chemical name for the six-carbon carboxylic acid, caproic acid. It is manufactured mostly from cyclohexane or phenol. All caprolactam is used to make Nylon 6 fibers, plastic resins, and film. Although not as predominant as Nylon 6,6, the use of Nylon 6 is growing rapidly, particularly in Japan.
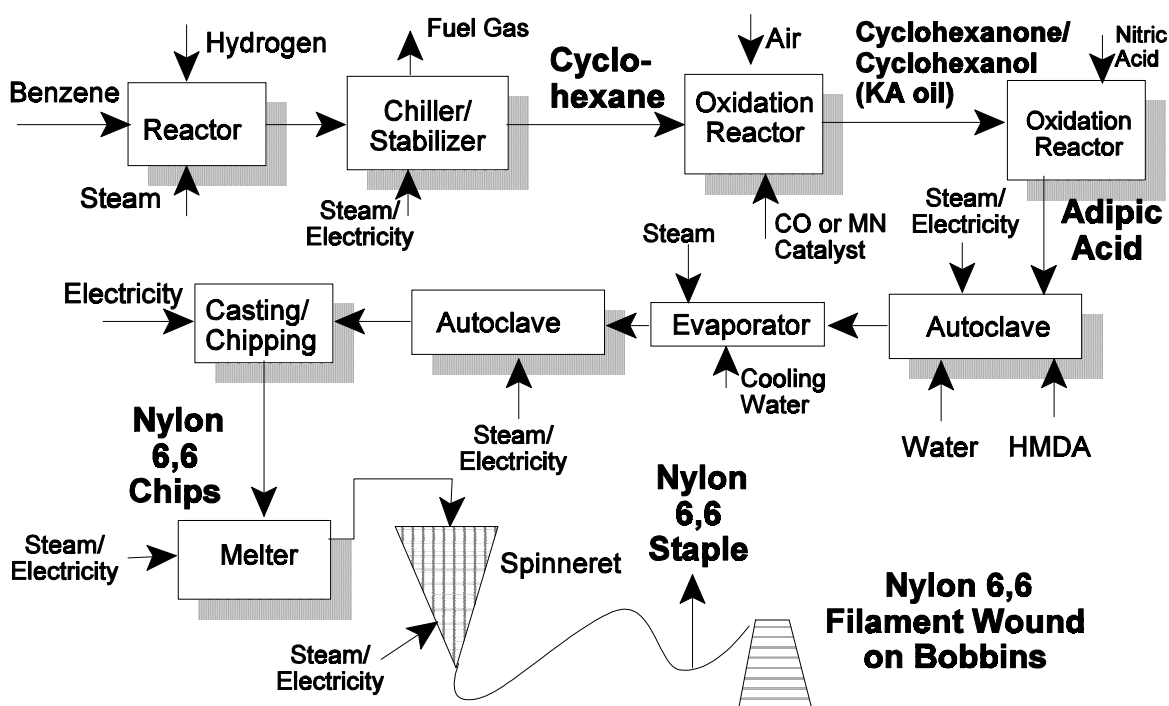

Figure 4-12. Nylon 6,6 Manufacture (EPA 1990, Chenier 1992, Brown 1996)

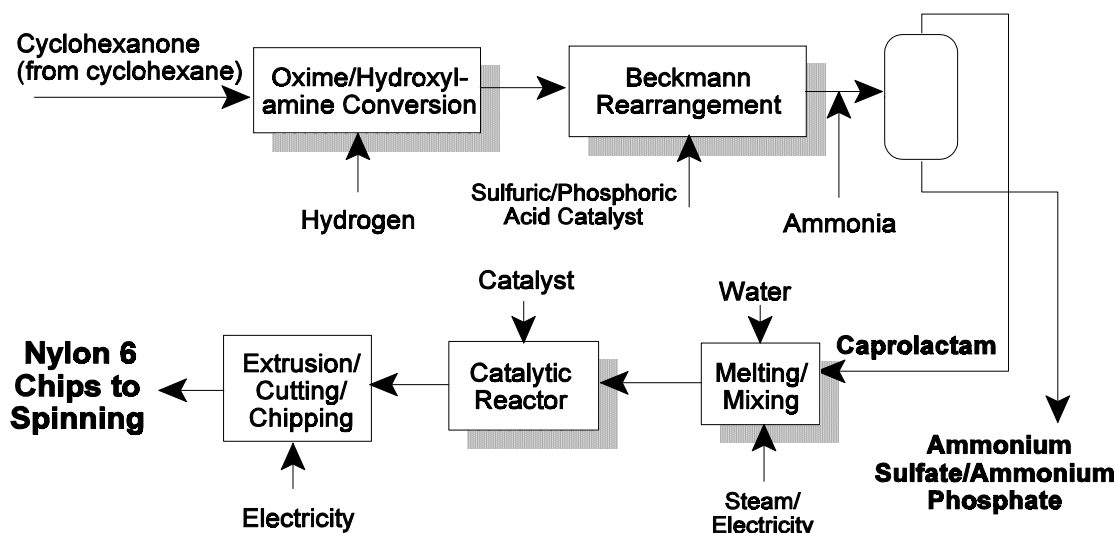| Key Energy and Environmental Facts - Nylon 6,6 Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Use: *Process: 17,166 Btu/lb* *Feedstock ΔHc: 23,080 Btu/lb*	*Largest source - fugitive emissions (volatilized monomers), oil vapors or mists*	*Largest source - wastewater*	*Fuel/vent gases*

Figure 4-13. Nylon 6 Manufacture (EPA 1990, Chenier 1992, Brown 1996, HP 1999)

Key Energy and Environmental Facts - Nylon 6 Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Use: *Process: 11,507 Btu/lb* *Feedstock ΔHc: 22,000 Btu/lb*	*Largest source - fugitive emissions (volatilized monomers), oil vapors or mists*	*Largest source - wastewater*	*Spent catalyst, ammonium sulfate, ammonium phosphate*

Adipic acid is made primarily by nitric acid oxidation of a cyclohexanone-cyclohexanol mixture called KA oil (ketone-alcohol) (see Figure 4-12).   Air oxidation of cyclohexane is first accomplished using a cobalt or manganese (II) naphthenate or acetate catalyst, which produces the KA oil mixture. The KA oil is then oxidized with 50 percent nitric acid with ammonium vanadate and copper present as catalysts. A new process has also been developed that use nitrous oxide oxidation of benzene to produce KA oil.

Nylon 6,6 is primarily made by the reaction of hexamethylene-diamine (HMDA) and adipic acid. The result is a salt, which is then washed in a methyl alcohol bath. Polymerization then takes place in a batch process under heat and pressure. A typical production process for producing Nylon 6,6, fiber from nylon polymer chips is shown in Figure 4-12. There are other possible routes for

production of Nylon 6,6 (e.g., the adipamide process), although the HMDA method is most commonly employed.

Caprolactam is made through a series of reactions in which cyclohexanone is converted into an oxime with hydroxylamine (see Figure 4-13). The oxime then undergoes the well-known acid-catalyzed reaction called the Beckmann rearrangement to produce caprolactam. Sulfuric or phosphoric acid compounds may be used as the catalyst, and after treatment with ammonia, a byproduct is created that can be sold as a fertilizer.

Nylon 6 is made directly from caprolactam by heating with a catalytic amount of water in a continuous polymerization process. It is then spun into fibers in a fashion similar to that for Nylon 6,6 (see Figure 4-12) (Process Description: ANL 1980, EPA 1990, Chenier 1992, Brown 1996, HP 1999).

4.2 Summary of Inputs/Outputs

The following summarizes the essential inputs and products, wastes, and byproducts of the chemicals and chemical products included in the BTX chain.

Benzene/Toluene/Xylene (BTX) from Naphtha

Inputs:	Outputs:
Naphtha or Pyrolysis Gasoline	Benzene/Toluene/Xylene Hydrogen
Ethylbenzene	Water
Solvent	Coke/Energy Export
Inert Gas	Purge/Flared Gases
Catalyst	Process Water
Water	Extraction Raffinate
Steam/Fuel	Spent Catalyst
Electricity	

Benzene from Toluene

Inputs:	Outputs:
Toluene	Benzene
Mixed Xylenes	Extraction Raffinate
Hydrogen	Hydrogen
Catalyst	Nonaromatic Byproducts
Steam/Fuel	Process Water
Electricity	

Ethylbenzene

Inputs:	Outputs:
Benzene	Ethylbenzene
Ethylene	Vent Gas
Polyethylbenzene	Bottom Residues
Catalyst	Water
Process Water	
Fuel/Steam	
Electricity	

Styrene

Inputs:	Outputs:
Ethylbenzene	Styrene
Benzene, Toluene	Off Gases
Catalyst	Steam
Inhibitors/Antioxidants	Condensate
Process Water	Tar Residues
Steam/Fuel	Wastewater
Electricity	

Polystyrene

Inputs:	Outputs:
Styrene	Polystyrene Pellets
Initiators	Purge Gases
Inhibitors	Process Water
Additives	Off-grade Polymer
Cooling Water	
Steam/Fuel	
Electricity	

Cumene

Inputs:	Outputs:
Benzene	Cumene
Propylene	Heavy Hydrocarbons
Catalyst	Light Gases
Process Water	Process Water
Steam/Fuel	
Electricity	

Phenol/Acetone

Inputs:	Outputs:
Cumene	Phenol
Air	Acetone
Acid Catalyst	α-Methylstyrene (AMS)
Solvent	Wastewater
Process Water	Spent Catalyst
Steam/Fuel	Organic Byproducts
Electricity	

Bisphenol A

Inputs:

Acetone
Phenol
Ion Exchange
  Resin
Process Water
Steam/Fuel
Electricity

Outputs:

Bisphenol A Flakes,
  Pellets, Pastilles, or Prills
Reaction-Produced Water
Tar
Heavy Components

Terephthalic Acid, Dimethyl Terephthalate

Inputs:

p-Xylene
Acetic Acid
p-Methyl Toluate
Sulfuric Acid
Methanol
Air
Catalyst
Process Water
Steam/Fuel
Electricity

Outputs:

Terephthalic Acid
Dimethyl Terephthalate
Heavy Components
Filtrate
Isomer Byproducts
Process Water
Acid Byproducts

Phthalic Anhydride

Inputs:

o-Xylene
Air
Catalyst
Process Water
Steam/Fuel
Electricity

Outputs:

Phthalic Anhydride
Heavy Components
High Pressure Steam
Low Pressure Steam
Spent Catalyst
Waste Gases
Process Water

Cyclohexane

Inputs:

Benzene
Hydrogen
Catalyst
Steam/Fuel
Electricity

Outputs:

Cyclohexane
Fuel Gas
Spent Catalyst

Adipic Acid

Inputs:

Cyclohexane
Air
Catalyst
Process Water

Outputs:

Adipic Acid
Spent Catalyst
Vent Gases
Wastewater

Caprolactam

Inputs:

Cyclohexane
Hydrogen
Acid Catalyst
Ammonia
Process Water
Steam/Fuel
Electricity

Outputs:

Caprolactam
Ammonium Sulfate
Ammonium Phosphate
Wastewater
Acid Waste

Nylon 6,6

Inputs:

Adipic Acid
HMDA
Process Water
Steam/Fuel
Electricity

Outputs:

Nylon 6,6 Filament or
  Staple
Process Water

Nylon 6

Inputs:

Benzene
Hydrogen
Catalyst
Steam/Fuel
Electricity

Outputs:

Cyclohexane
Fuel Gas
Spent Catalyst

4.3 Energy Requirements

Process Energy Requirements for the BTX Chain Are Relatively Low

The **process and feedstock energy** used for the production of benzene, toluene, xylene, and their derivatives are shown in Tables 4-3 through 4-15 (ANL 1980, EEA 1983, BIO 1988, Brown 1996, HP 1997d, HP 1999). Each table provides net processing energy, which is the energy used to provide heat and power for the process, in the form of fuels, electricity, or steam. Feedstock energy is comprised of two elements: (1) the net heat of combustion of the feedstock, and (2) the processing energy required to manufacture the feedstock. Each table provides the value of the heat of combustion for the feedstock chemical(s) at standard conditions (ΔHc).

The second component of feedstock energy, processing energy, is denoted as Feedstock Process Energy. This is the processing energy required to manufacture the feedstocks, beginning with the starting raw crude materials. For example, the Feedstock Process Energy

Table 4-3. Estimated Energy Use in BTX Manufacture - 1997			
Energy	**Specific Energy [f] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Chemical Industry Energy Use [g] (10^{12} Btu)**
Electricity[a]	62 - 99	81	2.4
Fuel Oil and LPG[b]	28 - 42	35	1.0
Natural Gas	718 - 1,090	904	226.4
Coal and Coke	93 - 142	117	3.4
Other[c]	93 - 142	117	3.4
NET PROCESS ENERGY	**994 - 1,515**	**1,255**	**36.6**
Electricity Losses	129	167	4.9
Energy Export	(127)	(230)	(6.7)
TOTAL PROCESS ENERGY	**996 - 1,388**	**1,192**	**34.8**
Heat of Feedstock (ΔHc) [d]	32,030	32,030	935.3
TOTAL PRIMARY ENERGY	**33,026 - 33,418**	**33,222**	**970.1**
Feedstock Process Energy[e]	390	390	11.4
TOTAL ENERGY EMBODIED IN BTX MFG	**33,416 - 33,808**	**33,612**	**981.5**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of naphtha, propane, and butanes (ANL 1980).
e   Energy for crude distillation to produce naphtha (EI 1997).
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including the IFP CCR Aromizing process and BP-UOP Cyclar process (HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values for benzene, toluene, and xylenes (29.2 billion lbs) (CMA 1998). This number captures the 80 percent of BTX produced from refinery stocks.

for propylene oxide includes the energy required to process ethylbenzene, propylene, ethylene, benzene, and raw crude.

Total net energy inputs include processing energy for the final product, plus the heat of combustion of the feedstocks, minus any steam or fuel generated by the process. The losses incurred during the generation and transmission of electricity (regardless of whether purchased or produced on-site) are shown as "electricity losses." These are added to total net energy to obtain Total Primary Energy, which is the total primary energy consumption associated with production of the individual chemical. Total Embodied Energy includes the Feedstock Process Energy, and represents all the energy consumption that is embodied in the manufacture of the product beginning with raw crude.

For every category, energy use for process heat is distributed according to the various fuel types used throughout the industry. Fuel distribution for 1997 was as follows: fuel oil and LPG - 3 percent, natural gas - 77 percent, coal and coke -

Table 4-4. Estimated Energy Use in Benzene Manufacture - 1997		
Energy	Average Specific [f] Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	64	0.2
Energy for Steam/Process Heat [f]		
Fuel Oil and LPG[b]	32	0.1
Natural Gas	811	2.4
Coal and Coke	105	0.3
Other[c]	105	0.3
NET PROCESS ENERGY	1,117	3.4
Electricity Losses	133	0.4
Energy Export	0	0.0
TOTAL PROCESS ENERGY	1,250	3.8
Heat of Feedstock (ΔHc) [d]	23,330	70.0
TOTAL PRIMARY ENERGY	24,580	73.7
Feedstock Process Energy[e]	433	1.3
TOTAL ENERGY EMBODIED IN BENZENE MFG	25,013	75.0

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of toluene (Perry 1984).
e   Energy used to manufacture toluene, including all steps from raw crude feed (see Table 4-3).
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including the ABB-Lummus Global process (HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values for benzene (3 billion lbs) (CMA 1998). This number captures the 20 percent of benzene produced directly from toluene.

10 percent, and other - 10 percent (CMA 1998). The "other" category includes any other fuel source (e.g., byproduct fuel gases).

With few exceptions, little energy is consumed to provide heat and power during the production of **BTX and derivatives**–usually less than 1,500 Btu/lb. The exceptions are for the production of styrene, phenol and acetone (which are co-produced), and caprolactam.

Energy requirements for **BTX** shown in Table 4-3 are based on production from naphtha (a

petroleum fraction) and mixtures of propane and butane; the feedstock energy data in Table 4-4 is based on production of **benzene** directly from toluene. Total process energy requirements are similar for both products. Most current production, however, is from refinery stocks, which are cheaper and more readily available. Feedstock energy requirements for BTX produced from refinery stocks are much higher, however, due to the highly combustible fuel content of the feed.

Table 4-5. Estimated Energy Use in Ethylbenzene Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	42	42	0.6
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	38 - 44	41	0.6
Natural Gas	971 - 1127	1,049	14.6
Coal and Coke	126 - 146	136	1.9
Other[c]	126 - 146	146	1.9
NET PROCESS ENERGY	**1303 - 1505**	**1,404**	**19.5**
Electricity Losses	87	87	1.2
Energy Export	(127) - (333)	(230)	(3.2)
TOTAL PROCESS ENERGY	**1,263 - 1259**	**1,261**	**17.5**
Heat of Feedstock (ΔHc) [d]	19,044	19,044	264.7
TOTAL PRIMARY ENERGY	**20,307 - 20,303**	**20,305**	**282.2**
Feedstock Process Energy[e]	2,978	2,978	41.4
TOTAL ENERGY EMBODIED IN ETHYLBENZENE MFG	**23,285 - 23,281**	**22,283**	**323.6**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of ethylene and benzene (Perry 1984). Stoichiometric ratios: 0.266 lbs ethylene and 0.739 lbs benzene for every lb of ethylbenzene (HP 1999).
e   Energy used to manufacture ethylene and benzene, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including CDTECH and Raytheon processes (HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (13.9 billion lbs) (CMA 1998).

Process and feedstock energy requirements for **ethylbenzene** are relatively low, in part because the process produces export steam (see Table 4-5). However, as shown in Table 4-6, energy used in the manufacture of its major derivative, **styrene**, is the highest in the BTX chain (about 14,000 Btu/lb). The majority of the energy is used in the form of steam for dehydrogenation, preheating, and separation processes. Although the amount of styrene produced is about one-fourth that of BTX, the annual energy consumption associated with its production is nearly three times that of BTX (110 trillion Btu compared with 39 trillion Btus for BTX).

Processing energy requirements for **polystyrene** are moderate, about 1,400 Btu/lb. A good portion of the energy is embodied in hot oil that is used to transfer heat. Small amounts of fuel and steam are used to supplement the hot oil. Electricity is used primarily for extruding, blending, and finishing of the polymer product.

Table 4-6. Estimated Energy Use in Styrene Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	0	0	0.0
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	431 - 582	507	3.3
Natural Gas	11,065 - 14,947	13,006	84.5
Coal and Coke	1,437 - 1,941	1,689	11.0
Other[c]	1,437 - 1,,941	1,689	11.0
NET PROCESS ENERGY	**14370 - 19,412**	**16,891**	**110.0**
Electricity Losses	0	0	0.0
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**14,370 - 19,412**	**16,891**	**109.8**
Heat of Feedstock (ΔHc) [d]	20,058 - 20,058	20,058	130.4
TOTAL PRIMARY ENERGY	**34,428 - 39,470**	**36,949**	**240.2**
Feedstock Process Energy[e]	4,501	4,501	29.3
TOTAL ENERGY EMBODIED IN STYRENE MFG	**38,929 - 43,971**	**41,450**	**269.5**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of ethylbenzene (Perry 1984). Stoichiometric ratios: 1.085 lbs ethylbenzene for every lb of styrene (Brown 1996).
e   Energy used to manufacture ethylbenzene, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (EEA 1983, Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (6.5 billion lbs) (CMA 1998). Does not include styrene co-produced with propylene oxide.

Table 4-7. Estimated Energy Use in Polystyrene Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	84 -195	140	0.9
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	40 - 88	64	0.4
Natural Gas	1,015 - 2,256	1,635	10.5
Coal and Coke	132 - 293	212	1.4
Other[c]	132 - 293	212	1.4
NET PROCESS ENERGY	1,402 - 3,125	2,264	14.5
Electricity Losses	174 - 405	290	1.9
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	1,576 - 3,530	2,553	16.3
Heat of Feedstock (ΔHc) [d]	20,058 - 20,058	20,058	128.4
TOTAL PRIMARY ENERGY	21,634 - 23,588	22,611	144.7
Feedstock Process Energy[e]	21,392	21,392	136.9
TOTAL ENERGY EMBODIED IN POLYSTYRENE MFG	43,026 - 44,980	44,003	281.6

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of styrene (Perry 1984). Stoichiometric ratios: 1.0 lbs styrene for every lb of polystyrene (Brown 1996).
e   Energy used to manufacture styrene, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (EEA 1983, Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (6.4 billion lbs) (CMA 1998).

The process for manufacturing **cumene** generates excess steam (about 400 Btu/lb of product). The annual energy contribution from this process is about 2.3 trillion Btu beyond the energy needed for manufacturing cumene (see Table 4-8). Feedstock requirements for cumene are based on stoichiometric quantities of benzene and propylene.

Production of the major derivatives of cumene, **phenol and acetone**, is very energy-intensive, and the cumene production unit is usually located in close proximity to phenol/acetone production facilities to make use of the excess steam. Most of the energy is consumed in distillation columns during the separation of acetone and phenol (see Table 4-9). Electricity is used primarily for compression and concentration of products.

Table 4-8. Estimated Energy Use in Cumene Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	5 - 17	11	0.1
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	17 - 24	21	0.1
Natural Gas	444 - 610	527	3.1
Coal and Coke	58 - 79	68	0.4
Other[c]	58 - 79	68	0.4
NET PROCESS ENERGY	582 - 809	696	4.0
Electricity Losses	10 - 35	23	0.1
Energy Export	(982) - (1243)	(1,113)	(6.5)
TOTAL PROCESS ENERGY	(390) - (399)	(394)	(2.3)
Heat of Feedstock (ΔHc) [d]	19,032	19,032	110.4
TOTAL PRIMARY ENERGY	18,642 - 18,633	18,638	108.1
Feedstock Process Energy[e]	1,643	1,643	9.5
TOTAL ENERGY EMBODIED IN CUMENE MFG	20,285 - 20,276	20,281	117.6

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of benzene and propylene (Perry 1984). Stoichiometric ratios: 0.651 lbs benzene and 0.351 lbs propylene for every lb of cumene (HP 1999).
e   Energy used to manufacture benzene and propylene including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including those licensed by CDTECH, Raytheon Engineers & Constructors, and UOP (HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (5.8 billion lbs) (CMA 1998).

Feedstock requirements for phenol/acetone production are also high. Approximately 1.3 tons of cumene are required for every ton of phenol/acetone product.

Process energy required for **terephthalic acid (TPA)**, another important derivative of cumene, can vary considerably depending on whether it is made directly from p-xylene and methanol, or from DMT (dimethyl terephthalate) (see Table 4-10). Electricity requirements can be significant, reaching nearly 50 percent of total energy use, primarily because of the filtering

and purification operations needed to produce a polymer-grade product, i.e., a product of 99.5 percent and greater purity). Feedstock requirements for TPA are based on production from p-xylene and methanol.

When electricity losses are excluded, the processes used for production of **phthalic anhydride** are net energy producers. The estimates published for utilities for these processes vary from a net energy export of about 958 Btu/lb to over 5,000 Btu/lb, depending on the feedstock used. Higher

Table 4-9. Estimated Energy Use in Phenol/Acetone Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	300 484	392	2.9
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	172 - 276	224	1.6
Natural Gas	4404 - 7081	5,743	41.9
Coal and Coke	572 - 920	746	5.4
Other[c]	572 - 920	746	5.4
NET PROCESS ENERGY	6020 - 9680	7,850	57.3
Electricity Losses	623 - 1005	814	5.9
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	6643 - 10685	8,664	63.3
Heat of Feedstock (ΔHc) [d]	15,112	15,112	110.3
TOTAL PRIMARY ENERGY	21,755 - 25,797	23,776	173.6
Feedstock Process Energy[e]	2,188	2,188	1.6
TOTAL ENERGY EMBODIED IN PHENOL/ACETONE MFG	23,943 - 27,985	25,964	175.2

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of cumene (Perry 1984). Stoichiometric ratios: 0.81 lbs cumene for every lb of phenol/acetone product (HP 1999).
e   Energy used to manufacture cumene, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (EEA 1983, Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (7.3 billion lbs) (CMA 1998).

amounts of electricity are derived from naphthalene feedstock, and lower amounts from o-xylene. Electricity requirements are estimated at about 1400 Btu/lb (ANL 1979, CEH 1999).

Process energy consumed for **cyclohexane** manufacture is low, primarily because the process is relatively uncomplicated and is a large net exporter of steam. Net process energy requirements after steam export, and including electricity losses, are only a little over 600 Btu/lb (see Table 4-11). However, the major derivatives of cyclohexane are energy-intensive, and account for a considerable amount of energy consumed.

Cyclohexane is used to make **adipic acid**, an intermediate in the production of Nylon 6,6. As seen in Table 4-12, the average energy requirements for adipic acid production are about 27 times greater per pound than those of cyclohexane. Annual energy consumption attributed to adipic acid production is about 35 trillion Btu without losses, and over 42 trillion Btu when losses are considered.

Table 4-10. Estimated Energy Use in Terephthalic Acid Manufacture - 1997

Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	620	620	6.2
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	22 - 48	35	0.4
Natural Gas	557 - 1227	892	8.9
Coal and Coke	72 - 159	116	1.2
Other[c]	72 - 159	116	1.2
NET PROCESS ENERGY	1,343 - 2,214	1,779	17.8
Electricity Losses	1,287	1,287	12.9
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	2,630 - 3,501	3,066	30.7
Heat of Feedstock (ΔHc) [d]	15,369 - 22,316	18,843	188.4
TOTAL PRIMARY ENERGY	17,999 - 25,817	21,908	219.1
Feedstock Process Energy[e]	903	903	9.0
TOTAL ENERGY EMBODIED IN TEREPHTHALIC ACID MFG	18,902 - 26,720	22,811	228.1

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of p-xylene and methanol (ANL 1980, Perry 1984). Stoichiometric ratios: 0.715 lbs p-xylene and 0.06 lbs methanol for every lb of terephthalic acid (HP 1999).
e   Energy used to manufacture p-xylene and methanol, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including those licensed by Degussa-Huls AG and others (EEA 1983, HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (10 billion lbs) (CMA 1998).

Another important derivative of cyclohexane is **caprolactam**, an intermediate in the production of Nylon 6. Average process energy requirements for caprolactam are also relatively high, about 13,000 Btu/lb when losses are considered, about 21 times greater than the process energy required for cyclohexane manufacture. Annual process energy consumed for caprolactam manufacture is over 22 trillion Btu (without considering losses).

Most of the energy consumed for both adipic acid and caprolactam manufacture is in the form of fuels combusted to produce steam for process heat. The thermal efficiencies of steam systems are variable, and can range from as low as 55 percent to as high as 85 percent, depending on heat losses from the stack and other areas. This variability creates a degree of uncertainty in data on energy consumption. Electricity is used for compression and pumping, but generally accounts for less than 10 percent of energy use.

Table 4-11. Estimated Energy Use in Cyclohexane Manufacture - 1997		
Energy	Average Specific [f] Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	150	0.3
Energy for Steam/Process Heat [f]		
Fuel Oil and LPG[b]	48	0.1
Natural Gas	1,227	2.7
Coal and Coke	159	0.4
Other[c]	159	0.4
NET PROCESS ENERGY	1,743	3.8
Electricity Losses	311	0.7
Energy Export	(1,416)	(3.1)
TOTAL PROCESS ENERGY	638	1.4
Heat of Feedstock (ΔHc) [d]	21,224	46.7
TOTAL PRIMARY ENERGY	21,862	48.1
Feedstock Process Energy[e]	1,680	3.7
TOTAL ENERGY EMBODIED IN CYCLOHEXANE MFG	23,542	51.8

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of benzene and hydrogen (ANL 1980, Perry 1984). Stoichiometric ratios: 0.93 lbs benzene and 0.075 lbs hydrogen for every lb of cyclohexane (ANL 1980).
e   Energy used to manufacture benzene and hydrogen, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (ANL 1980, Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (2.2 billion lbs) (CMA 1998).

Production of **Nylon 6,6** requires large quantities of steam for polymerization as well as melting of the polymer product (see Table 4-14). Fuel used for steam production can be as high as 17,000 Btu/lb. Large quantities of electricity are also used in the casting, chipping, melting, spinning, drawing, and winding of finished nylon fibers (over 3,000 Btu/lb).   On average, electricity accounts for about 20 percent of total energy consumed. The amount of energy consumed to produce Nylon 6,6 is significant–about 14 trillion Btu per year.

Nylon 6 production is also energy-intensive in terms of steam use. In the continuous polymerization process, most of the steam is used for melting, for carrying out the polymerization reaction, and for concentrating unreacted caprolactam to recycle it back into the process. Considerable amounts of steam are also expended for fiber processing (e.g., melting, drying). Electricity is used throughout the process for pumping, extraction, extruding, melting, spinning, drawing, and winding, and accounts for about 13 percent of total energy use. The greater share of electricity is used in production of the finished nylon fibers.

Table 4-12. Estimated Energy Use in Adipic Acid Manufacture - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	1,100 - 2,400	1,750	3.5
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	297 - 648	473	1.0
Natural Gas	7,623 - 16,632	12,128	24.3
Coal and Coke	990 - 2,160	1,575	3.2
Other[c]	990 - 2,160	1,575	3.2
NET PROCESS ENERGY	**11,000 - 24,000**	**17,500**	**35.0**
Electricity Losses	2,284 - 4,984	3,634	7.3
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**13,284 - 23,984**	**21,134**	**42.3**
Heat of Feedstock (ΔHc) [d]	14,414	14,414	28.8
TOTAL PRIMARY ENERGY	**27,698 - 43,398**	**35,548**	**71.1**
Feedstock Process Energy[e]	1,445	1,445	2.9
TOTAL ENERGY EMBODIED IN ADIPIC ACID MFG	**29,143 - 44,843**	**36,993**	**74.0**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of cyclohexane (Perry 1984). Stoichiometric ratios: 0.72 lbs cyclohexane for every lb of adipic acid (ANL 1980).
e   Energy used to manufacture cyclohexane, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (ANL 1980, BIO 1988).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (2.0 billion lbs) (CMA 1998).

Table 4-13. Estimated Energy Use in Caprolactam Manufacture - 1997			
Energy	**Specific Energy [f] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Chemical Industry Energy Use [g] (10^{12} Btu)**
Electricity[a]	624 - 1,239	932	1.6
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	249 - 487	368	0.6
Natural Gas	6,380 - 12,489	9,435	16.0
Coal and Coke	829 - 1,622	1,225	2.1
Other[c]	829 - 1,622	1,225	2.1
NET PROCESS ENERGY	**8,910 - 17,459**	**13,185**	**22.4**
Electricity Losses	1,296 - 2,573	1,934	3.3
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**10,206 - 20,032**	**15,119**	**25.7**
Heat of Feedstock (ΔHc) [d]	21,027	21,027	35.8
TOTAL PRIMARY ENERGY	**31,233 - 41,059**	**36,146**	**61.5**
Feedstock Process Energy[e]	2,107	2,107	3.6
TOTAL ENERGY EMBODIED IN CAPROLACTAM MFG	**35,448 - 43,166**	**38,253**	**65.1**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of cyclohexane (Perry 1984). Stoichiometric ratios: 1.05 lbs cyclohexane for every lb of caprolactam (ANL 1980).
e   Energy used to manufacture cyclohexane, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including those licensed by SNIA BPD, Sp.A (BIO 1988, HP 1999).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (1.7 billion lbs) (CMA 1998).

Table 4-12. Estimated Energy Use in Manufacture of Nylon 6,6 - 1997			
Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	2,606 - 3,914	3,260	2.6
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	334 - 501	417	0.3
Natural Gas	8,560 - 12,855	10,708	8.6
Coal and Coke	1,112 - 1,670	1,391	1.1
Other[c]	1,112 - 1,670	1,391	1.1
NET PROCESS ENERGY	13,723 - 20,609	17,166	13.7
Electricity Losses	5,411 - 8,127	6,769	5.4
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	19,134 - 28,736	24	19.2
Heat of Feedstock (ΔHc) [d]	23,080	23,080	18.5
TOTAL PRIMARY ENERGY	42,214 - 51,816	47,015	37.6
Feedstock Process Energy[e]	15,928	15,928	12.7
TOTAL ENERGY EMBODIED IN NYLON 6,6 MFG	58,142 - 67,744	62,943	50.3

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of adipic acid and HMDA (Perry 1984). Stoichiometric ratios: 0.63 lbs adipic acid and 0.53 lbs HMDA for every lb of Nylon 6,6 (ANL 1980, Brown 1996).
e   Energy used to manufacture adipic acid and HMDA, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (ANL 1980, Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (0.8 billion lbs) (CMA 1998). Assumes 2/3 of nylon market is Nylon 6,6.

Table 4-15. Estimated Energy Use in Manufacture of Nylon 6 - 1997		
Energy	**Average Specific [f] Energy (Btu/lb)**	**Chemical Industry Energy Use [g] (10^{12} Btu)**
Electricity[a]	1,520	0.6
Energy for Steam/Process Heat [f]		
Fuel Oil and LPG[b]	300	0.1
Natural Gas	7,690	3.1
Coal and Coke	999	0.4
Other[c]	999	0.4
NET PROCESS ENERGY	**11,507**	**4.6**
Electricity Losses	3,156	1.3
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**14,663**	**5.9**
Heat of Feedstock (ΔHc) [d]	22,000	8.8
TOTAL PRIMARY ENERGY	**36,663**	**14.7**
Feedstock Process Energy[e]	16,821	6.7
TOTAL ENERGY EMBODIED IN NYLON 6 MFG	**53,484**	**21.4**

a   Does not includes losses incurred during the generation and transmission of electricity.
b   LPG includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed.
d   Feedstock energy based on heat of combustion of caprolactam (estimated). Stoichiometric ratios: 1.1 lbs caprolactam for every lb of Nylon 6 (Brown 1996).
e   Energy used to manufacture caprolactam, including all steps beginning with raw crude.
f   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (Brown 1996).
g   Calculated by multiplying average energy use (Btu/lb) by1997 production values (0.4 billion lbs) (CMA 1998). Assumes 1/3 of nylon market is Nylon 6.

4.4 Air Emissions

Fugitive Emissions Are the Primary Source of Air Contaminants in the BTX Chain

The primary sources of emissions in the BTX chain are fugitive and point air source emissions from volatile compounds emitted from equipment and process operations. Fugitive emissions of volatile compounds arise from leaks in valves, pumps, tanks, flanges, and similar sources. While individual leaks may be minor, the combined fugitive emissions from various sources can be substantial in amount.

Benzene is considered a human carcinogen and is highly toxic and flammable. It is among the top twenty toxic chemicals released every year, primarily from point air and fugitive emission sources. **Toluene, xylene, cumene, styrene**, and **phthalic anhydride** are also toxic chemicals that are released by fugitive and point air sources during their manufacture and use in chemical processing. Styrene is also a suspected human carcinogen.   Emissions of these compounds are reported annually in the Toxic Release Inventory (TRI) (e.g., EPA 1993a, 1994b, 1998).

Air releases of **benzene** from the entire organic chemical sector (SIC 286) that were reported to the TRI were 1.4 million pounds in 1995. Air releases of **toluene (**a non-carcinogenic toxin) from the organic chemicals sector that were reported to the TRI were about 2.2 million pounds in 1995, although many of these releases originated from the use of toluene as a solvent, rather than in chemical reactions. Releases of p-xylene were also significant in 1995–about 1.5 million pounds (EPA 1998).

Volatile emissions from the production of **polystyrene** include styrene, ethylbenzene, additives, and small amounts of other volatile organic compounds. Table 4-16 lists estimated emission factors for volatile compounds emitted during polystrene production by the continuous bulk polymerization process (EPA 1991b). The major vent is the devolatilizer condenser, with emissions consisting of unreacted styrene, which is flashed from the polymer in a vacuum but becomes extremely dilute through air leakage. The stream is exhausted through a vacuum system and an oil demister to remove the organic mist before being vented to the atmosphere. The extruder quench vent is a large source of emissions, consisting primarily of styrene in water vapor. This stream is usually vented through a forced draft hood and then passed through a mist separator or electrostatic precipitator before passing to the atmosphere.

Emissions from **polystyrene plants** vary considerably, depending on the type of vacuum system employed. Plants using steam ejectors typically produce VOC emissions at an elevated rate. Condenser operating parameters also have a substantial impact on emissions, and these vary greatly between plants. Most polystyrene plants do not use VOC control devices other than condensers (EPA 1991b).

Combustion of fuels in boilers to produce steam and in process heaters or furnaces also produce criteria air pollutants that are regulated under the Clean Air Act. The burning of cleaner fuels such as natural gas in these heating units creates relatively low emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons. Present-day emission factors for process heaters and boilers are discussed in Section 7, Supporting Processes.

4.5 Effluents

Liquid Wastes Are Primarily Process Wash Water

Effluents emitted during the production of BTX and its derivatives consist primarily of wash waters from crystallization operations, process water from distillation towers, and cooling water. Much of this process water is recycled for reuse. Wash waters containing solvents are usually sent to solvent recovery systems to recover water and control volatile solvent emissions. Wastewater containing hazardous or toxic components is often subjected to stripping to separate contaminants so water can be reused.

Allowable limits for toxic or hazardous compounds contained in these wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, Part 414, which was promulgated in 1974 and revised several times since. The chemicals in the BTX chain are covered under Subparts C, D, F, and G in Part 414 of the CFR. The limitations for BTX chemicals are summarized together in Section 7, Supporting Processes, of this present document, where there is a discussion of general water treatment processes. Specific limitations are given for benzene, ethylbenzene, and toluene, and for their chlorinated derivatives, as shown in Table 4-17.

Table 4-16. Air Emission Factors for Continuous Processing of Polystyrene (Grams VOC/kilogram product)		
Type of Fiber	**Nonmethane Volatile Organics**	
	Uncontrolled	**Controlled**
Styrene monomer storage	0.08	
Additives General Purpose High Impact	0.002 0.001	
Ethylbenzene Storage	0.001	
Dissolvers	0.008	0.04[d]
Devolatilizer Condenser Vent	0.05[a] 2.96[b]	
Styrene Recovery Unit Condenser Vent	0.05[a] 0.13[b]	
Extruder Quench Vent	0.01[a] 0.13[b,c]	
Pellet Storage	negligible	
General Purpose Storage	0.008	
High Impact Storage	0.007	
TOTAL PLANT	0.21[a] 3.34[b]	

Source: EPA 1991b.

a   For plants using vacuum pumps.
b   For plants using steam injector jets.
c   Plant uses an organic scrubber to reduce emissions, and nonsoluble organics are burned as fuel. This factor may vary significantly depending on overall process.
d   Condenser is used downstream of primary process condensers; includes emissions from dissolvers; plant uses vacuum pumps.

Table 4-17. Effluent Pretreatment Standards		
Effluent	**Maximum for any 1 day (micrograms/liter)**	**Maximum for Monthly Average (micrograms/liter)**
Benzene	134	57
Ethylbenzene	380	142
Toluene	74	28
Chlorobenzene	380	142
1,2,4-Trichlorobenzene	794	196
Hexachlorobenzene	794	196
1,2-Dichlorobenzene	794	196
1,3-Dichlorobenzene	380	142
1,4-Dichlorobenzene	380	142
Nitrobenzene	6,402	2,237
2-Nitrophenol	231	65
4-Nitrophenol	576	162

Source: 40 CFR Chapter 1, Part 414, *Organic Chemicals, Plastics and Synthetic Fibers*

4.6 Wastes, Residuals, and Byproducts

Hazardous Wastes Are Associated with Production of BTX and Derivatives

The EPA classifies a number of the wastes associated with the production of BTX and its derivatives as hazardous under Title 40 Code of Federal Regulations (CFR), Part 261, Section 32 (see Table 4-18). Some of these wastes are produced during the manufacture of these chemicals, and some are produced during their use as solvents. Toluene, benzene, xylene, phthalic anhydride, phenol, and acetone (as well as chlorinated derivatives of these compounds) are all hazardous constituents and any waste stream containing these compounds must be treated as a hazardous waste.

Some of the hazardous wastes listed in Table 4-18 are not the products of specific chemical

processes discussed in this section, but are products of the BTX chain. These include dinitrotoluene, toluenediamine, toluene diisocyanate, and others. While these are relatively minor products, they contribute significantly to the waste management burden associated with BTX derivatives. Further, the chlorinated BTX derivatives (chlorinated benzenes, phenols) are not included in this table.

There are many options available for the management of hazardous wastes, ranging from incineration, which destroys the hazardous components, to various treatment technologies that convert hazardous to non-hazardous components. For information on specific treatment processes for hazardous wastes, refer to one of the many sources published on this topic.

Table 4-18. Hazardous Wastes from Production and Use of BTX and Derivatives

Waste Number	Description	Hazardous Constituents
F003	Spent non-halogenated solvents, including xylene and acetone. Includes all spent solvent mixtures/blends containing, before use, one or more of the aforementioned spent non-halogenated solvents; a spent solvent mixture/blend containing a total of 10 percent or more (by volume) of one of the solvents; and still bottoms from the recovery of these spent solvents and solvent mixtures.	Xylene, acetone
F005	Spent non-halogenated solvents including toluene and benzene. Includes all solvent mixtures/blends containing a total of 10 percent or more (by volume) of one or more of the aforementioned spent solvents; and still bottoms from the recovery of these spent solvents and solvent mixtures.	Toluene, benzene
K022	Distillation bottom tars from the production of phenol/acetone from cumene	Phenol, tars (polycyclic aromatic hydrocarbons)
K023	Distillation light ends from the production of phthalic anhydride from naphthalene	Phthalic anhydride, maleic anhydride
K024	Distillation bottoms from the production of phthalic anhydride from naphthalene	Phthalic anhydride, 1-4, naphthoquinone
K025	Distillation bottoms from the production of nitrobenzene from benzene	Meta-dinitrobenzene, 2,4-dinitrotoluene
K093	Distillation light ends from the production of phthalic anhydride from o-xylene	Phthalic anhydride, maleic anhydride
K094	Distillation bottoms from the production of phthalic anhydride from o-xylene	Phthalic anhydride
K111	Product washwaters from the production of dinitro-toluene via nitration of toluene	2,4-dinitrotoluene
K112	Reaction by-product water from the drying column in the production of toluenediamine via hydrogenation of dinitro-toluene	2,4-Toluenediamine, o-toluidine, p-toluidine, aniline
K113	Condensed liquid light ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene	2,4-Toluenediamine, o-toluidine, p-toluidine, aniline
K114	Vicinals from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene	2,4-Toluenediamine, o-toluidine, p-toluidine, aniline
K115	Heavy ends from the purification of toluenediamine in the production of toluenediamine via hydrogenation of dinitrotoluene	2,4-Toluenediamine
K116	Organic condensate from the solvent recovery column in the production of toluene diisocyanate via phosgenation of toluenediamine	Carbon tetrachloride, tetrachloroethylene, chloroform, phosgene

Source: BNA 1995.