3

The Propylene Chain

3.1 Overview of the Propylene Chain

Propylene Is a Building Block for Polymers, Fibers, and Solvents

Propylene ranks sixth on the list of the top 50 chemicals produced in the United States, with a production of about 28.7 billion pounds in 1997. It is a feedstock for many important chemical products, and is used to make such widely available plastics and fibers as polypropylene and acrylic (see Figure 3-1). Propylene is co-produced as a prime product with ethylene in steam cracking (see Section 2, The Ethylene Chain) and as a minor co-product in refinery operations.

About a third of the propylene produced is used in the manufacture of **polypropylene (PP)**, a thermoplastic that is used to manufacture a myriad of consumer products (e.g., tableware, mixing bowls, washing machine parts, outdoor furniture, automotive components, building components, food packaging, film, and fibers for woven tape, ropes, and twine). About 13 billion pounds of polypropylene were produced in 1997.

U.S. Production of Propylene and Its Major Derivatives (1997)

Propylene	(28.7 billion lbs)
Polypropylene	(13.3 billion lbs)
Propylene Oxide	(3.9 billion lbs)
Propylene Glycol	(1.1 billion lbs)
Acrylonitrile	(3.3 billion lbs)
Acrylic Fibers	(0.44 billion lbs)
ABS Resins	(1.4 billion lbs)

Sources: CMA 1998, SPI 1998.

Propylene oxide is another important propylene derivative, and ranked thirty-fourth in U.S. chemicals production in 1997. About 25 percent of propylene oxide is used to make **propylene glycol**, which is used in the production of suntan lotions, pharmaceuticals, cosmetics, and deicing fluids. U.S. production of propylene glycol was about 1.1 billion pounds in 1997.

A small percentage of propylene (about 13 percent) is used to make **acrylonitrile**, a feedstock for the production of various polymers, including **acrylic fibers and ABS (acrylonitrile-butadiene-styrene) resins**. About 60 percent of the 3.3 billion pounds of acrylonitrile produced

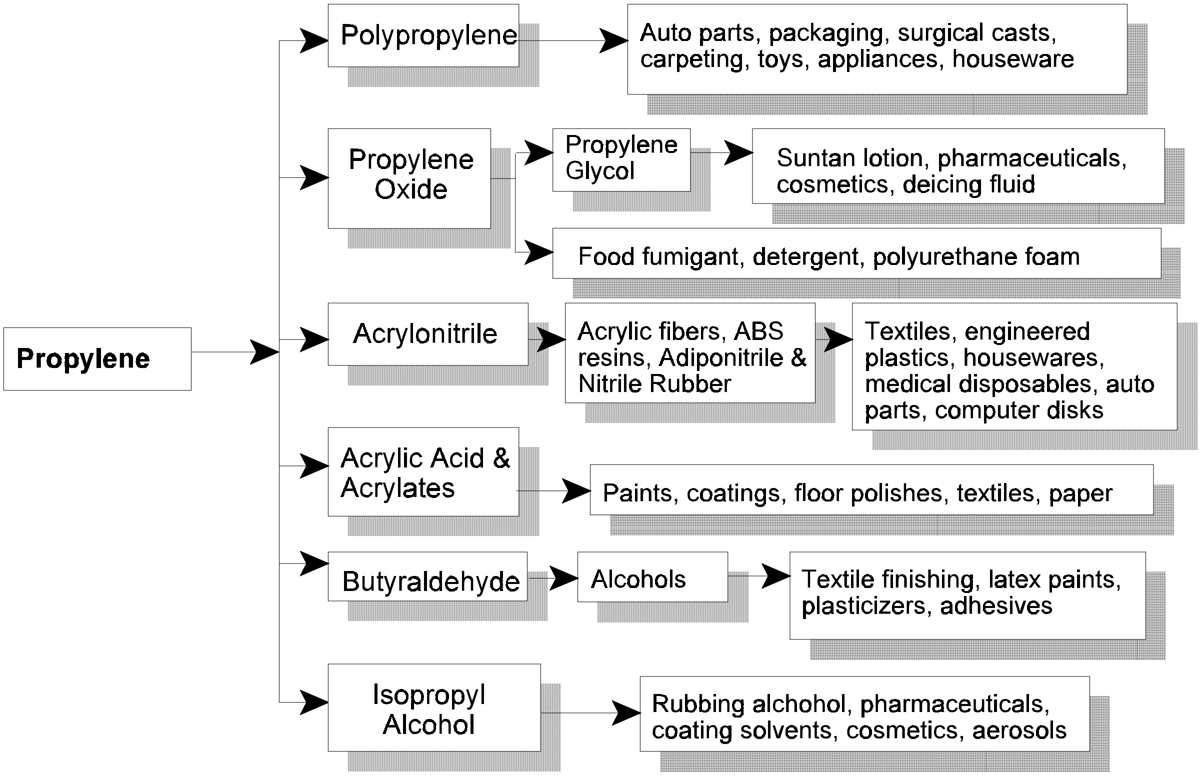

Figure 3-1. The Propylene Products Chain (CMA 1998)

in 1997 went into the production of these two polymers. Acrylic fibers are manufactured into textiles for apparel, carpet, drapes, and blankets. ABS resins are the starting materials for many common plastic products such as telephones and computer disks.

Growth in Demand for Propylene Exceeds Production Capacity

Worldwide **demand for propylene** has been rising steadily over the last 10 years, particularly from Southeast Asia, the Middle East, Africa, and Latin America. Current sources of propylene (mostly steam crackers) do not meet this growth in demand. It is predicted that the price of propylene will have to be relatively higher in the future to justify additional "on-purpose" production or the development of new technologies to enhance current production (OGJ 1998).

Some Asian countries (China, Thailand) are investing in processes that increase propylene production, such as deep catalytic cracking. In the United States and Germany, some firms are moving toward construction of metathesis reactors to maximize propylene production rather than ethylene.[1] In other areas, including Europe, Asia, and Mexico, propane dehydrogenation plants are used for additional propylene production.

During the current shortage, the propylene market is a "seller's market" and it is promoting numerous expansion plans around the world. The global growth in demand is expected to reach 6 percent this year (OGJ 1998). The capacity for propylene production in the United States (for chemical purposes) is currently about 30 billion pounds. About 50 percent of propylene capacity is located at refineries or plants integrating refining and petrochemical activities (OGJ 1998, CHEMX 1999).

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[1] Through metathesis, N-butenes can be reacted in the presence of ethylene to produce propylene.

The global demand for **polypropylene** is also strong, but it may be weakened by an over-supply in the near future, based on additions in capacity anticipated in Asia, the Middle East, and Western Europe. New market opportunities may be created for polypropylene as the catalyst technology for polyolefins (e.g., the metallocene catalysts) advances. However, there is also significant competition from other "new-generation"polymers.

Markets for **propylene oxide** and its derivatives (**propylene glycol, urethane polyether polyols, urethane foam**) are generally favorable, primarily because of continual increases in demand from Southeast Asia, in spite of Asian financial crises. U.S. markets for **propylene glycol** are being driven by strong demand for skin-care and sunscreen products, as well as the use of polyester resins (CHEMX 1999).

3.1.1 Propylene Manufacture

Nearly All Propylene Is Co-produced with Ethylene by Steam Cracking of Hydrocarbons

Propylene is co-produced as a prime product with ethylene in steam cracking and as a byproduct of refinery operations. The principal process (see Section 2 for a process description) is steam cracking of hydrocarbons, such as ethane, propane, naphtha, and gas oil. Lower molecular weight feedstocks (e.g., ethane, propane) yield a higher percentage of ethylene. Heavy molecular weight feedstocks like naphtha and gas oil are used to obtain more propylene.

The product stream also contains significant quantities of C4 compounds (containing four carbons), which include butane, isobutane, 1-butene (butylene), cis- and trans-2-butene, isobutene (isobutylene), and butadiene. Typical yields from steam cracking according to feedstock are shown in Table 3-1. From 50 to 75 percent of the propylene produced by steam cracking is consumed in petroleum refining for alkylation and production of gasoline additives. The remainder (nearly 30 billion pounds) is diverted to the manufacture of chemicals and plastics. The energy requirements for producing propylene are discussed in Section 3-3.

The propylene produced from an ethylene steam cracker is of sufficient purity to produce polypropylene directly. Propane/propylene streams produced from a refinery fluid catalytic cracking (FCC) unit contain about 60 percent propylene, and must be subjected to distillation to produce chemical grade propylene.

Propylene can also be produced by propane dehydrogenation from methanol, or by metathesis reactions, where n-butenes are reacted in the presence of ethylene to produce propylene. As demand for propylene continues

Table 3-1. Typical Olefin Yields From Steam Cracking Based on Feedstock (Percent Yield)

	Feedstock			
Product	**Ethane**	**Propane**	**Naphtha**	**Gas Oil**
Ethylene	76	42	31	23
Propylene	3	16	16	14
C4 Compounds	2	5	9	9

Source: Chenier 1992.

to grow rapidly, technologies like these will grow in popularity as a means for supplementing the propylene supply produced in steam cracking. Some capacity additions have already been planned for U.S. refineries, although there is some uncertainty about the type of technology that will be used.

A typical flow for a metathesis reaction process for propylene production is shown in Figure 3-2. In this process ethylene and butenes are introduced into a catalytic metathesis reactor. The catalyst promotes the reaction of ethylene and 2-butene to form propylene, and simultaneously isomerizes 1-butene to 2-butene. Effluent from the reactor is fractionated to yield high purity polymer grade propylene. Ethylene and butenes can come from steam crackers, other refinery sources, or from ethylene dimerization. Conversion to propylene is usually greater than 98 percent (Process Description: HP 1999).

A typical method for dehydrogenation of propane to propylene is shown in Figure 3-3. In this process, propane is sent to a reactor section where dehydrogenation occurs over a catalyst. Catalyst activity is maintained by continuous regeneration. The effluent from the reactor is compressed and sent to cryogenic separation to remove hydrogen, which is recovered and recycled. The olefin product, which contains propylene, unreacted propane, and some byproducts, is fed to a selective hydrogenation process to remove dienes and acetylenes.

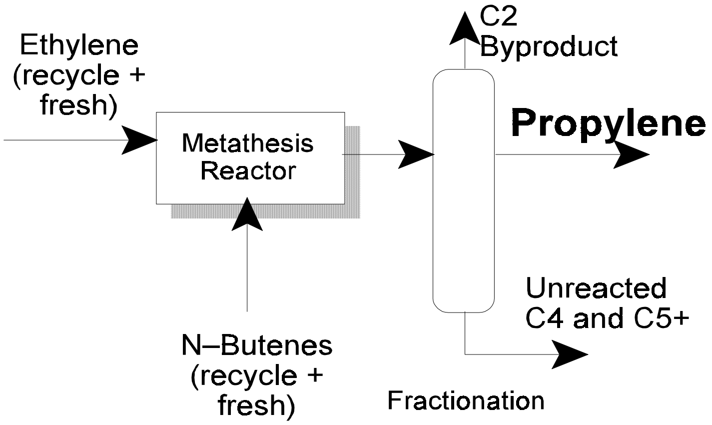

Figure 3-2. Propylene Production by Metathesis (HP 1999)

Key Energy and Environmental Facts - Propylene Manufacture/Metathesis			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 2,273 Btu/lb* *Feedstock ΔHc: 21,625 Btu/lb*	*Largest source - fugitive emissions (ethylene, butenes, propylene, C4 and C5 compounds)*	*Largest source - process water from fractionation*	*C2 compounds*

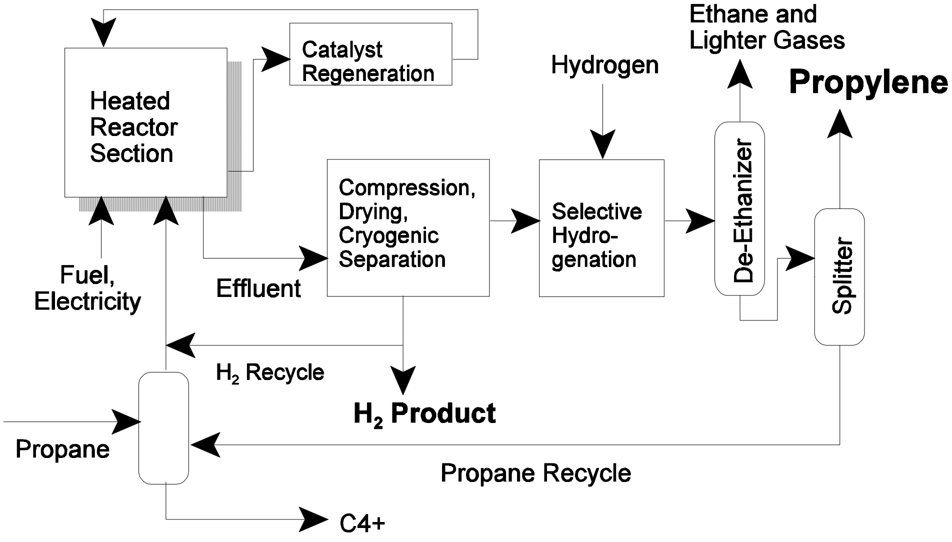

Figure 3-3. Dehydrogenation of Propane To Yield Propylene
(HP 1999)

Key Energy and Environmental Facts - Propylene Manufacture/Dehydrogenation			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy Exporter: *Net Steam Export: 497 Btu/lb*	*Largest source - fugitive emissions (C4 and C5 compounds)*	*Largest source - process water*	*Hydrogen, light gases*

During selective hydrogentation, dienes and acetylenes are converted to mono-olefins (ethylene and propylene). If hydrogenation is not selective, they are converted to paraffins (ethane or propane). The propylene/propane stream is finally sent to a C3 splitter to separate propane (which is recycled to the reactors) and propylene product. The yield of propylene is about 85 percent by weight (Process Description: HP 1999).

Another technology that optimizes propylene production is **deep catalytic cracking**. This process was developed by the Research Institute of Petroleum Processing and Sinopec International, both located in China, and was recently licensed for use in the United States by an American equipment manufacturer (Meyers 1997, HP 1999). Similar or superior technology is also available from other U.S. companies.

Deep catalytic cracking is similar to fluid catalytic cracking, with somewhat different operating conditions. With this process, yields of propylene can be increased to over 20 percent. The deep catalytic cracking technology is targeted for use at petroleum refineries rather than chemical manufacturing facilities. In most cases it can be retrofitted on existing catalytic cracking units to provide product flexibility.

3.1.2 Polypropylene Manufacture

Polypropylene Can Now Be Produced Using Ziegler-Natta or Metallocene Catalysts in the Gas Phase

Polypropylene was first invented in the 1950s by Karl Ziegler in Germany and Giulio Natta in Italy through the polymerization of propylene in the presence of titanium tetra chloride ($TiCl_3$) and triethyl aluminum ($AlCl_3$), a combination developed by Karl Ziegler (Orica 1999). Both scientists received the Nobel Prize for this discovery. With the Ziegler-Natta catalyst, polypropylene is produced as a mixture of forms, mostly isotactic, with very small amounts of atactic and syndiotactic polymer.[2]

Until the 1980s, the Ziegler-Natta catalyst was the only means of producing polypropylene. Since the advent of metallocene catalysts in the mid-1980s (see Section 2, Polyethylene Manufacture), it is possible to produce syndiotactic polypropylene as a pure polymer. The syndiotactic polypropylene is softer but much tougher and clearer than isotactic polypropylene. It is expected to compete, not as a replacement for isotactic polypropylene, but as a replacement for other polymers currently used in film, medical, adhesive, and extrusion applications.

With moderate modifications, it is possible to use metallocene catalysts in existing equipment and this has been carried out successfully. However, metallocene catalysts are currently more expensive than the Ziegler-Natta catalyst, so very little polypropylene is currently being produced using them. An advantage of metallocene catalysts is their significantly increased productivity compared to the traditional catalyst, and the ability to produce one to two orders of magnitude more polymer per pound of catalyst in some instances (C&E 1995).

There are companies in the United States and abroad that are currently operating pilot operations to produce polypropylene with metallocene catalysts on a relatively small scale. A number of firms are also seeking ways to optimize production and lower costs, and use of the new catalysts is expected to greatly expand in the near future as demand for polypropylene continues to grow (C&E 1995, Malhotra 1997).

Regardless of the type of catalyst used, the manufacture of polypropylene can be accomplished in either the gas or liquid phase. Most newer capacity utilizes the gas phase process, such as that shown in Figure 3-4. Here, propylene with a purity of greater than 99.5 percent is fed to a continuously stirred reactor along with hydrogen and catalyst. In the reactor, the propylene reacts with the active catalyst to form long chains of propylene. The length of the chains is controlled by temperature and hydrogen concentration. When the reaction is terminated by a change in the temperature and/or hydrogen, polypropylene is formed.

Block high impact copolymers (polymers based on a mix of ethylene and propylene polymers) can be produced using the product stream from this process and reacting it in another reactor with ethylene and additional propylene. Most plants are versatile enough to produce homopolymers as well as impact copolymers, including rubber contents of up to 50 percent, depending on market demand.

The polymer (or copolymer) is discharged from the reactor system as a powder containing polypropylene, $AlCl_3$, $TiCl_3$, and/or other catalyst residues. Many new processes do not require removal of catalyst residues and amorphous polymer. In some cases, however, the powder must be subjected to a dechlorination process to remove these residues, as they can cause degradation of the polymer's properties. During dechlorination, the powder enters a fluidized bed where it reacts with a mixture of nitrogen, propylene oxide, and water.

The dechlorination process converts the catalyst residues to hydroxides and hydrochloric acid by water; hydroxides break down further into

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[2] Isotactic indicates a regularly arranged structure, as opposed to atactic (random) or syndiotactic (alternating) structures.

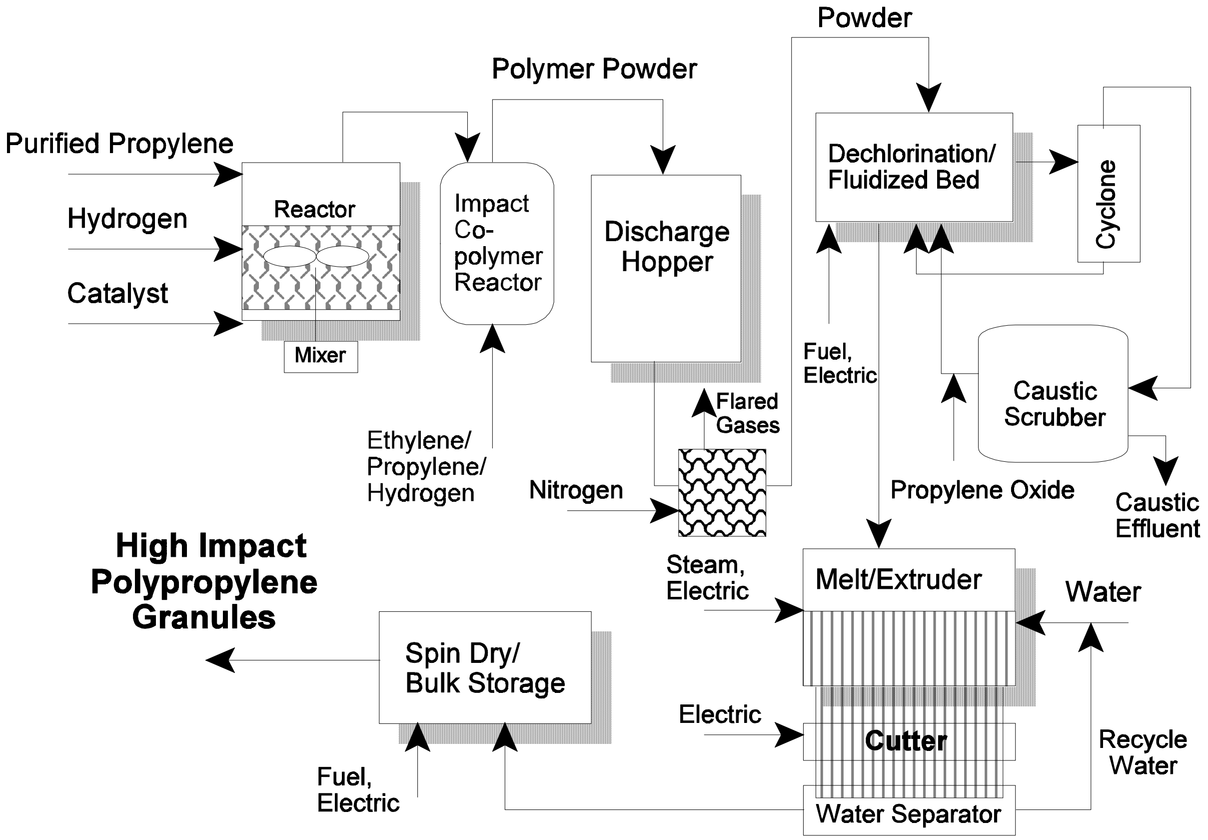

Figure 3-4. Polypropylene Manufacture
(ANL 1980, Brown 1996, HP 1999, Orica 1999)

Key Energy and Environmental Facts - Polypropylene Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 514 Btu/lb* *Feedstock ΔHc: 21,137 Btu/lb* *Fiber Manufacture:* *Process Energy: 16,345 Btu/lb*	*Largest source - fugitive emissions, airborne polymer powder, fumes containing carbon monoxide, formaldehyde and acrolein.*	*Largest source - process water, caustic streams*	*Off-grade or contaminated polymer scraps; spent catalyst.*

oxides and water. The oxides remain dispersed throughout the polymer powder. The hydrochloric acid reacts with the propylene oxide to form propylene chlorohydrin, which is passed through a caustic scrubber. In the scrubber the chlorohydrin is converted back to propylene oxide, which is recycled back to the system, and sodium chloride (salt). The "clean" powder exiting the fluidized bed is mixed in with a master batch containing an antioxidant (to prevent degradation when exposed to air or heat). The master batch and the incoming powder are mixed under specific conditions to yield a final product with the desired characteristics. This final mix is melted and extruded through dies to form laces that are quenched and cooled by water. The solidified laces are then cut to form granules that are shipped in bulk. Polypropylene can also be spun into fibers.

To achieve the desired polymer properties, the master batch may include ethylene copolymers, additives to enhance color, stability, flame retardance, and clarity, and fillers to add strength and rigidity (Process Description: ANL 1980, Brown 1996, HP 1999, Orica 1999).

3.1.3 Manufacture of Propylene Oxide and Propylene Glycol

Propylene Oxide Can Be Produced by Two Methods

Before 1969 almost all **propylene oxide** was produced by the reaction of propylene with chlorine and water to form a **propylene chlorohydrin**[3] solution. The major drawback of the chlorohydrin process is the requirement for large amounts of chlorine, which increases the cost of the process and necessitates handling of large volumes of chlorine water and disposal of calcium chloride waste.

During the **chlorohydrin process** (see Figure 3-5), propylene, water, and chlorine enter a tower that is maintained at about 120°F (49°C). The chlorine dissolves in the water to form hydrochloric and hypochlorous acids. The latter reacts with propylene to form propylene chlorohydrin. The major byproduct of this reaction is propylene dichloride, and amounts of this product are minimized by keeping the concentration of chlorohydrin low. Any unreacted propylene is scrubbed with caustic and returned to the tower. A variation of this process uses *tert*-butyl hypochlorite as the chlorinating agent, which permits the waste brine solution to be converted back to chlorine and caustic using an electrolytic cell, avoiding wasted chlorine.

In the final stage, the propylene chlorohydrin intermediate is steam-heated and contacted with a lime slurry (10 percent milk of lime). The resulting products are propylene oxide gas and waste calcium chloride. The gas is condensed and distilled to obtain the purified product.

The second process, based on **peroxidation of propylene**,[4] gained popularity during the 1970s and is now used to manufacture about half of the propylene oxide produced. In this process, oxygen is used to oxidize a hydrocarbon (isobutane, ethylene benzene) to the tertiary or secondary hydroperoxide (see Figure 3-6). The hydroperoxide is then put in contact with propylene to produce propylene oxide. Yields range from 80 to 90 percent.

Both stages of this process require a catalyst. A homogeneous catalyst, such as molybdenum naphthenate catalyst, or a tungsten, vanadium, or molybdenum heterogeneous catalyst have been successfully used.

The process produces an alcohol byproduct (t-butyl alcohol, methylbenzyl alcohol). In some cases the byproducts can be used as gasoline additives, or in alkylation reactions. Methybenzyl alcohol can be dehydrated to styrene, which can be economically advantageous as it entirely offsets total costs of raw materials. About 2.5 pounds of styrene can be produced for every pound of propylene oxide that is manufactured.

A route for the direct oxidation of propylene, such as that used to manufacture ethylene oxide from ethylene and oxygen (see Section 2), has been sought for many years without success.
The methyl group is highly sensitive to oxidation conditions, and direct oxidation usually leads to the formation of acrolein rather than propylene oxide (Process Description: ANL 1980, Chenier 1992, HP 1999).

Propylene Glycol and Ethylene Glycol Are Made by Similar Processes

Propylene glycol is made by the direct hydration of propylene oxide, in a process nearly identical to that used in the production of ethylene glycol. For a description of this process, see Section 2, Figure 2-10.

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[3] The chlorohydrin structure contains both an alcohol group (-OH) and a Cl molecule attached to the carbon backbone.

[4] The Oxirane process, developed jointly by Halcon International and Arco Chemical.

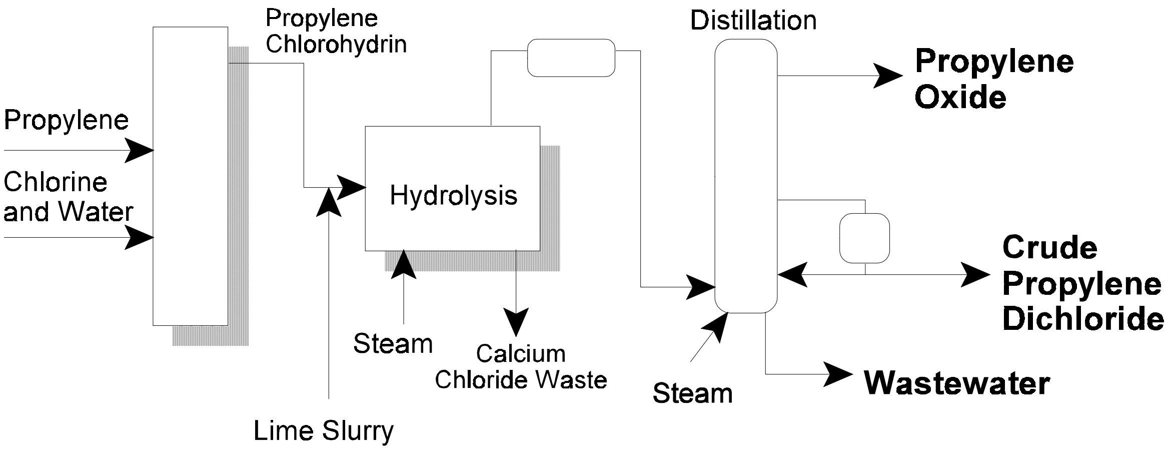

Figure 3-5. Manufacture of Propylene Oxide through Chlorohydrin Formation
(ANL 1980, Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Propylene Oxide Manufacture/Chlorohydrin Method			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Not available	*Largest source - fugitive emissions (propylene)*	*Largest source - Chlorine-containing process water*	*Calcium chloride waste; propylene dichloride*

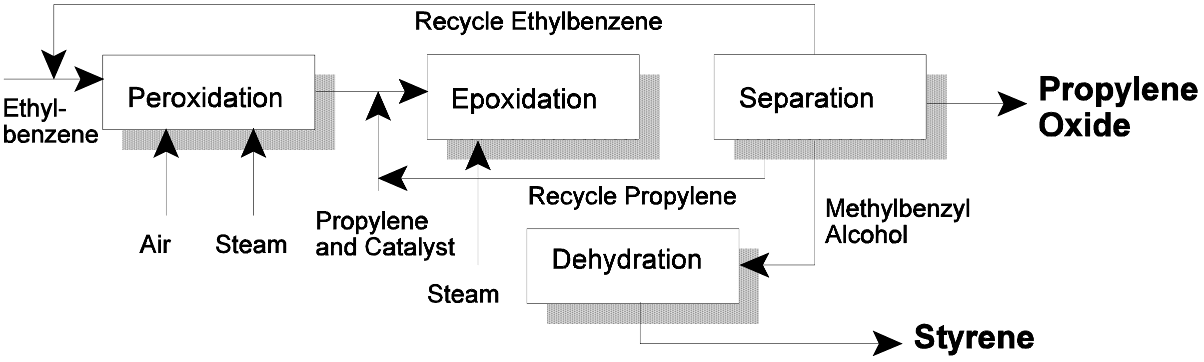

Figure 3-6. Manufacture of Propylene Oxide by Peroxidation
(ANL 1980, Chenier 1992)

Key Energy and Environmental Facts - Propylene Oxide Manufacture/Peroxidation			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 2,567 Btu/lb* *Feedstock ΔHc: 26,772 Btu/lb*	*Largest source - fugitive emissions (propylene, ethylbenzene)*	*Largest source - process water*	*Catalyst residues; styrene.*

Propylene glycol is a monomer used to produce unsaturated polyester resins, which are found in boat and automobile bodies and other plastic goods for consumers. A more important use of propylene glycol is for polymerization of the glycol to polypropylene glycol, a polyether used as an intermediate in the production of high molecular weight **polyurethane foams**. These widely used foams can be flexible or rigid, and can be found in automobile seats, furniture, bedding, and carpets.

3.1.4 Manufacture of Acrylonitrile and Acrylic Fibers

Acrylonitrile Can Be Produced from Either Propylene or Propane

Acrylonitrile and other three-carbon analogs (acrylic acid, acrolein, acrylamide) are named for the word *acrid* after the strong, disagreeable odor by which they are characterized. About 1960, all acrylonitrile was made from acetylene by a reaction occurring in the presence of hydrogen cyanide. By 1970, the industry had switched to the Sohio[5] process for **ammoxidation of chemical-grade propylene**, which involves the reaction of propylene, ammonia, and oxygen at high temperatures. The Sohio process was considered a breakthrough in chemistry when it was developed. Today over 90 percent of acrylonitrile is produced in this way (Chenier 1992, ICETT 1997, CHEMX 1999).

In 1998, BP Chemicals, Inc. announced the planned construction of a demonstration plant for a proprietary process to manufacture acrylonitrile directly from propane. The new plant will be integrated with its successful pilot-scale facility that was brought on-line in 1997. The new process is said to have numerous advantages over the ammoxidation process, including up to a 30 percent lower production cost, fewer byproducts, and more valuable coproducts (CHEMNEWS 1998).

In the ammoxidation process, chemical-grade propylene and anhydrous fertilizer-grade ammonia are fed into a catalytic fluidized bed reactor (see Figure 3-7). The original Sohio catalyst was based on molybdenum, bismuth, and phosphorus, and has undergone several improvements. The current catalyst utilizes molybdenum, bismuth, iron, and other proprietary components. The yield of acrylonitrile by this route is about 70 percent (ICETT 1997).

In the reactor, the reaction is carried out at high temperatures and low pressure: 750ºF–950ºF (399ºC–510ºC) and1-2 atmospheres, respectively. The reaction is exothermic and generates high-pressure steam from cooling water passing through the reactor in tubes. The reactor effluent is scrubbed and neutralized in an absorber to remove unreacted ammonia. Organic products are stripped from the water solution, and hydrogen cyanide (a byproduct) is removed through fractionation.

Azeotropic or extractive distillation columns are used to separate and purify the acrylonitrile and acetonitrile. The configuration shown in Figure 3-7 illustrates a steam reduction strategy devised by Monsanto Corporation to improve the Sohio process. The amount of steam required to produce 1 ton of acrylonitrile is reduced by about 3 tons using this scheme.

Hydrogen cyanide and acetonitrile are major byproducts, and acrylonitrile production is a primary source for these two chemicals, which are important intermediates in other chemical processes. Hydrogen cyanide, for example, is used in the manufacture of methyl methacrylate, which is used for paper coatings, floor polishes, leather finishes, and other consumer products (Process Description: ANL 1980, Chenier 1992, ICETT 1997).

Acrylic (or Polyacrylonitrile) Can Be Made by Suspension or Solution Polymerization

The manufacture of **polyacrylonitrile**, commonly called **acrylic**, can be accomplished through polymerization in a water solution or in suspension. The reaction is started and driven by a free-radical or anionic initiator. A typical process flow is shown in Figure 3-8. In the first stage, a weak water solution of acrylonitrile of

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[5] Standard Oil Company of Ohio

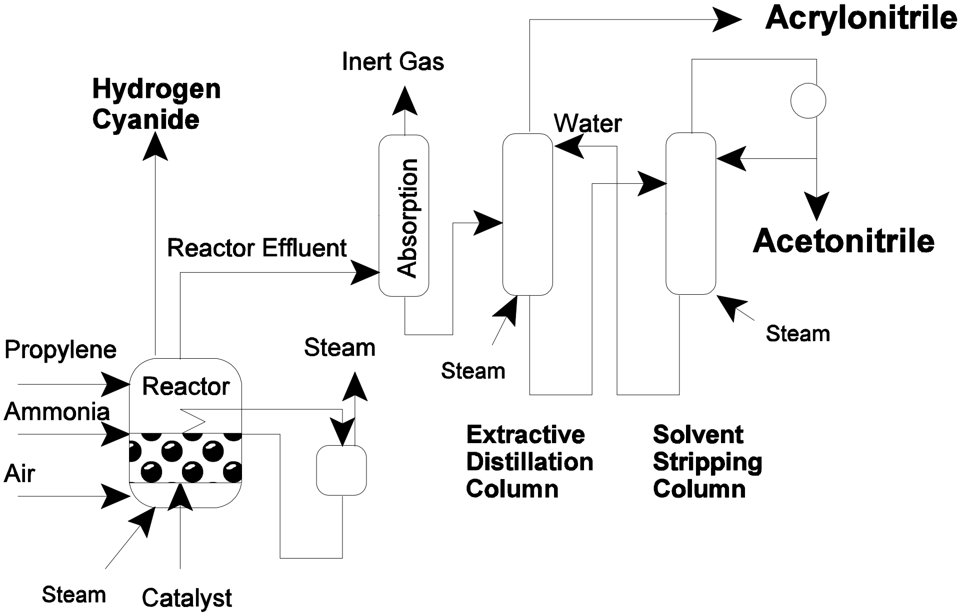

Figure 3-7. Acrylonitrile Manufacture from Propylene
(ANL 1980, Chenier 1992, ICETT 1997)

Key Energy and Environmental Facts - Acrylonitrile Production			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 956 Btu/lb* *Feedstock ΔHc: 24,283 Btu/lb*	*Largest source - fugitive emissions (ammonia, propylene, acrylonitrile, acetonitrile)*	*Largest source - process water*	*Catalyst residues, hydrogen cyanide gas, acetonitrile*

about 5 to 6 percent is combined with a small amount of initiator and enough sulfuric acid to reduce the value of the pH to about 3. The reaction is exothermic and requires cooling/heat removal to maintain temperatures at about 100ºF-120ºF (38ºC–49ºC). The polymer precipitates as an ivory powder, which is then separated and dried.

Acrylic fibers are composed of about 85 percent acrylonitrile; **modacrylic fibers** are about 35 to 85 percent acrylonitrile. The remaining components can include methyl-methacrylate, methyl acrylate, vinyl acetate, vinyl chloride, or vinyldene chloride. It is not possible to melt-spin acrylic fibers (as is done with polyester) because the fibers degrade at or below the melting point. To produce fibers, the polymer powder is first dissolved in a highly polar organic solvent, such as dimethyl formamide or dimethyl acetamide. At this point additives and delusterants are added, and the solution is filtered and pumped through a manifold to a bank of spinnerettes containing 30-50 per unit. The fibers can then be spun using dry or wet methods.

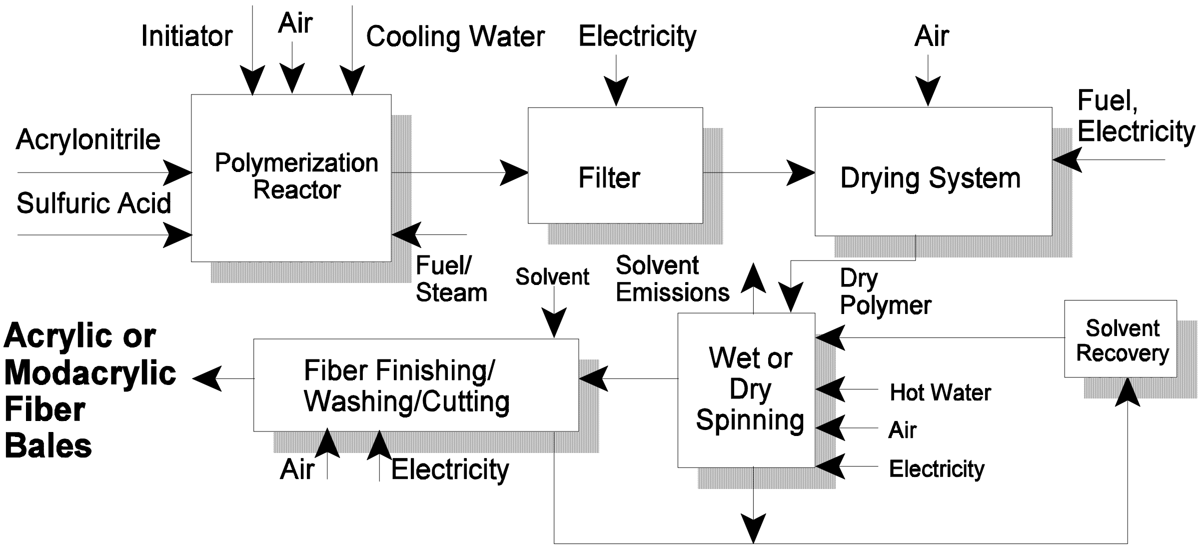

Figure 3-8. Acrylic/Modacrylic Fiber Production
(ANL 1980, EPA 1990)

Key Energy and Environmental Facts -Acrylic/Modacrylic Fibers			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 21,520 Btu/lb* *Feedstock ΔHc: 23,855 Btu/lb*	*Largest source - fugitive emissions (acrylonitrile, solvents, additives)*	*Largest source - process water*	*Hydrogen cyanide gas, acetonitrile, off-grade polymer*

In dry spinning, the solution is forced through the spinnerettes with the solvent evaporating during the process. In the wet spinning process, the fiber from the spinnerettes is coagulated in a bath and pulled out on take-up wheels, then washed to remove solvent. After washing, the filaments are gathered into a tow band.

Fibers are stretched at elevated temperatures to as much as eight times their original length to orient the molecules parallel to the fiber axis, which imparts strength. The final step, regardless of spinning method, is drying, crimping, heat-setting, and cutting (Process Description: ANL 1980, EPA 1990).

3.2 Summary of Inputs/Outputs

The following summarizes the essential inputs and products, wastes, and byproducts of the chemicals and chemical products included in the propylene chain (except propylene). For information on co-production of propylene and ethylene, see Section 2, The Ethylene Chain.

Propylene

By Metathesis

Inputs:	Outputs:
Ethylene	Propylene
N-Butenes	C2 Byproducts
Catalyst	Unreacted C4 and C5+
Process Water	Process Water
Steam/Fuel	
Electricity	

By Dehydrogenation of Propane

Inputs:	Outputs:
Propane	Propylene
Catalyst	Ethane/Light Gases
Hydrogen	Dienes, Acetylenes, C4
Process Water	Hydrogen
Steam/Fuel	Process Water
Electricity	

Polypropylene

Inputs:	Outputs:
Purified Propylene	High Impact Polypropylene
Ethylene	Purge/Flared Gases
Hydrogen	Caustic Effluent
Catalyst	Process Water
Nitrogen	Off-grade Polymer
Propylene Oxide	Spent Catalyst
Cooling Water	
Steam/Fuel	
Electricity	

Propylene Oxide

Chlorohydrin Formation Method

Inputs:	Outputs:
Propylene	Propylene Oxide
Chlorine	Propylene Dichloride
Pure Water	Calcium Chloride Waste
Lime	Process Water
Process Water	
Steam/Fuel	
Electricity	

Peroxidation Method

Inputs:	Outputs:
Propylene	Propylene Oxide
Ethylbenzene	Styrene
Air	Spent Catalyst
Catalyst	
Fuel/Steam	
Electricity	

Acrylonitrile

Inputs:	Outputs:
Propylene	Acrylonitrile
Anhydrous Ammonia	Acetonitrile
Air	Hydrogen Cyanide
Catalyst	Inert Gas
Process Water	Spent Catalyst
Solvent	Steam
Steam/Fuel	Wastewater
Electricity	

Acrylic/Modacrylic Fibers

Inputs:	Outputs:
Acrylonitrile	Acrylic/Modacrylic Fibers
Sulfuric Acid	Process Water
Initiator	Solvent Emissions
Cooling Water	Off-grade Polymer
Solvent	
Fiber Bath (Wet Spin)	
Cooling Water	
Steam/Fuel	
Electricity	

3.3 Energy Requirements

The **process and feedstock energy** used for the production of propylene, polypropylene, propylene oxide, acrylonitrile, and acrylic fibers are shown in Tables 3-2 through 3-8 (ANL 1980, EEA 1993, 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 heat of combustion value of 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 Processing Energy for propylene oxide includes the energy required to process ethylbenzene, propylene, ethylene, benzene, and raw crude feedstocks.

Table 3-2. Estimated Energy Use in Propylene Manufacture - 1997

Energy	Average Specific[f] Energy (Btu/lb)	Chemical Industry Energy Use[g] (10^{12} Btu)
Electricity[a]	243	7.0
Energy for Steam/Process Heat[f]		
Fuel Oil and LPG[b]	33	1.0
Natural Gas	853	24.5
Coal and Coke	111	3.2
Other[c]	111	3.2
NET PROCESS ENERGY	**1,351**	**38.8**
Electricity Losses	505	14.5
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**1,856**	**53.3**
Heat of Feedstock (ΔHc)[d]	20,297	582.5
TOTAL PRIMARY ENERGY	**22,153**	**635.8**
Feedstock Process Energy[e]	95	2.7
TOTAL ENERGY EMBODIED IN PROPYLENE MFG	**22,248**	**638.5**

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 a mix of feedstock (ethane, propane, naphtha, gas oil) (ANL 1980).
e Energy used to process crude oil feedstocks (ANL 1980).
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 ethylene production (see Table 2-1). Assumes 15% propylene yield.
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (28.7 billion lbs) (CMA 1998).

Table 3-3. Estimated Energy Use in Propylene Manufacture By Alternate Processes

	Metathesis (Btu/lb)	Dehydrogenation of Propane (Btu/lb)
Electricity[a]	1,229	435
Steam/Fuel	1,044	2,310
NET PROCESS ENERGY	2,273	2,746
Heat of Feedstock (ΔHc)[b]	21,625	21,490
Fuel Recovered	--	3,243
TOTAL NET ENERGY	23,898	20,993
Electricity Losses	2,552	903
TOTAL PRIMARY ENERGY	26,450	21,896

[a] Does not includes losses incurred during the generation and transmission of electricity.

[b] Feedstock energy based on heat of combustion of ethylene (metathesis) or propane (dehydrogenation) (Perry 1984).

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 the total net energy to obtain Total Primary Energy, which is the total primary energy consumption associated with production of an 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 among the various types of fuel used throughout the industry. Fuel distribution in the chemicals industry for1997 was as follows: fuel oil and LPG - 3%; natural gas - 77%; coal and coke - 10%; and other - 10% (the latter category includes any fuel source not already mentioned, such as byproduct fuel gases) (CMA 1998).

As described in Section 3.1.1, most propylene is co-produced with ethylene by an energy-intensive steam-cracking process. The energy consumption shown for **propylene** manufacture in Table 3-2 reflects production by this method only, although there is some small capacity for producing propylene by metathesis or direct dehydrogenation. Energy consumption for these less-used processes is shown in Table 3-3. These latter processes are more energy-intensive and have higher operating costs than co-production of propylene with ethylene. The cost of propylene would need to be significantly higher to stimulate additional capacity for these dedicated processes.

The amount of processing energy consumed to produce heat and power for propylene production is generally relatively small, with steam accounting for the greatest share. Feedstocks represent the largest energy input, since these materials are hydrocarbon fuels or fuel precursors. In Table 3-2, it is assumed that propylene is produced from a mix of feedstocks (e.g., ethane, propane) introduced into ethylene units at chemical plants.

Table 3-4. Estimated Energy Use in Polypropylene Manufacture - 1997

Energy	Specific Energy[f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use[g] (10^{12} Btu)
Electricity[a]	178 - 201	190	2.5
Energy for Steam/Process Heat[f]			
Fuel Oil and LPG[b]	9 - 10	10	0.1
Natural Gas	237 - 263	250	3.3
Coal and Coke	31 -34	32	0.4
Other[c]	31 - 34	32	0.4
NET PROCESS ENERGY	**486 - 542**	**514**	**6.8**
Electricity Losses	370 - 417	393	5.2
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**856 - 959**	**907**	**12.1**
Heat of Feedstock (Δhc)[d]	21,137	21,137	281.1
TOTAL PRIMARY ENERGY	**21,993 - 22,096**	**22,044**	**293.2**
Feedstock Process Energy[e]	1,453	1,435	19.3
TOTAL ENERGY EMBODIED IN POLYPROPYLENE MFG	**23,446 - 23,549**	**23,497**	**312.5**

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 propylene (Perry 1984).
e Energy used to manufacture propylene feedstock (see Table 2-1).
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 Mitsui Petrochemical and Montell Technology Company processes (Source: HP 1999).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (13.3 billion lbs) (SPI 1998).

Table 3-5. Estimated Energy Use in Polypropylene Fiber Manufacture

Process	Electricity (Btu/lb)	Steam/Fuel (Btu/lb)
Melting/Extruding	78	4,787
Cutting	625	-
Pelletizing	78	7,024
Spinning	235	-
Drawing	704	-
Winding	547	-
TOTAL NET ENERGY USE	2,267	14,078

Source: Brown 1996.

Table 3-6. Estimated Energy Use in Propylene Oxide Manufacture - 1997		
Energy	Average Specific[f] Energy (Btu/lb)	Chemical Industry Energy Use[g] (10^{12} Btu)
Electricity[a]	462	1.8
Energy for Steam/Process Heat[f]		
Fuel Oil and LPG[b]	63	0.2
Natural Gas	1,621	6.3
Coal and Coke	211	0.8
Other[c]	211	0.8
NET PROCESS ENERGY	**2,567**	**10.9**
Electricity Losses	959	3.7
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**3,526**	**13.8**
Heat of Feedstock (ΔHc)[d]	26,772	104.4
TOTAL PRIMARY ENERGY	**30,298**	**118.2**
Feedstock Process Energy[e]	2,342	9.1
TOTAL ENERGY EMBODIED IN PROPYLENE OXIDE MFG	**32,640**	**127.3**

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 propylene and ethylbenzene (ANL 1980).
e Energy used to process propylene and ethylbenzene feedstocks, including all steps from raw crude (ANL 1980).
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 peroxidation processes (ANL 1980).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (3.9 billion lbs) (CMA 1998).

The **synthesis of polypropylene** requires relatively low amounts of process energy compared to other products of the propylene chain. However, significant amounts of energy may be expended in fabrication of the polymer into fiber (see Table 3-5). The bulk of processing energy in this case is expended in the form of steam or fuel for melting, extruding, and drying. A considerable amount of electricity is also required for spinning, winding, and drawing of fibers.

Production of **acrylonitrile** is one of the least energy-intensive of the propylene derivatives, requiring less than 1000 Btu/pound of product for processing. However, feedstock energy required to produce acrylonitrile is substantial (over 24,000 Btu/pound), and is based on material inputs of ammonia and propylene. When the processing energy associated with the feedstocks is considered, total energy embodied in production of acrylonitrile is nearly 34,000 Btu/pound.

Table 3-7. Estimated Energy Use in Acrylonitrile Manufacture - 1997

Energy	Average Specific[f] Energy (Btu/lb)	Chemical Industry Energy Use[g] (10^{12} Btu)
Electricity[a]	172	0.6
Energy for Steam/Process Heat[f]		
Fuel Oil and LPG[b]	24	0.1
Natural Gas	604	2.0
Coal and Coke	78	0.3
Other[c]	78	0.3
NET PROCESS ENERGY	**956**	**3.2**
Electricity Losses	357	1.2
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**1,313**	**4.3**
Heat of Feedstock (ΔHc)[d]	24,283	80.1
TOTAL PRIMARY ENERGY	**25,596**	**84.5**
Feedstock Process Energy[e]	2,235	7.4
TOTAL ENERGY EMBODIED IN ACRYLONITRILE MFG	**27,831**	**91.8**

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 propylene and ammonia (ANL 1980). Stoichiometric ratios: 1.15 lbs propylene and 0.52 lbs ammonia for every lb of acrylonitrile.
e Energy used to process propylene and ethylbenzene feedstocks, including all steps from raw crude (ANL 1980).
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 (ANL 1980).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (3.3 billion lbs) (CMA 1998).

The manufacturing of **acrylic fibers**, one of the major uses for acrylonitrile, requires the second largest amount of processing energy among the propylene derivatives, or more than 23,000 Btu/pound of finished fiber. The bulk of this energy is used for heating and drying raw polymer powder and spun fibers. Considerable amounts of electricity are required for the numerous intermediate polymer- and fiber-processing steps, which include washing, grinding, dissolving, spinning, cutting, and baling. Feedstock energy to produce acrylic fibers is based on acrylonitrile, and includes the smaller amounts of solvent used for dissolving and washing the polymers and fibers.

Table 3-8. Estimated Energy Use in Acrylic Fibers Manufacture - 1997			
Energy	**Specific Energy[f] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Chemical Industry Energy Use[g] (10^{12} Btu)**
Electricity[a]	1,707 - 2,769	2,238	1.0
Energy for Steam/Process Heat[f]			
Fuel Oil and LPG[b]	540 - 617	578	0.3
Natural Gas	13,860 - 15,834	14,847	6.5
Coal and Coke	1,800 - 2,056	1,928	0.9
Other[c]	1,800 - 2,056	1,928	0.9
NET PROCESS ENERGY	**19,707 - 23,333**	**21,520**	**9.5**
Electricity Losses	3,545 - 5,750	4,647	2.0
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**23,252 - 29,083**	**26,167**	**11.5**
Heat of Feedstock (ΔHc)[d]	23,855	23,855	10.5
TOTAL PRIMARY ENERGY	**47,107 - 52,938**	**50,022**	**22.0**
Feedstock Process Energy[e]	2,246	2,246	1.0
TOTAL ENERGY EMBODIED IN ACRYLIC FIBERS MFG	**49,353 - 55,184**	**52,286**	**23.0**

[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 propylene and ammonia used to make acrylonitrile (see Table 3-7) (Perry 1984).
[e] Energy used to manufacture propylene and ammonia feedstocks, beginning with raw crude feedstocks.
[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 (ANL 1980, Brown 1996). Includes spinning, drying, and drawing of fibers.
[g] Calculated by multiplying average energy use (Btu/lb) by1997 production values (0.44 billion lbs) (SPI 1998).

3.4 Air Emissions

Fugitive Emissions Are the Leading Sources of Air Contaminants in the Propylene Chain

The primary sources of emissions in the propylene chain are fugitive and point air source emissions of volatile compounds emitted from equipment during process operations. Fugitive emissions of volatile compounds arise from leaks in valves, pumps, tanks, flanges, and similar components of the process equipment.

The primary toxic air emissions from production of **propylene** and its derivatives include ammonia, propylene glycol, propylene, propylene oxide, methanol, acrylonitrile, acetonitrile, and polar solvents (e.g., dimethylformamide, dimethylacetamide, lithium bromide). Emissions of these compounds are reported annually in the Toxic Release Inventory (TRI).

Releases of **propylene** from the entire organic chemical sector (SIC 286) were 4.5 million pounds in 1995, as reported to the TRI. Reported releases of known or suspected carcinogens were also substantial in 1995, including 412,897 pounds of propylene oxide; 224,000 pounds of acrylonitrile from the plastics and synthetic fibers industry (SIC 2823 and 2824); and 1.1 million pounds of acrylonitrile from organic chemicals manufacture. Releases of the solvent dimethylformamide, also a known carcinogen and used to produce acrylic fibers, were moderate–a total of about 57,000 pounds in 1995 from the plastics and organic chemicals manufacturing sectors (EPA 1997c).

Volatile emissions during the production of **acrylic fibers** include acrylonitrile (as a volatilized monomer), solvents, additives, and other organic compounds that may be used in processing and finishing the fibers. During the wet spinning process, washing and spinning are the primary sources of volatile emissions. The spinning and post-spinning units (up to and including drying operations) are the main sources for volatile emissions in dry spinning. Solvent recovery operations are also a significant source of emissions. Table 3-9 lists the estimated emission factors for volatile compounds during acrylic fiber production (EPA 1990).

Effective control and reduction of solvent emissions from both wet and dry spinning is accomplished through the use of a solvent recovery system. In wet spinning, distillation may be used to recover and recycle solvent from the water-solvent stream that circulates throughout the spinning, washing and drawing operation. In dry spinning, scrubbers and condensers can be used to recover solvent emissions from spinning cells as well as from drying units. Carbon absorption is also used to recover solvent emissions from vents on storage tanks, and from mixing and filtering units. Distillation can also be used in dry spinning to recover solvent from wash water as well as from condensers and scrubbers (EPA 1990).

Table 3-9. Air Emission Factors for Melt Spinning of Acrylic and Modacrylic Fibers
(lbs/1000 lbs fiber spun, including waste fiber)

Type of Fiber	Nonmethane Volatile Organics	Particulates
Acrylic, Dry Spun		
Uncontrolled	40	nil
Controlled	32[a]	nil
Modacrylic, Dry Spun	125[b]	nil
Acrylic/Modacrylic, Wet Spun	6.75[c]	nil
Acrylic, Inorganic Wet Spun		
Hompolymer	20.7[d]	nil
Copolymer	2.75[e]	nil

Source: AP 42, Chapter 6.9.1, *Synthetic Fibers*.

a After recovery from spin cells.
b Uncontrolled.
c After solvent recovery from the spinning, washing, and drawing stages (includes acrylonitrile emissions).
d Uncontrolled. Average emission factor; range is from 13.9 to 27.7 pounds.
e Uncontrolled. Average emission factor; range is from 2.04 to 16.4 pounds.

The combustion of fuels in boilers to produce steam and in process heaters or furnaces also produces criteria air pollutants that are regulated under the Clean Air Act. Burning cleaner fuels (e.g., natural gas) in these heating units creates relatively low emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons. If fired with lower grade fuels (e.g., fuel oils, coke, coal) or operated inefficiently, attaining incomplete combustion, heaters can be a significant source of emissions. Current emission factors for process heaters and boilers are discussed later in this document (see Section 7, Supporting Processes).

3.5 Effluents

Liquid Wastes Are Comprised Primarily of Process Wash Water

Effluents emitted during the production of propylene and its derivatives consist primarily of **wash waters** from spinning operations, process water from distillation towers, and cooling water. Much of this water is recycled for reuse in the process. 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 are often subjected to stripping to separate contaminants so water can be reused.

Limitations for the 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 originally promulgated in 1974 and has been subsequently revised several times. The chemicals in the propylene chain are covered under Subparts C, D, F, and G in Part 414. Since these Subparts also discuss numerous other chemicals, the limitations are presented together in Section 7, where general water-treatment processes are covered.

3.6 Wastes, Residuals, and Byproducts

Hazardous Wastes Are Associated with Production of Acrylonitrile

The EPA classifies a number of wastes associated with the production of acrylonitrile as **hazardous waste** under Title 40 Code of Federal Regulations (CFR), Part 261, Section 32 (see Table 3-10). These wastes are primarily associated with the purification system for acrylonitrile and its co-product acetonitrile, which are both listed as hazardous (and toxic) materials. Hydrocyanic acid may also be present in the wastewater from the water stripping and recovery system.

Many options are 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 more information, refer to one of many sources published on this topic.

Table 3-10. Hazardous Wastes from Production of Acrylonitrile

Waste Classification	Description	Hazardous Constituents
K011	Bottom stream from the wastewater stripper in the production of acrylonitrile	Acrylonitrile, acetonitrile, hydrocyanic acid
K013	Bottom stream from the acetonitrile column in the production of acrylonitrile	Acrylonitrile, acetonitrile, hydrocyanic acid
K014	Bottom stream from the acetonitrile purification column in the production of acrylonitrile	Acetonitrile, acrylamide

Source: BNA 1995.