Energy and Environmental Profile of the U.S. Chemical Industry

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This report was written by Joan L. Pellegrino of Energetics, Inc. in Columbia, MD. It was prepared under the general direction of Lou Sousa, Office of Industrial Technologies (OIT), U.S. Department of Energy, in cooperation with Hank Kenchington, OIT's Chemical Team Leader. This report represents the first attempt to take a comprehensive look at the industry and identify energy use for a wide number of individual processes. The report was reviewed by several experts in the chemical industry and community. However, due to the great complexity of the industry and its products, we acknowledge that we may not have the best or most up-to-date information available in every instance. We welcome comments that would add to the substance of the report. Comments can be forwarded to:

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FOREWORD

In 1996, the U.S. Department of Energy's Office of Industrial Technologies (DOE/OIT) began work on a series of reports in support of DOE/OIT's Industries of the Future strategy. Under this industry-led strategy, DOE/OIT works with U.S. industry to develop technology partnerships and support collaborative RD&D projects that enhance energy efficiency, competitiveness and environmental performance.

Though the profiles are intended primarily to better inform collaborative industry-DOE R&D planning, they provide a valuable resource that can be widely used by many others who are not directly involved in these efforts. Through these profiles, research managers, policymakers, industry analysts and others can gain a general perspective of energy use and environmental characteristics of the industry. The profiles do not attempt to recreate sources that already exist; rather, they provide a "snap-shot" of the industry and an excellent source of references on the topic.

The profiles synthesize into a single document information that is available in many different forms and sources. Aggregated data for the entire industry as well as data at the process level is presented according to the major unit operations of each industry. Data is obtained from the most currently available published sources, industry experts, and government reports. Prior to publication, profiles are reviewed by those working in the industry, trade associations, and experts in government and the national laboratories.

To date, energy and environmental profiles have been published for the aluminum, steel, metalcasting, petroleum refining, and chemical industries. Development of profiles for the glass, mining, and forest products industries is currently underway, and a similar report is planned for the renewable bioproducts area of agriculture.

1 Overview

1.1 Chemicals: A Huge, Complex, and Highly Diverse Industry

The Industry Produces Over 70,000 Products

The chemical industry is an integral component of the U.S. economy, converting various raw materials (e.g, metals, minerals, coal, oil, natural gas, air, water) into more than 70,000 diverse products. Many of its contributions are not highly visible, however, because most chemical companies are not directly involved in the production of consumer products. The industry itself consumes a large portion of the chemicals it produces–about 24 percent. Since very few goods can be manufactured without some input from the chemical industry, many of the industry's products become essential raw materials for the rest of the manufacturing sector, which purchases about 30 percent of these products. Manufacturers who use large amounts of chemicals represent rubber and plastic products, textiles, apparel, petroleum, paper and allied products, and primary metals. Non-manufacturing sectors also require chemical products, and large purchasers represent the agriculture, construction, and service industries (such as health care), as well as consumer goods (CMA 1998).

The industry creates its diverse slate of products using materials in two forms: organic and inorganic. Organic raw materials (oil, natural gas) are comprised of hydrocarbons that form the building blocks for final organic products. Inorganic chemicals are made from

Examples of Products Created with Chemical Industry Inputs

Paints
Food Packaging
Pharmaceuticals
Detergents
Adhesives
Cleaners
Waste Bags
Packaging Film
Toys
Plastic Bottles
Antifreeze
Printing Inks
Clothing
Carpets
Insulation
Auto Parts
Solvents
Paper

The U.S. Department of Energy and the Chemical Industry of the Future

The U.S. Department of Energy's (DOE's) Office of Industrial Technologies has formed a partnership with the U.S. chemical industry to accelerate the development of technologies and processes that will improve the industry's energy efficiency and environmental performance. This report is intended to support the DOE/chemical industry partnership.

ores or elements taken from the earth (e.g., phosphate, sulfur, potash), air (e.g., nitrogen, oxygen) and water (e.g., chlorine).

In the 1930s, the chemical industry was divided into various categories that were coded under the Standard Industrial Classification (SIC) System, based on the type of chemical processing used and the final products generated (OMB 1987). In 1997, the Office of Management and Budget (OMB) reclassified all U.S. industries under a new coding system, the North American Industry Classification System (or NAICS) (OMB 1997). NAICS recognizes new technologies and industries, and creates a uniform system for the three North American countries. These new classifications will be used in the next census of manufactures conducted by the Department of Commerce, and by other Federal agencies that collect data from industry. At present, however, all industry data is still classified under SIC codes. Appendix A contains an abbreviated list of the new classifications. The individual segments of the SIC code that will be examined in this study are shown in Table 1-1 (the NAICS codes are shown in parentheses).

Table 1-1. Major U.S. Chemical Industry SIC (and NAICS) Codes and Their Corresponding Products

SIC	Major Products
281 Industrial Inorganic Chemicals ***(32518 Other Basic Inorganic Chemical Manufacturing)*** [b]	
2812 Alkalies and Chlorine *(325181 Alkalies and Chlorine Manufacturing)* [b]	Caustic soda (sodium hydroxide), chlorine, soda ash, potassium, and sodium carbonates
2813 Industrial Gases *(32512 Industrial Gas Manufacturing)* [b]	Inorganic and organic gases (acetylene, hydrogen, nitrogen, oxygen)
2819 Industrial Inorganic Chemicals, nec[a] *(325188 Other Basic Inorganic Chemicals Manufacturing)*[b]	Compounds of aluminum, ammonium, chromium, magnesium, potassium, sodium, sulfur, and numerous other minerals; inorganic acids.
282 Plastics and Rubbers ***(32521 Resin and Synthetic Rubber Manufacturing)*** [b]	
2821 Plastics Materials and Resins *(325211 Plastics Material and Resin Manufacturing)* [b]	Synthetic resins, plastics, and elastomers (acrylic, polyamide, vinyl, polystyrene, polyester, nylon, polyethylene)
2822 Synthetic Rubber *(325212 Synthetic Rubber Manufacturing)* [b]	Vulcanizable rubbers (acrylic, butadiene, neoprene, silicone)
286 Industrial Organic Chemicals ***(32511 Petrochemical Manufacturing)*** [b]	
2865 Cyclic Crudes and Intermediates *(325192 Cyclic Crude and Intermediate Manufacturing and 325110 Petrochemical Manufacturing)* [b]	Distilling coal tars; cyclic intermediates, i.e., hydrocarbons, aromatics (benzene, aniline, toluene, xylenes); and organic dyes and pigments. (Note: in the NAICS codes, aromatics have been moved to petrochemical manufacturing.)
2869 Industrial Organic Chemicals, nec[a] *(325110 Petrochemical Manufacturing)* [b]	Aliphatic/acyclic organics (ethylene, butylene, organic acids); solvents (alcohols, ethers, acetone, chlorinated solvents); perfumes and flavorings; rubber processors and plasticizers. (The NAICS codes include aromatics here.)
287 Agricultural Chemicals ***(32531 Fertilizer Manufacturing)*** [b]	
2873 Nitrogenous Chemicals *(325311 Nitrogeneous Fertilizer Manufacturing)* [b]	Ammonia fertilizer compounds, anhydrous ammonia, nitric acid, urea and natural organic fertilizers.
2874 Phosphatic Chemicals *(325312 Phosphatic Fertilizer Manufacturing)* [b]	Phosphatic materials, phosphatic fertilizers

[a] nec means “not otherwise classified”; [b] NAICS codes are shown in parentheses.
Sources: OMB 1987, 1997.

The nine industrial segments represented by the four-digit SICs shown in Table 1-1 account for about 90 percent of the energy consumed and nearly 80 percent of the toxic waste generated by the chemical industry. Industry segments that are not covered in this report are primarily small energy users and/or represent a relatively small share of chemical product shipments. The exception is SIC 283, Drugs, a segment that is a small energy user but one producing very high-value products. It is not included primarily because energy data for this segment is not readily available. Energy data is also not available for SIC 284, Soap, Detergents, Cosmetics, and SIC 285, Paints, Varnishes, Lacquers and Enamels.

1.2 Industry Performance and Market Trends

Industry Has Experienced Substantial Growth

The chemical industry is one of the oldest U.S. industries, with roots going back to 1635. It is a dynamic, internationally competitive industry that invests billions of dollars annually in research and development (R&D), and relies on advanced technologies and innovative products to capture and maintain market share. The industry's composition has changed over the last decade to reflect more diversification into high technology areas (e.g., pharmaceuticals, biotechnologies, advanced materials). Along with this diversification has come an increased emphasis on R&D spending.

The industry accounts for about 5 percent of U.S. gross domestic product (GDP), and about 11.8 percent of the value added to GDP by all U.S. manufacturing. The industry has grown steadily over the last 10 years, and in 1997 achieved record shipments of over $392 billion. Capacity utilization over the same period has risen only slightly (less than 1 percent). The industry's gross investment in new plants and equipment has risen steadily along with R&D funding, a direct result of industry growth and record profits. Table 1-2 summarizes the trends in shipments, investments, and employment for the U.S. chemical industry during the past decade.

The chemical industry is the largest employer in the manufacturing sector, with more than a million workers on its payroll. The complex nature of the industry requires a large number of technically skilled production workers, as well as chemists, chemical and other types of engineers, and professionals from a variety of other technical disciplines (e.g., agronomists, toxicologists, biologists). About 4 of every 10 employees in the chemical industry are in R&D, administration, sales, technical servicing, and clerical positions. Nearly 89,000 scientists and engineers are involved just in R&D–or nearly 14 percent of all those employed in R&D in the entire U.S. manufacturing sector (CMA 1998).

Along with more emphasis on R&D, this highly technical and rapidly changing industry is also increasing its technical services and the amount of automation in its production processes. This has led to a slight decrease in production workers over the last few years, although the remaining labor pool has steadily increased its productivity. Because of the technical nature of the production workforce and its increasing productivity, these workers receive average hourly wages that are about 27 percent higher than those of manufacturing workers as a whole.

Organics Lead the Industry in Shipments

In terms of the value of shipments, SIC 2869, Industrial Organic Chemicals, is ranked first among the four-digit SICs examined for this study (see Figure 1-1). Combined shipments for SIC 2865, Cyclic Crudes, and SIC 2869, Industrial Organic Chemicals (which comprise most of organic chemicals manufacture), were valued at nearly $76 billion in 1996. SIC 2821, Plastic Materials and Resins, which relies heavily on the organic chemical segment for raw materials and intermediates, ranked second with shipments of about $40 billion in 1996. Several segments not covered in this study are shown in Figure 1-1 for comparison, notably pharmaceuticals, soaps and cleaners, and paints.

Together, SIC 2869, 2865, and 2821 accounted for a total of nearly $44 billion in "value added by manufacturing" (DOC 1994). The *value added* by manufacturing essentially represents

Table 1-2. U.S. Chemical Industry Trends in Shipments, Investments, and Employment (SIC 28)

	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
Value of Shipments ($billion)	230	261	283	293	299	305	314	334	362	373	392
Investment in Plant & Equipment ($billion)	9.8	12.4	15.4	17.5	18.5	18.4	18.0	17.8	23.1	23.4	n/a
R&D Spending ($billion)	9.5	10.8	11.5	13.2	14.4	15.1	16.7	16.7	17.3	17.7	18.7
Capacity Utilization (%)	81.3	84.0	83.7	83.0	80.1	80.2	78.6	78.8	78.9	78.4	79.1
Employment (1000s)	1025	1057	1074	1086	1076	1084	1081	1057	1038	1034	1034
Average Hourly Wages $/Hour (Production)	12.36	12.71	13.09	13.54	14.04	14.51	14.82	15.12	15.62	16.17	16.58

Source: CMA 1998.

the value of shipments minus the cost of materials, supplies, containers, fuels, purchased electricity, and other costs encountered during production. It is considered to be the best measure of value available for comparing the relative economic importance of manufacturing and other industries.

Another commonly used chemical industry indicator is "production of the top 50 chemicals." The list of the top 50 chemicals is compiled based on the annual production of selected chemicals throughout all segments of the chemical industry. Although about 30 of the chemicals have been on this list for decades, significant increases or decreases have been noted as changes occurred in consumer demands or external markets (e.g., the production of MTBE, a gasoline additive, increased as the Federal Government changed requirements for transportation fuels). The current top 50 chemicals according to 1997 data are shown in Table 1-3. It should be noted that many of the chemicals on this list are co-produced or are used almost entirely as intermediates in the production of other chemicals on the list.

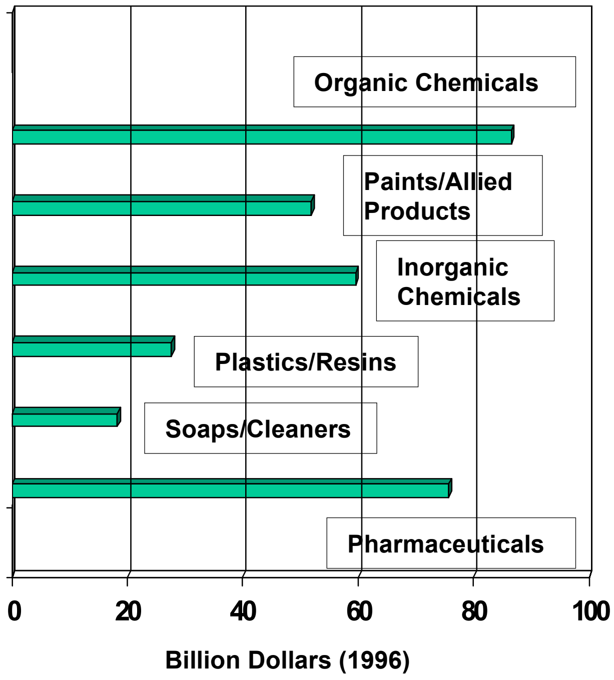


Figure 1-1. 1996 Shipments in Selected Chemical Segments

Examples are oxygen and nitrogen, which are derived from one process, air separation, and ethylbenzene, which is used almost entirely to produce styrene, often in the same plant.

Table 1-3. U.S. Production of Top 50 Chemicals, 1997 (1000 short tons)

Rank	Chemical	Production	Rank	Chemical	Production
1	Nitrogen	47,708	26	p-Xylene	3,963
2	Sulfuric Acid	35,707	27	Ethylene Oxide	3,550
3	Oxygen	30,068	28	Cumene	2,913
4	Ethylene	24,125	29	Ethylene Glycol	2,813
5	Lime	21,175	30	Acetic Acid	2,425
6	Propylene	14,350	31	Phenol	2,175
7	Ammonia	14,204	32	Ammonium Sulfate	2,045
8	Chlorine	12,997	33	Butadiene (1,3-)	2,038
9	Sodium Carbonate (Soda Ash)	11,838	34	Propylene Oxide	1,963
10	Caustic Soda (Sodium Hydroxide)	11,371	35	Carbon Black	1,750
11	Ethylene Dichloride	10,088	36	Acrylonitrile	1,663
12	Phosphoric Acid	9,909	37	Vinyl Acetate	1,500
13	MTBE	9,038	38	Titanium Dioxide	1,478
14	Vinyl Chloride	8,763	39	Acetone	1,463
15	Benzene	7,463	30	Aluminum Sulfate	1,181
16	Ethylbenzene	6,950	41	Sodium Silicate	1,155
17	Nitric Acid	6,765	42	Cyclohexane	1,100
18	Ammonium Nitrate	6,147	43	Bisphenol A	863
19	Methanol	6,013	44	Caprolactam	825
20	Urea	5,918	45	Aniline	713
21	Styrene	5,700	46	Isopropyl Alcohol	700
22	Terephthalic Acid	5,000	47	Sodium Sulfate	639
23	Hydrochloric Acid	4,219	48	Methyl Chloride	563
24	Formaldehyde	4,188	49	Propylene Glycol	538
25	Toluene	4,138	50	Methyl Methacrylate	313
TOTAL PRODUCTION, 1997: 364, 171,000 tons					

Source: CMA 1998.

Plastics Are a Billion-Dollar Industry

Many of the commodity organic chemicals are used as feedstocks in the production of plastics (e.g., polymers). The properties and use of plastics are highly diverse, and they are found in tens of thousands of consumer products. The estimated annual trade in plastics and plastic products is about $274 billion (SPI 1998).

Plastics (i.e., polymers) can be **thermoplastic** or t**hermosetting**. Thermoplastic polymers can be heated and remolded, and are therefore recyclable. Major thermoplastics include polyethylene, polypropylene, acrylonitrile-butadiene-styrene (ABS), polystyrene, nylon, and poly vinyl chloride (PVC).

Thermosetting plastics degrade upon heating and cannot be remolded. Major thermosets include resins of unsaturated polyester, urea, melamine, and phenol.

Engineering resins include fluoropolymers, polycarbonate, thermoplastic polyester, polyamide, and numerous others. These can be thermoplastic or thermosetting.

Recent data on U.S. plastics production is summarized in Table 1-4. About 92 billion pounds of polymeric materials were produced in the United States in 1998. Of this, more than 71 billion pounds were thermoplastics, while a much smaller quantity were thermosets (about 9 billion pounds). About 11 billion pounds of engineering resins and other plastics were also produced (SPI 1998).

Table 1-4. U.S. Plastics Production, 1997–1998 (millions of pounds, dry weight basis)

Plastic	1998	1997	% Change 98/97
Thermosets (TOTAL)	9,163	8,647	6.0
Epoxy	639	654	-2.3
Polyester (Unsaturated)	1,713	1,621	5.7
Urea	2,581	2,335	10.5
Melamine	290	303	-4.3
Phenolic Resins	3,940	3,734	5.5
Thermoplastics (TOTAL)	71,209	78,142	2.9
Low Density Polyethylene (PE)	7,578	7,691	-1.5
Linear Low Density PE	7,227	6,888	4.9
High Density PE	12,924	12,557	2.9
Polyproplyene (PP)	13,825	13,320	3.8
Acrylonitrile-Butadiene-Styrene (ABS)	1,432	1,374	4.2
Styrene-Acrylonitrile Rubber	122	96	27.1
Other Styrenics	1,654	1,623	1.9
Polystyrebe (PS)	6,237	6,380	-2.2
Nylon	1,285	1,222	5.2
Poly Vinyl Chloride	14,502	14,084	3.0
Thermoplastic Polyester	4,423	4,260	3.8
Engineering Resins	2,766	2,619	5.6
All Other Plastics	8,547	8,045	6.2
GRAND TOTAL	91,685	88,806	3.2

Source: SPI 1998.

The plastics industry has increasingly become globalized, and is primarily comprised of large, vertically integrated, multi-national chemical companies. Considerable consolidation has occurred in the industry, with the major products manufactured by fewer than five large companies. With globalization has come a shift in the production of many of the basic commodity resins to Saudi Arabia, China, South Korea, and other countries. The more highly industrialized countries such as the United States, Western Europe, and Japan have responded to this competition by increasing their production of specialty and higher-value-added products and adjusting their production capacity to improve profitability. By taking advantage of their advanced technology and research, highly developed producers can reduce the impacts of market cycles (DOC 1999).

Mature producers of plastics are increasing their exports to fast-growing parts of the world such as Mexico, South America, and Asia. Economic trends in these countries in turn can have a significant impact on future exports from the United States (as seen during the recent economic downturn and currency crisis in Asia). It is expected, however, that U.S. producers will continue to find opportunities for growth in these markets, despite economic fluctuations in the areas (DOC 1999).

The largest change in polymer chemistry in this decade has been the development and commercialization of **metallocene catalysts**, which make it possible to refine and even design the structure of polymers. Since these catalysts were first discovered in the 1980s, as much as $3 billion has been spent on research to modify, improve, and extend them (C&E 1995). Metallocene-based polymers demonstrate increased impact strength and toughness, better melt characteristics, and improved film clarity compared to earlier polymers.

Polymers made with metallocene catalysts have been available commercially since 1991 when Exxon first used its Exxpol catalysts to produce them. At the present time, Exxon Chemical and Dow Plastics are the major producers of these polymers in the United States, with over 1 billion pounds of capacity on-line (see Table 1-5 for a summary of the worldwide capacity for producing metallocenc-based polymers).

Metallocene catalysts are being used to produce improved polymers as well as entirely new kinds of polymers. Some compete with conventional polymers for use in packaging, medical equipment, and other applications. In other cases, new polymers are being produced that have unique densities and that will compete in entirely different markets than those where conventional plastics have been used.

The manufacture of metallocene-catalyzed thermoplastics has been growing at a rapid pace, both in the United States and globally. It remains, however, a small portion of total resin production. Market share is expected to rise worldwide as new technical advances are made and prices for the products fall (DOC 1999).

U.S. Is the World's Largest Chemical Producer and Second Largest Exporter

U.S. industry is now the largest producer of chemicals worldwide, accounting for about 25 percent of the $1.5-trillion global chemicals market. Japan, Germany, and France rank next in total production. The U.S. chemical industry's share of the global market is increasingly focused on specialty chemical products, particularly those where the industry has developed a technological advantage.

The U.S. chemical industry began exporting goods in the 18th century, when it established a limited export trade in potash and naval stores with the United Kingdom. The industry has historically maintained large trade surpluses, even during the late 1980s when the nation as a whole experienced huge trade deficits that were often over $100 billion. In 1997 the U.S. trade surplus in chemicals was $19.2 billion.

The United States is currently the second largest exporter of chemicals (after Germany), capturing about 15 percent of total world exports in 1997. Canada is the single largest market for U.S. chemical exports, followed by Japan. Exports to developing countries (e.g., Mexico, Latin America, Asia) are large in number and growing. Exports of U.S.

Table 1-5. Global Capacity for Metallocene-Based Polymers

Company	Location	Capacity[a] (millions of lbs per year)
Polyethylenes		
Dow Plastics	U.S.	250
Dow Plastics	Spain	125
Exxon Chemical	U.S.	253
Mitsubishi	Japan	220
Nippon Petrochemicals	Japan	110
Ube Industries	Japan	44
Total		**1,002**
Polypropylenes		
BASF	Germany	26
Chisso	Japan	44
Exxon Chemical	U.S.	220
Hoechst	Germany	220
Mitsui Toatsu	Japan	165
Total		**675**
EPDM[b]		
Dow/DuPont	U.S.	198
Cyclic Olefins		
Dow Plastics	U.S.	Pilot
Hoechst	Germany	Pilot
Mitsui Petrochemical	Japan	7
Polystyrene		
Idemitsu Petrochemical	Japan	22
TOTAL WORLDWIDE		**1,904**

[a] Forecasted by 1996

[b] Ethylene-propylene-diene monomer rubber

Source: C&E 1995.

chemicals to Mexico grew 196 percent between 1989 and 1997. Overall, exports of U.S. chemicals have grown at a rate of more than10 percent annually over the last 10 years (CMA 1998).

Despite U.S. Productivity, All Industry Sectors Face Increased Competition

U.S. imports of chemicals have also risen steadily during this period. This was particularly true for organic chemicals, where imports increased by nearly 14 percent from 1996 to 1997. Nearly $25 billion worth of products were imported into the United States in 1997, the majority from Western Europe. The global trade in organic chemicals is among the most competitive in the industry. While developed countries (United States, Western Europe, Japan) have traditionally dominated this sector of the industry, developing regions are also experiencing rapid growth rates. Countries increasing their chemical trading include Asia, the Middle East, and Latin America (DOC 1999). Figure 1-2 summarizes the value of the U.S. chemical trade over the last 10 years.

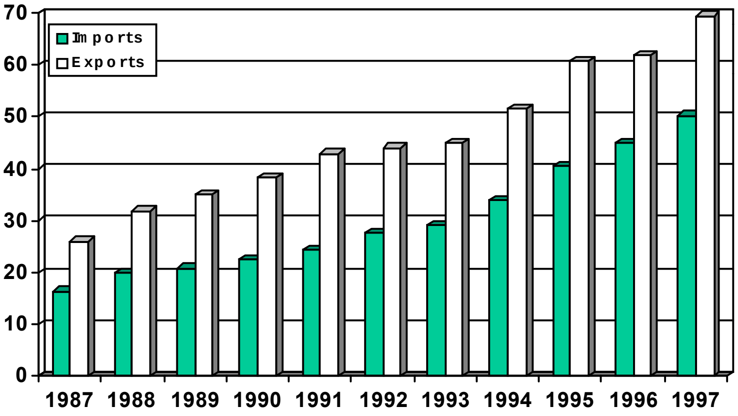


Figure 1-2. Value of U.S. Chemical Trade (CMA 1998)

Worldwide, the United States is the largest producer of phosphate fertilizers and the second largest producer of nitrogen fertilizers. Other countries, however, have large phosphate rock resources, and are expected to increase production of these products. Morocco, for example, has over 50 percent of the world's phosphate rock reserves, and is the largest phosphate rock exporter, primarily to European markets. A significant amount of phosphate fertilizer is also produced in China, India, and the former Soviet Union.

Figure 1-3 shows U.S. exports and imports of chemicals in 1997 according to Standard International Trade Classification categories (CMA 1998). A list of these categories can be found in Appendix A and they correlate fairly well with U.S. SIC/NAICS codes.

Despite a growing demand for petrochemicals worldwide, there is increasing competition in the export market for these raw materials also. It is anticipated that products from the Gulf Cooperation Council and Pacific Rim countries, including China and Korea, will begin to compete with U.S. products in current export markets as new facilities become operational in these developing areas.

Globalization has also become a key element in the inorganic chemicals sector. About one-third of the inorganic chemicals produced in the United States are exported, primarily to Canada, Japan, Mexico and Asia. About one-third of these total exports go to Asia, although they have been affected recently by economic slowdowns in the region (DOC 1999).

Foreign trade is an important aspect of the agricultural chemicals sector, representing about a third of shipments from U.S. manufacturers. China is the largest importer of U.S. fertilizers (30 percent), followed by the Asian Pacific markets (33 percent) and Latin America (25 percent). Despite their fluctuating economies, the developing countries, particularly Asia and Latin America, are high-growth markets for U.S. fertilizers (DOC 1999).

The North American Free Trade Agreement (NAFTA) and the Uruguay Round of the General Agreement on Tariffs and Trade (GATT) have reduced trade barriers and helped contribute to increased competition. U.S. firms are adapting by increasing their emphasis on specialty chemicals and higher value-added products (EPA 1995b).

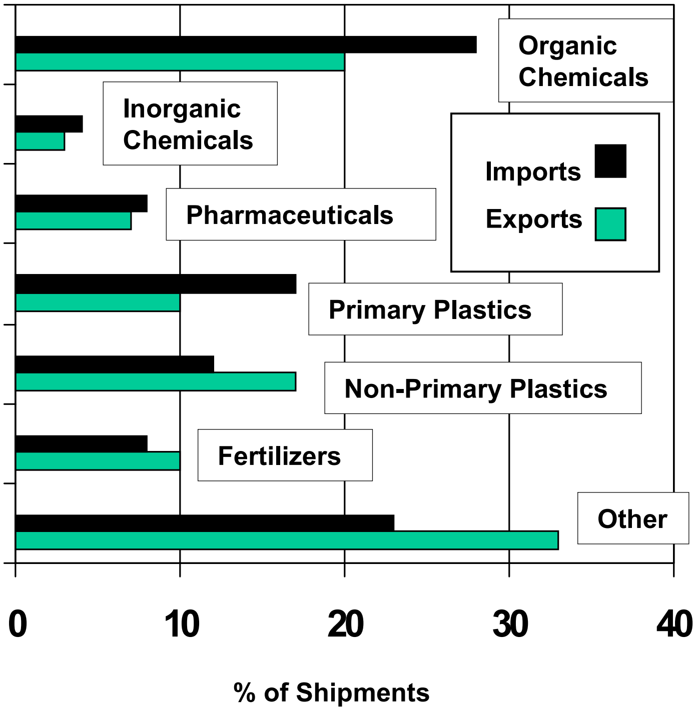


Figure 1-3. U.S. Exports and Imports of Chemicals by Product Area, 19997 (CMA 1998**)**

1.3 Energy and Materials Consumption

Energy Is Used Both as Fuel and Feedstock

In this report, the term “energy”will include energy used to supply heat and power for manufacturing processes as well as energy feedstocks such as natural gas and petroleum used as raw materials to produce a range of petrochemicals, plastics, and synthetic fibers. Moreover, certain chemical, physical, and biological separation and synthesis processes are required to transform these (and other) raw materials into salable products. These in turn consume large amounts of energy in the form of heating, cooling, or electrical power.

According to the most recent Manufacturing Energy Consumption Survey (MECs) conducted by the Energy Information Administration of the U.S. Department of Energy, the U.S. chemical industry consumed 5.051 quads (quadrillion Btu, or 10^{15} Btu) of energy (excluding electricity generating and transmission losses) in 1994 (EIA 1997). This represents about 7 percent of all domestic energy use that year, and approximately 25 percent of all U.S. manufacturing energy use.

The Chemical Manufacturers Association (CMA) also estimates and publishes energy data on the industry, and its most recent study indicates that the chemical industry’s energy consumption was 6.283 quads in 1997 (CMA 1998). Historical data on energy consumption from both CMA and MECs is shown in Tables 1-6 and 1-7 respectively. The discrepancy between these sets of data is attributed to differences in the methods used to collect and estimate the data.

The industry uses a diversity of fuel sources for its energy needs (e.g., electricity, natural gas, coal, crude oil, and derivatives), with nearly 50 percent of the total used as feedstocks. The chemical industry is the largest consumer of natural gas in the United States, requiring more than 10 percent of the total amount used domestically, and accounts for nearly 7 percent of all U.S. petroleum products consumed (equivalent to about 1.5 million barrels of oil per day). Table 1-8 provides a breakdown of the chemical industry’s energy use by fuel type and feedstock category for 1997.

Although they vary widely from product to product, energy expenditures can represent a significant portion of manufacturing costs in the chemical industry. For some products, energy for heat, power, and feedstocks can consume up to 85 percent of total production costs. In 1997 the industry spent about $29 billion on energy for all purposes, including feedstocks. These energy expenditures, however, represent only 9 percent of the value of chemical shipments. Purchases of fuels and electric energy across the industry for heat and power are shown in Figure 1-4, based on data from the Bureau of the Census (DOC 1998).

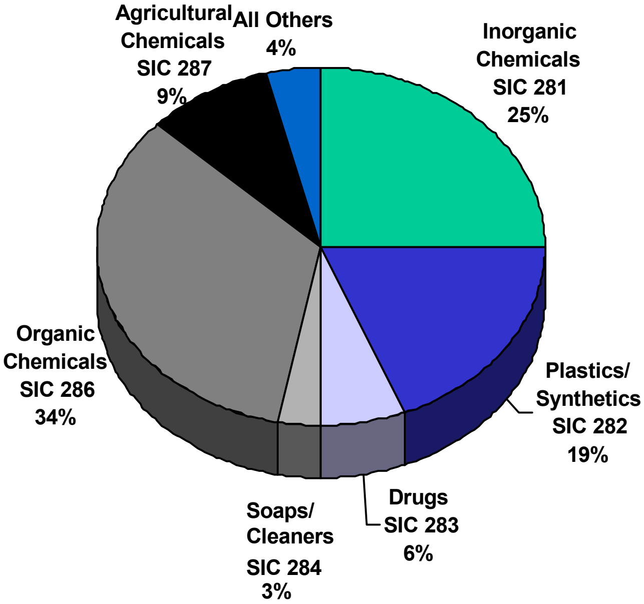


Figure 1-4. Purchases of Fuel and Electric Power in the U.S. Chemical Industry (SIC 28), by Industry Segment - 1996 (DOC 1998)

Table 1-6. U.S. Chemical Industry (SIC 28) Energy Use 1987–1997; CMA Estimates (Trillion Btu)

Year	Fuels	Purchased Electricity	Feedstocks	Net Energy Use	Electricity Losses[a]	TOTAL ENERGY USE
1987	2,014	409	2,215	4,638	850	5,488
1988	2,124	423	2,332	4,879	879	5,758
1989	2,153	444	2,290	4,887	922	5,809
1990	2,214	454	2,488	5,156	943	6,099
1991	2,200	474	2,610	5,284	985	6,269
1992	2,264	488	2,689	5,441	1014	6,455
1993	2,337	498	2,740	5,575	1035	6,610
1994	2,367	522	2,899	5,788	1084	6,872
1995	2,465	515	2,852	5,832	1070	6,902
1996	2,499	540	3,042	6,081	1122	7,203
1997	2,489	545	3,248	6,282	1132	7,414

[a] Electricity losses incurred during the generation, transmission, and distribution of electricity are based on a conversion factor of 10,500 Btu/kilowatt-hour.
Source: CMA 1998.

Table 1-7. U.S. Chemical Industry (SIC 28) Energy Use, 1985, 1988, 1991, and 1994: MECS Estimates (Trillion Btu)

Year	Fuels	Purchased Electricity	Feedstocks	Net Energy Use	Electricity Losses[a]	TOTAL ENERGY USE
1985	1,781	432	1,354	3,567	897	4,464
1988	2,266	416	1,678	4,360	864	5,224
1991	2,253	440	2,358	5,051	914	5,965
1994	2,345	520	2,463	5,328	1,080	6,408

[a] Electricity losses incurred during the generation, transmission, and distribution of electricity are based on a conversion factor of 10,500 Btu/kilowatt-hour.
Sources: EIA 1988, 1991, 1994b, 1997.

Table 1-8. U.S. Chemical Industry (SIC 28) Energy Use by Fuel and Feedstock Category, 1997 (Trillion Btu)

Energy Used for Heat and Power		
Electricity (excludes losses)	545	18%
Natural Gas	1,927	64%
Coal and Coke	250	8%
Fuel Oil and LPG	61	2%
Other	251	8%
TOTAL	3,034	100%
Feedstock Energy		
Liquefied Gases	1,106	34%
Heavy Liquids	1,513	47%
Natural Gas	598	18%
Coal	32	1%
TOTAL	3,248	100%

Sources: EIA 1997, CMA 1998.

On-Site Cogeneration and Direct Generation Supply One-Fourth of Industry's Electricity for Manufacturing

Electricity for chemical manufacturing can be purchased from utilities and independent power producers, or it can be produced on-site by **cogeneration** or **direct generation**. Cogeneration is the co-production of electricity and process heat. Cogenerating systems use fossil fuels or other combustibles (e.g., wood, process wastes) to power a gas or steam turbine, which runs a generator to produce electricity. Waste heat that is otherwise discarded is captured to produce steam for process needs and to power steam turbines to generate additional electricity.

Chemical plants are second only to pulp and paper mills as the largest industrial cogenerators in the manufacturing sector. Electricity produced by cogeneration often provides a competitive advantage to purchased electricity, since efficient systems can operate at greater than 90 percent thermal efficiency compared to 30–35 percent efficiency for direct generation. If pertinent regulations allow, any excess electricity can be sold back to the utility, providing additional cost benefits to the chemical plants.

As illustrated in Figure 1-5, the cogeneration capacity in chemical plants more than doubled between 1985 and 1994, with the electricity supplied by cogeneration systems increasing an average of 14 percent per year. This has helped improve the chemical industry's efficiency and profitability (CE 1992a, EIA 1997).

Table 1-9 shows how the demand for electricity is currently met in six of the chemical segments that are significant cogenerators or direct generators of electricity. Most cogenerating capacity is found in four segments: Plastics Materials and Resins, Organic Chemicals, Inorganic Chemicals, and Fertilizers.

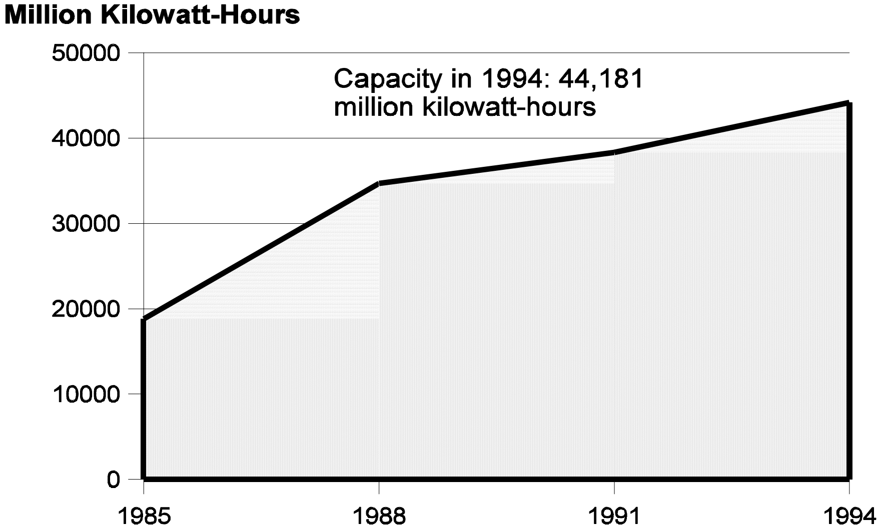


Figure 1-5. Trends in Cogeneration Capacity in the Chemical Industry
(CE 1992a, EIA 1997)

Table 1-9. Components of Electricity Use in the U.S. Chemical Industry, 1994: Selected Segments (Million Kilowatt-hours)

Segment	Purchased Electricity	Cogeneration	Direct Generation	Sales/Transfers Off-site	Total Demand
SIC 2813 Industrial Gases	23,525	512	-	-	24037
SIC 2819 Industrial Inorganic Chemicals	42,861	2,794	283	622	45,315
SIC 2821 Plastics Materials and Resins	16,976	4,616	36	568	21,060
SIC 2865 Cyclic Crudes and Intermediates	4,794	817	1	5	5,607
SIC 2869 Industrial Organic Chemicals	22,537	23,522	2,072	3,751	44,380
SIC 2873 Nitrogenous Fertilizers	3,851	653	35	14	4,505
SIC 2874 Phosphatic Fertilizers	2,185	2,963	-	1,053	4,095

Source: EIA 1997.

Fuel and Feedstock Use Vary Considerably among Industry Segments

With thousands of processes used to produce the more than 70,000 products of the chemical industry, it is not surprising that manufacturing energy use varies significantly among different segments of the industry.

Within individual industry segments, energy use is closely tied to product configurations and whether fuels are used as a raw material (feedstock). Inorganic chemicals (alkalies and chlorine compounds, industrial gases, acids, salts of aluminum, bauxite, sodium, and other minerals) are not usually produced from energy feedstocks (with the exception of urea). Since they do not contain organic carbon, they are made primarily from mineral ores taken from the earth or through the liquefaction of air.

Organic chemicals, on the other hand, begin with raw materials that contain hydrocarbons, such as crude oil derivatives, natural gas, and coal. Large manufacturing plants producing primary olefins (e.g., ethylene, propylene, butadiene) require a substantial and reliable supply of petroleum-based feedstocks–gas oil, naphtha, propane, or ethane. These plants are often located near petroleum refineries to ensure an adequate supply of these materials.

Availability of feedstock is a primary concern for many chemical producers. The industry is highly susceptible to volatility in price and supply of energy feedstocks, a fact made evident during the oil embargo of 1973. The U.S. chemical industry posted a substantial trade surplus of more than $21 billion in 1995, but imports of large quantities of energy-based organic chemicals grew sharply in the last five years and this trend is continuing. To reduce the risk of interruptions in feedstock supply, chemical companies are examining ways to become more flexible in their choice of feedstocks, for example, by shifting from gas feeds to oil feeds. Some firms are also investigating the use of renewable resources such as biomass and processing wastes as alternative feedstocks.

Feedstock requirements can also be reduced by increasing conversion efficiencies and product yields. Some firms have accomplished this by implementing better process monitoring and control. For example, they choose to more accurately control the distillation process in order to decrease both feedstock and fuel requirements. This may also be achieved through new, more efficient production processes. A good example is the direct production of acetaldehyde from ethylene, rather than through a process that converted ethane to ethylene to ethanol and finally to acetaldehyde, as carried out prior to 1980. The direct process has resulted in a 15 percent improvement in the acetaldehyde-to-ethane yield ratio (EEA 1983).

Figure 1-6 compares the use of feedstock energy with the use of fuels for producing heat and power by the major segments of the chemical industry. It is clear that the segments producing organic chemicals depend on feedstock most heavily. Not all 4-digit SICs are represented in Figure 1-6, only those for which energy data is available or significant.

Figure 1-6 shows that the use of energy feedstocks was significant (between 25 and 55 percent) in three major chemical segments in 1994. Within these segments, primary energy feedstocks as well as intermediate products manufactured from primary energy feedstocks comprise a large portion of the raw materials used.

2821 Plastics Materials and Resins. Within this segment, natural gas, still gas (gas produced by distillation processes and comprised mostly of methane and other light gases), and a variety of organic intermediates derived from energy feedstocks are used as building blocks in the production of polymers, elastomers, and synthetic resins.

A breakdown of the primary raw materials used in this segment is shown in Table 1-10, based on the latest Census of Manufactures (1992). Major organic intermediates consumed include ethylene, propylene, and vinyl monomers (chloride and acetate). The use of energy-based intermediate feedstocks accounts for a substantial 73 percent of raw material costs in this segment.

SIC 2865 Cyclic Crudes and Intermediates. This segment consumes natural gas and other hydrocarbons as well as a number of organic and inorganic intermediates to produce aromatic organic chemicals (benzene, toluene, naphthalene), and organic dyes and pigments. The products from this segment are subsequently used in the production of a myriad of consumer products ranging from packaging to paints to pharmaceuticals.

As shown in Table 1-11, organic intermediates and hydrocarbon gases account for a large share of raw material costs (66 percent). Organic chemicals (benzol, xylenes, acetone, other cyclic crudes) account for the largest portion of energy-based feedstocks (about 54 percent).

SIC 2869 Industrial Organic Chemicals. This very diverse segment consumes large quantities of natural gas and other energy-based organic intermediates to manufacture high-volume commodity chemicals that are used as intermediates in many chemical processes. The most important products manufactured include ethylene, butylene, butadiene, alcohols and many other solvents, rubber processing chemicals, plasticizers, and organic acids.

As shown in Table 1-12, hydrocarbon gases account for a large share of energy-based raw materials used in this segment (37 percent).

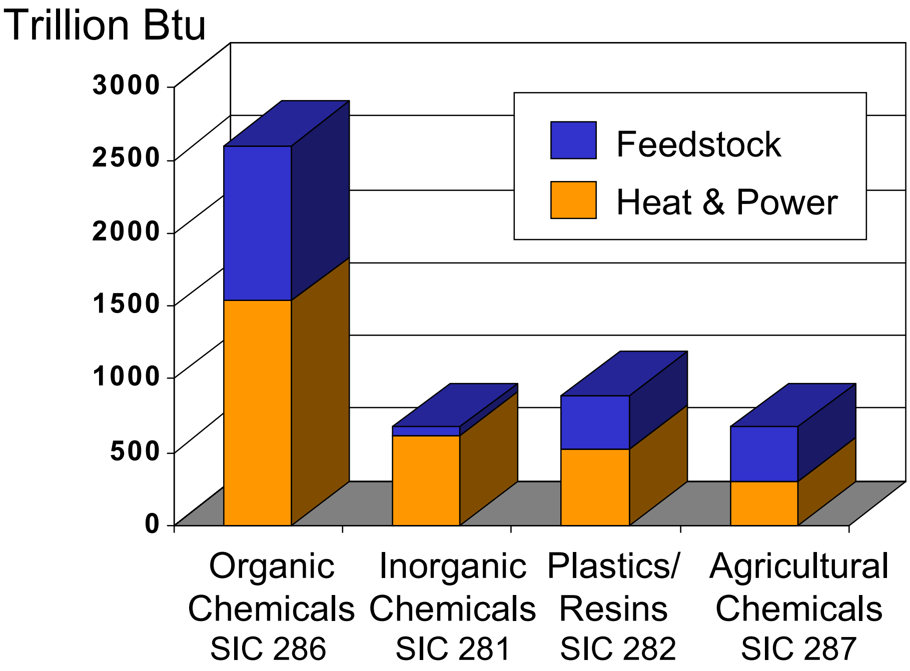


Figure 1-6. Fuel Versus Feedstock Consumption in Selected Chemical Industry Segments, 1994 (Source: EIA 1997)

Table 1-10. Feedstock and Materials Use in SIC 2821, Plastics Materials and Resins (1992)

Material	Delivered Cost ($millions)	% of Total Raw Materials Cost
Total Raw Materials and Supplies	**$16,946.8**	**100**
Hydrocarbons used as raw materials or feedstocks:		
Natural gas, ethane, ethylene, propane, propylene, butane, butylene, and others	4,867.5	29
Synthetic organic chemicals:		
Styrene	1,345.6	8
Other cyclic crudes and intermediates (phenol, benzene, others)	920.0	6
Alcohols	188.3	1
Organic dyes	22.8	<1
Acrylates and methacrylates, monomers	774.8	4
Vinyl chloride monomer	1,017.6	6
Vinyl acetate monomer	278.8	2
Rubber processing chemicals	194.5	1
Other organics (acrylonitrile, formaldehyde, etc)	1,986.3	12
Plastic resins (granules, pellets, powders)	620.1	4
Carbon Black	14.5	<1
TOTAL ENERGY-BASED RAW MATERIALS	**12,230.8**	**73**
Inorganic chemicals	412.6	2
Miscellaneous packaging	4303.4	26
TOTAL NON-ENERGY BASED RAW MATERIALS	**4,716.0**	**28**

Source: DOC 1995b, *Industry Series, Plastics Materials, Synthetic Rubber, and Manmade Fibers*.

Synthetic organic chemicals (alcohols, aromatics, other solvents) are also consumed in large quantities (24 percent of total raw materials). Overall, the use of energy-based raw materials represents about 61 percent of total raw material costs in this segment. In terms of Btus, this segment is the largest consumer of energy feedstocks and combustible energy for heat and power in the chemicals industry.

SIC 2873 Nitrogenous Fertilizers. The primary energy feedstock used in this segment is natural gas, which is necessary for the production of ammonia, a major component in nitrogenous fertilizers. This segment also relies on already-manufactured ammonia, which is purchased or is available from on-site inventories. As shown in Table 1-13, a substantial portion of the raw material costs for this segment–67 percent– is derived from the combined use of natural gas and manufactured ammonia. Inorganic materials including phosphate compounds, potassic compounds, inert fillers, sulfur, and sulfuric acids also comprise a portion of this segment's raw material costs.

Table 1-11. Feedstock and Materials Use in SIC 2865, Cyclic Crudes and Intermediates (1992)

Material	Delivered Cost ($millions)	% of Total Raw Materials Cost
Total Raw Materials and Supplies	**$5,604.1**	**100**
Hydrocarbons used as raw materials or feedstocks:		
Natural gas, ethane, ethylene, propane, propylene, butane, butylene, and others	673.5	12
Organic chemicals:		
Alcohols	54.2	1
Benzol	436.5	8
Tar, crude	131.3	2
Other cyclic crudes and intermediates	517.0	9
Other organics	760.8	14
Plastic Resins	7.7	<1
Other energy feedstocks, nec	455.2	8
TOTAL ENERGY-BASED RAW MATERIALS	**3,036.2**	**54**
Inorganic chemicals (acids, sulfur, chlorine)	350.9	6
Industrial gases	20.6	<1
Miscellaneous Materials	2,196.4	39
TOTAL NON-ENERGY-BASED RAW MATERIALS	**2,567.9**	**46**

Source: DOC 1995b, *Industry Series, Industrial Organic Chemicals.*

Table 1-12. Feedstock and Materials Use in SIC 2869, Industrial Organic Chemicals (1992)

Material	Delivered Cost ($millions)	% of Total Raw Materials Cost
Total Raw Materials and Supplies	**$26,535.5**	**100**
Hydrocarbons used as raw materials or feedstocks:		
Natural gas, ethane, ethylene, propane, propylene, butane, butylene, and others)	9,742.7	37
Organic chemicals:		
Alcohols	1,183.8	5
Toluene and xylenes	657.9	2
Benzol	573.8	2
Phenol	481.8	2
Other cyclic crudes and intermediates	698.2	3
Acetone	175.1	1
Other synthetic organic chemicals	2,382.3	9
TOTAL ENERGY-BASED RAW MATERIALS	**15,895.6**	**61**
Inorganic chemicals (acids, ammonia, chlorine, caustic soda)	1,780.4	6
Industrial gases	162.1	1
Miscellaneous Materials	8,697.3	32
TOTAL NON-ENERGY-BASED RAW MATERIALS	**10,639.8**	**39**

Source: DOC 1995b, *Industry Series, Industrial Organic Chemicals.*

Table 1-13. Feedstock and Materials Use in SIC 2873, Nitrogenous Fertilizers (1992)

Material	Delivered Cost ($millions)	% of Total Raw Materials Cost
Total Raw Materials and Supplies	$1,189.4	100
Natural gas	514.2	43
Ammonia and ammonia compounds	287.0	24
TOTAL ENERGY-BASED RAW MATERIALS	**801.2**	**67**
Inorganic chemicals (phosphatic materials, potassic materials, sulfuric acid, sulfur, phosphate rock)	59.8	5
Miscellaneous Materials	328.4	28
TOTAL NON-ENERGY-BASED RAW MATERIALS	**388.2**	**33**

Source: DOC 1995a, *Industry Series, Agricultural Chemicals.*

Minerals Are Also Important Feedstocks in Chemicals Production

The chemical industry is one of the largest consumers of minerals in the United States, using about $6 billion worth of minerals as raw materials for a wide variety of chemical products in 1995. The actual quantities of minerals consumed in 1995 are shown in Table 1-14. Phosphate, salt, sulfur, potash, lime, and gypsum account for about 98 percent of the minerals used (CMA 1996)

Table 1-14. Chemical Industry (SIC 28) Minerals Use (1995)

Mineral	Quantity (1000 tons)
Phosphate	52,645
Salt	21,850
Sulfur	13,405
Potash	9,970
Lime	4,935
Gypsum	3,340
Clay	1,455
Titanium	880
Fluorspar	435
Bauxite	280
Talc	235
Zinc	225
Magnesium	210
Diatomite	140
Bromine	75

Source: CMA 1996.

Improvements in Energy Efficiency Are Relatively Flat

The U.S. chemical industry has made significant improvements in energy efficiency over the last two decades. As shown in Figure 1-7, energy consumed for heat and power per unit of output declined by more than 39 percent between 1974 and 1995, a trend that was precipitated by the oil crises of 1973 (CMA 1996). Improvements in efficiency have remained relatively flat, however, since the late 1980s, primarily because of the availability of inexpensive energy for heat, power, and feedstocks. When energy prices are low, investments made to improve energy efficiency are far less attractive than investments made to increase market share (such as new product development). Figure 1-7 reflects trends in fuels purchased for heat and power, and does not reflect trends in feedstock consumption.

Much of the improved efficiency achieved over the last two decades has resulted from aggressive energy management and housekeeping programs instituted during the early 1970s, which are now an integral and established part of operations management at many firms. Many of these housekeeping improvements have focused on steam generation and distribution and operating practices for fueled reactors and fired heaters.

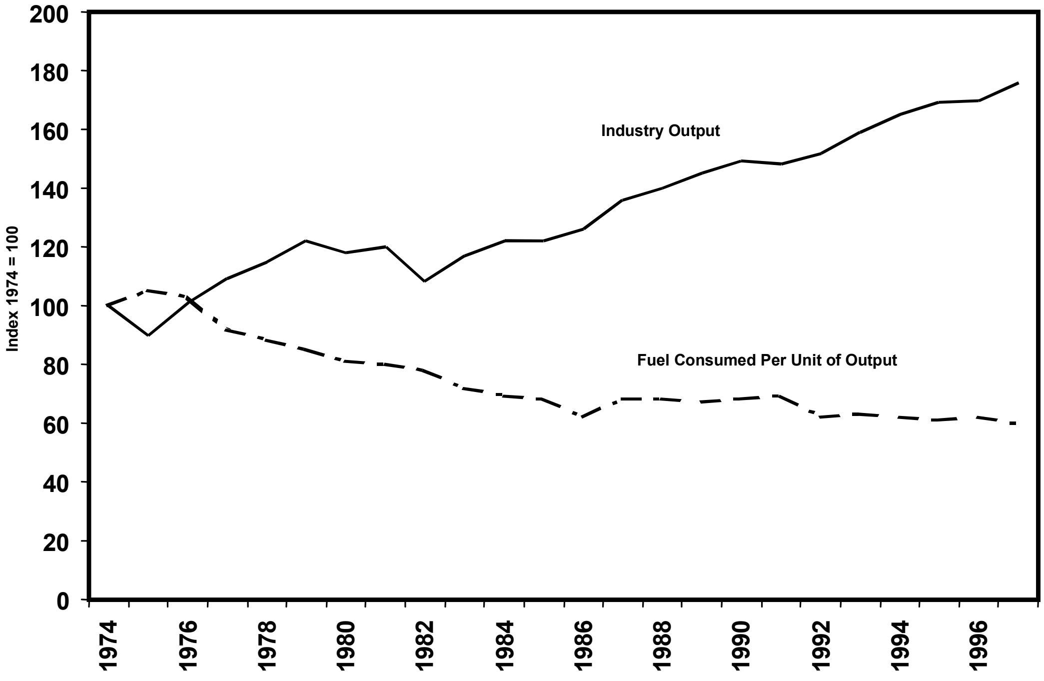


Figure 1-7. Energy Intensity Trends Related to Heat and Power in the U.S. Chemical Industry, 1974 - 1997 (Source: CMA 1998)

Improvements in process and equipment design have also contributed to gains in energy efficiency (e.g., more efficient designs for distillation, absorption, and other separation processes). The increased adoption of energy-efficient practices such as cogeneration and on-site recovery of waste heat and energy, including heat recovery from exothermic reactions, have also helped to reduce overall energy intensity.

More recent gains in energy and material efficiency have resulted from the realization that waste minimization could help decrease the cost of environmental compliance. (End-of-the-pipe waste treatment and disposal options often carry a heavy energy burden.) However, as regulations grow more stringent, the largest percentage of funds continues to be diverted toward non-productive investments on end-of-the-pipe controls to avoid the penalties of non-compliance.

Nonetheless, further efficiency gains could play an important role in the industry's ability to maintain its competitive edge in global markets. The increasing complexities of environmental compliance, changing product configurations, and growing competition from resource-rich developing countries are all challenges to the industry. These challenges can be met in part through improved efficiency, the use of innovative processing routes, and decreased dependence on petroleum-based feedstocks.

Many of the low-cost, high-return investments (e.g., housekeeping, improved operating practices) have already been made. Further gains may require more dramatic changes in process design and in innovative R&D.

Chemical Process Efficiency Is Limited by Thermodynamic and Other Constraints

The efficiency of any individual process used in chemicals manufacture is dependent on optimizing a number of process variables (e.g., temperature, pressure) that may be constrained by thermodynamic, kinetic, or transport limitations. Thermodynamic limitations, for example, dictate allowable conversions for catalytic reactions, requiring that several passes be made over the catalyst before an acceptable yield is obtained. These additional passes require energy for heating/cooling or separating the feedstocks, which increases energy intensity.

Thermodynamic constraints also place practical limits on many commonly used separation processes such as distillation. Some reactions are kinetically limited due to the production of unwanted byproducts. Transport limitations arise with some highly exothermic reactions as heat is generated at a faster rate than it can be effectively removed.

Chemical processing is further complicated by the fact that a series of unit operations is often required to reach the final end product. For example, ammonia is produced by the Haber process, which converts air and methane to ammonia and carbon dioxide. In this process, methane and air must first be passed through a steam reformer to yield hydrogen and nitrogen gas along with carbon dioxide. These gases must then be passed through a separator to remove the carbon dioxide.

Once this is accomplished, the hydrogen and nitrogen gases are sent to a catalytic reactor where they require about four passes over a catalyst to attain a yield of about 88 percent ammonia. The energy efficiency of this process depends on the combined efficiency of all these operations, as well as the operating conditions within individual plant sites.

Given these complexities, it is often difficult to accurately assess the overall efficiency of chemical processes. Typically, a range of energy intensities is reported in the literature based on actual operating experiences. While this can provide an average assessment of energy requirements, it gives little insight into potential efficiency gains. Theoretically, minimum energy requirements for producing any chemical can be determined based on the net chemical reaction used to produce the chemical. While this technique does not consider the individual unit operations and auxiliary equipment requirements, it may provide a simplistic gauge for evaluating the efficiency of actual operating practices.

A study done several years ago by Argonne National Laboratory (ANL 1991) compared the theoretical minimum energy requirements for producing 31 of the top 50 chemicals with published ranges of production energy intensity. In this study, theoretical minimum energy requirements were derived by determining the reversible work for the reaction, based on Gibbs free energy at ambient conditions. (See the sidebar on the next page for further explanation of minimum theoretical energy and Gibbs free energy.) The actual net production energy intensity (Btu/ton) was then compared with theoretical energy intensity to determine efficiency as a percent of the theoretical minimum requirements. For exothermic processes that produce energy, energy requirements were determined based on the percentage of available energy that was not recovered.

Figures 1-8 through 1-11 show the theoretical versus the actual energy requirements for producing various chemicals that were determined during this study (ANL 1991 and updates). These chemicals represent four different 4-digit SICs. These results illustrate that a range of efficiencies occurs within all chemical segments.

By calculating the difference between the minimum theoretical energy required and the energy consumed in practice, it is possible to estimate the potential energy savings if these chemicals were produced under “minimized” or ideal conditions. However, in commercial applications, it is unlikely that ideal conditions can be achieved. Moreover, energy beyond the theoretical minimum will be required to operate auxiliary equipment such as pumps, compressors, and fans, and to carry out other unit operations such as separations to recover the final product.

Finally, there are always some irreversibilities associated with chemical reactions as well as heat transfer operations that place practical and economic limitations on reaching the minimum theoretical energy use.

Keeping these limitations in mind, the results of this study still provide a preliminary analysis of the potential for improved energy efficiency and reduced energy consumption. Figure 1-12 compares theoretical and actual energy requirements using this methodology, broken out by 4-digit SIC codes. The graph shows there is considerable room for improvement in many chemical processes.

The largest potential for energy savings is evident in the organic chemicals segment, which relies heavily on energy-based feedstocks. This segment accounts for production of high volume chemicals (e.g., ethylene, propylene, benzene) that are important as intermediates in many other chemical processes. The difference between actual and theoretical energy requirements in this segment (for the selected chemicals reviewed in the study) is nearly 80 million Btu per ton of product.

The inorganic chemicals segment exhibits the next highest potential, primarily because sulfuric acid, nitrogen, oxygen, and lime are among the top five chemicals produced in the United States. Given their volume of production, energy inefficiencies in the processes used to produce these chemicals can have a significant impact on energy use. Energy dependence in these segments is on fuels used for heat and power rather than feedstock energy. The difference between actual and theoretical energy requirements in this segment (for the chemicals reviewed) is about 30 million Btu per ton of product.

The agricultural chemicals segment, which included some of the most inefficient chemical processes, such as production of ammonium

Minimum Theoretical Energy and Gibbs Free Energy

Minimum theoretical energy *can be defined as the minimum energy required to synthesize a substance in its standard state from substances also in a standard state*. It can also be defined as the maximum work or available energy that can be attained when the substance is brought from its standard state to complete thermodynamic equilibrium. A system closed to heat and mass transfer is at thermal equilibrium if there are no temperature gradients in the system. A closed system is at thermal equilibrium if no pressure gradients exist. The closed system is in chemical equilibrium if it is in mechanical and thermal equilibrium, and no work can be derived at the given system temperature and pressure.*

The concept of equilibrium is closed associated with the idea of spontaneity of a chemical reaction: when will a chemical reaction occur in a closed system without the addition of heat or work? For a long time it was believed that a chemical reaction was spontaneous if the reaction was exothermic (heat releasing) at a fixed temperature and pressure. In the 1870's J.W. Gibbs showed that this idea was not complete, since heat may be derived from a chemical reaction even though work may not be derived from that heat at the system temperature and pressure. Gibbs thus defined the ***free energy*** *of a system at a fixed temperature and pressure as the work that was capable of being extracted (or the amount of work needed to bring the system to equilibrium).*

For a chemical reaction, minimum theoretical energy (or maximum work) can be calculated based on the change in Gibbs Free Energy (ΔG) occurring during the reaction, assuming both reactants and products are in their standard states (GIBBS 1961). In short, the equilibrium state of the chemical system is that state for which total Gibbs Free Energy is a minimum with respect to all possible changes at a given temperature and pressure. The following equations define the relationship between optimum work and Gibbs Free Energy:

$$\text{Work} = -(\Delta G_{\text{products}} - \Delta G_{\text{reactants}})$$

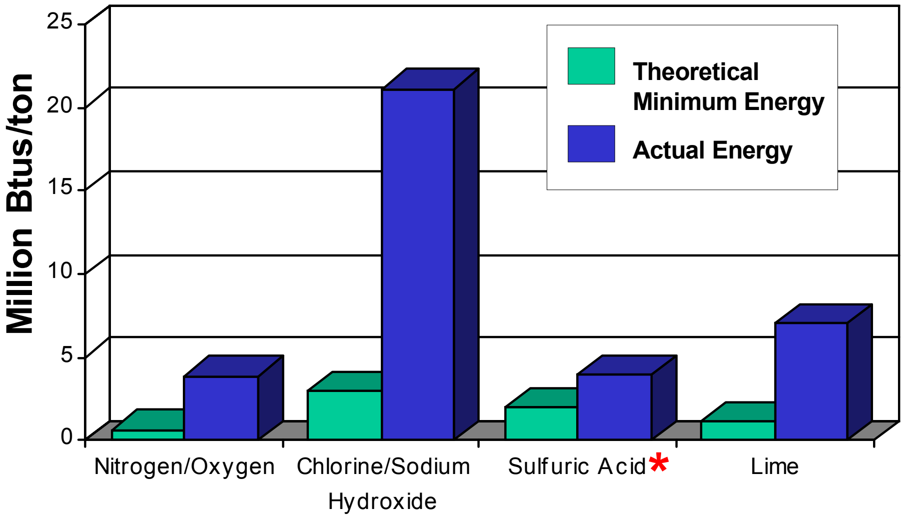
$$\text{and } \Delta G = \Delta H - T(\Delta S)$$

H = the heat of the reaction
S = the entropy of the system.

A negative result indicates that the chemical reaction requires work (energy); a positive result indicates that net work (energy) is produced by the chemical reaction.

**A standard state at ambient temperature and pressure is commonly used to calculate theoretical minima based on Gibbs Free Energy.*

nitrate and urea, scored low in terms of energy savings potential. This occurred because the agricultural chemicals are produced in less volume using comparatively lower energy-intensity processes, compared to chemicals in other segments. The difference between actual and theoretical energy requirements in this segment (for the chemicals reviewed) is about 26 million Btu per ton of product.



*Energy Generated (Exothermic)

Figure 1-8. Theoretical vs. Actual Energy Requirements for SIC 281, Industrial Inorganic Chemicals (ANL 1991)

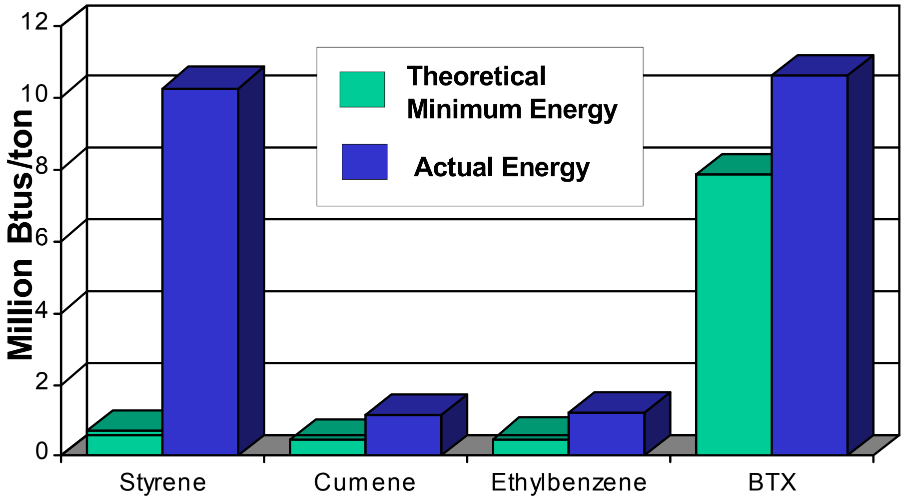


Figure 1-9. Theoretical vs. Actual Energy Requirements for SIC 2865,Cyclic Crudes and Intermediates (ANL 1991)

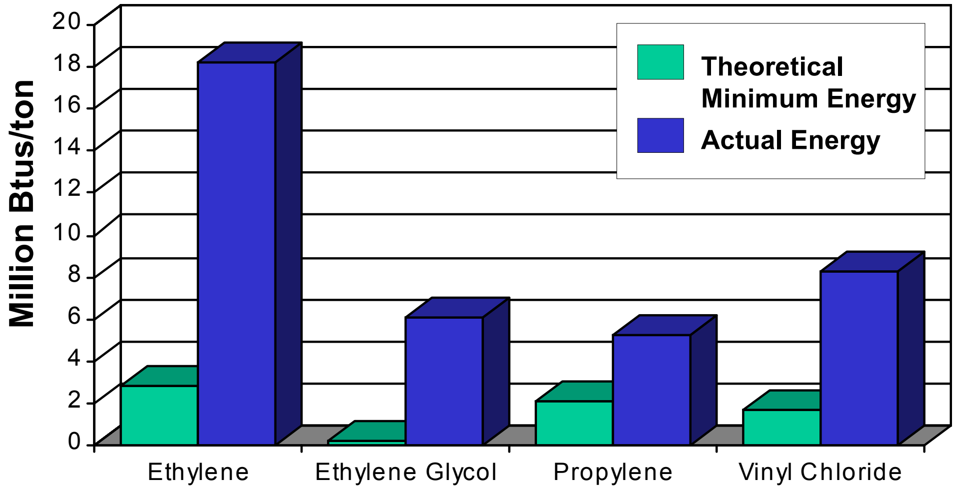


Figure 1-10. Theoretical vs. Actual Energy Requirements for SIC 2869, Industrial Organics (ANL 1991)

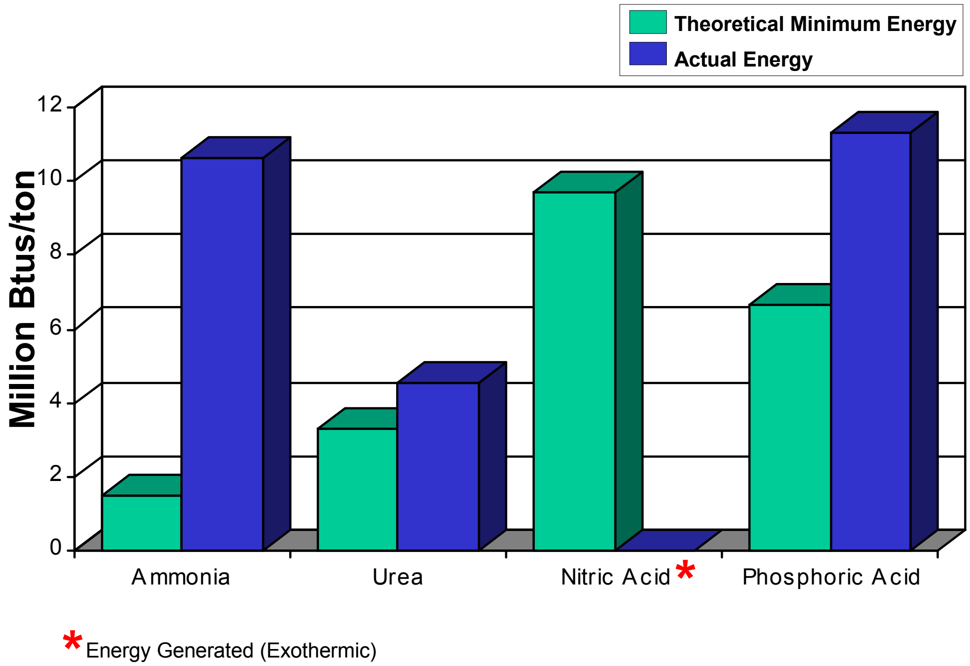


Figure 1-11. Theoretical vs. Actual Energy Requirements for SIC 287, Agricultural Chemicals (ANL 1991)

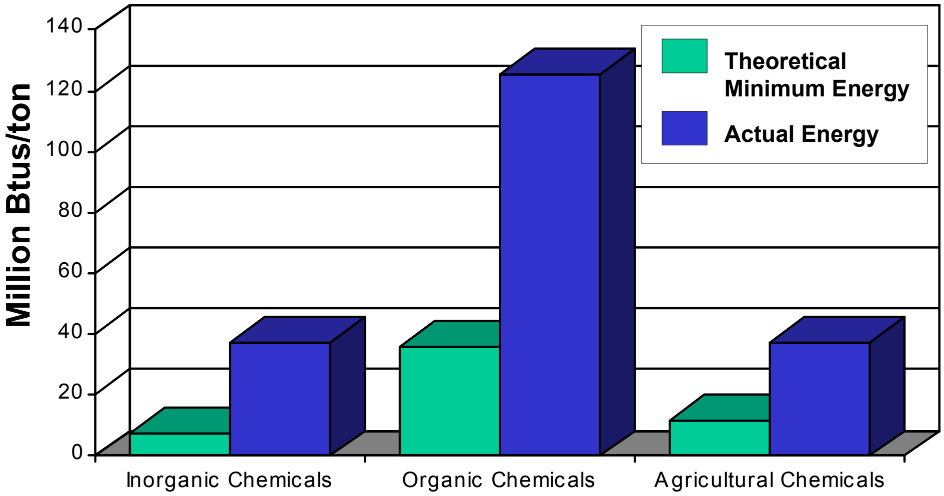


Figure 1-12. Potential Energy Savings - Theoretical Energy Minima Versus Operating Practice (ANL 1991)

Several other studies have also examined the potential for energy savings in production of the top 50 chemicals. One study by Pacific Northwest National Laboratory (PNNL), which ranked the top 50 chemicals by energy intensity, energy consumption, revenues, and other parameters, identified process inefficiencies in a number of areas (PNNL 1994). The top 20 chemicals ranked by the study in terms of total energy consumption are shown in Table 1-15.

It should be noted that the energy intensities used for this study were based on average process and feedstock energy requirements, not on the measured values for actual operations. In fact, in 1993, the total energy consumption for these 20 chemicals was higher than the estimated consumption value for the entire segment for that year, as reported by CMA. Part of the discrepancy can be attributed to PNNL's use of average energy intensity values, which do not account for differences between plant sites.

The study does, however, provide a means for ranking chemical production by the approximate level of energy consumed. A companion study (see Table 1-16) examined the potential for energy savings achievable through improved catalytic processes (PNNL 1995). This study identified the loss of 830 trillion Btu of energy due to process inefficiencies during the production of 30 major chemicals. The study also discovered that over $2 billion were spent to purchase feedstocks that were subsequently converted to waste.

Table 1-15. Energy Consumed in Production of Major Chemicals, PNNL Estimates (Trillion Btus)

Chemical	Rank	Energy for Heat and Power	Feedstock Energy	Total Energy
Ethylene	1	400	1010	1410
Ammonia	2	290	460	750
Propylene	3	160	540	700
Benzene	4	10	420	430
Vinyl Chloride	5	100	300	400
Sodium Hydroxide	6	380	0	380
Styrene	7	50	280	330
Ethylbenzene	8	10	310	330
Ethylene Dichloride	9	30	290	320
Methy t-Butyl Ether	10	60	240	300
Urea	11	20	220	240
Chlorine	12	230	0	230
p-Xylene	13	60	140	200
Phosphoric Acid	14	150	50	200
Phenol	15	20	160	180
Ammonium Nitrate	16	30	150	180
Terephthalic Acid	17	30	140	170
Ethylene Oxide	18	0	160	160
Carbon Black	19	40	120	160
Butadiene	20	70	80	150
TOTAL ENERGY CONSUMED: 7,220 Trillion Btu				

Source: PNNL 1994.

Table 1-16. Potential Energy Savings through Improved Catalysts, PNNL Estimates (trillion Btus)

Chemical	Rank	Total Energy Savings
Ammonia	1	294
Propylene	2	98
p-Xylene	3	94
Butadiene	4	81
Vinyl Chloride	5	44
Methanol	6	37
Ethylene Oxide	7	29
Acrylonitrile	8	24
Adipic Acid	9	20
Styrene	10	20
Vinyl Acetate	11	16
Propylene Oxide	12	16
Phenol	13	12
Ethylene Dichloride	14	11
Acetone	15	8
Terephthalic Acid	16	8
Formaldehyde	17	6
Ethylbenzene	18	4
Cumene	19	3
Acetic Acid	20	2
Nitric Acid	21	1
MTBE	22	1
Caprolactam	23	1
Ethylene Glycol	24	1
Sulfuric Acid	25	1
Isobutylene	26	0.3
TOTAL ESTIMATED ENERGY SAVINGS: 832.2 Trillion Btu		

Source: PNNL 1995.

Six Chemical Chains Capture the Most Energy-Intensive Chemicals

The chemical reactions associated with six **chemical chains** account for a substantial share of the energy consumed in the chemical industry. These chains include ethylene, propylene, BTX (benzene-toluene-xylene), butadiene, agricultural chemicals, and caustics. As shown in Table 1-17, roughly 70-80 percent of the products of the chains account for about 54 percent of current energy consumption in the chemical industry. Tables 1-18 through 1-24 illustrate the major products within these chemical chains, and summarize the related energy use, production, and common manufacturing processes involved.

Production data for most chemicals was taken from current statistics published by the Chemical Manufacturers Association (CMA 1998). Data for polymers and a few chemicals was obtained from several other sources (SPI 1998, CHEMX 1999). Data on energy consumption and specific processes was obtained from a number of studies and literature describing licensed technologies (Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999). The data represents estimated, approximate values, based on averages throughout the industry, and may not represent the most current and state-of-the art technologies available for production of these chemicals.

Tables 1-18 through 1-23 help to identify where the largest portion of process energy is consumed throughout the chemical chain, and the distribution of the primary feedstock to various end-products. As shown in Table 1-22, the chain accounting for the most energy consumed annually is **agricultural chemicals**. This is attributed to the large energy requirements for ammonia production, which is a largely inefficient, low-yield process. Other energy-intensive processes in this chain include production of phosphoric acid by the wet process. Overall this chain accounts for about 26 percent of energy use attributed to the six chemical chains.

Table 1-18 illustrates that nearly half of **ethylene** produced is used to manufacture polyethylene, one of the most highly consumed plastics. However, production of polyethylene requires the least processing energy among all of the products produced from ethylene, and accounts

Table 1-17. Summary of Process Energy Use for Six Chemical Chains

Chemical Chain (% of Products Represented)	Estimated Process Energy Use (Trillion Btu/year)
Ethylene (80%)	406
Propylene (73%)	80
BTX (87%)	400
Butadiene (50%)	45
Agricultural Fertilizers (75%)	424
Caustics (100%)	291
TOTAL ESTIMATED ENERGY USE FOR SIX CHAINS	1646
Process Energy Use by the Chemical Industry in 1997	3,034
Percentage of Chemical Industry Use in 1997: ~ 54%	

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-18. Ethylene Chain Production, Processing Energy, and Associated Processes

	% of Ethylene	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
Ethylene 48.3 billion lbs **(8,107 Btu/lb)** *- Steam Cracking* *- Catalytic Hydrogenation* *- Distillation* **Annual Energy Use:** **392 Trillion Btu** **Attributed to chemical industry:** **196 Trillion Btu**	45	Polyethylene (100%) 27.0 billion lbs **(1,178 Btu/lb)** *Addition Polymerization*	---	32
	15	Ethylene Dichloride 20.2 billion lbs **(3,410 Btu/lb)** *Catalytic Chlorination*	Poly Vinyl Chloride (100%) 10.9 billion lbs **(1,246 Btu/lb)** *Addition Polymerization*	83
	20	Ethylene Oxide 7.1 billion lbs **(1,711 Btu/lb)** *Catalytic Oxidation*	Ethylene Glycol (69%) → 5.63 billion lbs **(2,045 Btu/lb)** *- Hydrolysis* *- Distillation* Polyester (56%) 5.9 billion lbs **(12,128 Btu/lb)** *- Condensation Polymerization*	95
	TOTAL ENERGY USE (Including Ethylene)			**406**
	20	Other Products: Vinyl Acetate, Acetaldehyde, Ethanol, Ethylbenzene, Styrene/Polystyrene, Antifreeze		

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-19. Propylene Chain Production, Processing Energy, and Associated Processes

	% of Propylene	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
Propylene 28.7 billion lbs **(1,351 Btu/lb)** *- Steam Cracking* *- Distillation* **Annual Energy Use:** **39 Trillion Btu**	36	Polypropylene 13.3 billion lbs **(514 Btu/lb)** *Liquid Phase or Gas Phase Catalytic Polymerization*	---	7
	20	Propylene Oxide 3.9 billion lbs **(2,557 Btu/lb)** *Epoxidation Reactor*	Propylene Glycol (25%) → Urethane Polyol Ethers 1.1 billion lbs (60%) No Data **(2,045 Btu/lb)** *Direct Hydration, Evaporation, Distillation*	12
	13	Acrylonitrile 3.3 billion lbs **(956 Btu/lb)** *Catalytic Fluidized Bed Reactor*	Acrylic Fibers (42%) 0.44 billion lbs **(21,520 Btu/lb)** *Suspension Polymerization* ABS resins (19%) 1.4 billion lbs **(1,221 Btu/lb)** *Continuous Mass, Emulsion and Suspension Polymerization*	15
	4	Isopropyl Alcohol 1.4 billion lbs **(4,693 Btu/lb)** *Sulfuric Acid Oxidation*	Coating Processes (70%) Pharmaceuticals (15%) Miscellaneous Uses (15%)	7
	TOTAL ENERGY USE (including propylene)			**80**
	27	Other Products: Cumene (see BTX chain), Acrylic Acid & Acrylates, Butyraldehyde		

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-20. BTX (Benzene-Toluene -Xylene) Chain Production, Processing Energy, and Associated Processes

	% of Benzene	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
Benzene 14.9 billion lbs **(1,255 Btu/lb)** *- Steam Cracking* *- Distillation* **Annual Energy Use for BTX:** **40.4 Trillion Btu**	53	Ethyl Benzene 13.9 billion lbs **(1,404 Btu/lb)** *Acid Catalyzed Friedal Crafts Alkylation*	Styrene → Polystyrene (66%) 11.4 billion lbs; 6.4 billion lbs **(16,891 Btu/lb)**; **(2,264 Btu/lb)** *Dehydrogenation, Vacuum Distillation*; *Bulk Polymerization*	228
	22	Cumene 5.8 billion lbs **(696 Btu/lb)** *Catalytic Alkylation*	Phenol/Acetone (100%) → Bisphenol A (35%) 7.3 billion lbs; 1.6 billion lbs **(7,850 Btu/lb)**; **(9,410 Btu/lb)** *Oxidation, Vacuum Separation*	76
	12	Cyclohexane 2.2 billion lbs **(1,743 Btu/lb)** *Catalytic Hydrogenation*	Cyclohexanone → Caprolactam (90%) 1.7 billion lbs **(13,185 Btu/lb)** *Oxime production*	26
	13	Dodecylbenzene, Maleic Anhydride		--
Toluene 8.3 billion lbs (co-produced)	8	Toluene Diisocyanate 0.93 billion lbs **(11,279 Btu/lb)** *Conversion to diamine, then reaction with phosgene*	Polyurethane (85%) 4.6 billion lbs **(138 Btu/lb)** *Continuous process*	11
	92	Benzene (57%), medicines, solvents, high octane gasoline, explosives		--
o-Xylene 1.1 billion lbs (co-produced)	~100	Phthalic Anhydride 1.3 billion lbs (small net producer)	Plasticizers (53%) Unsaturated Polyester Resins (21%)	--
p-Xylene 7.9 billion lbs	~100	Purified Terephthalic Acid (PTA) 10.0 billion lbs **(1,779) Btu/lb)**	Polyester (see ethylene chain)	18
TOTAL ENERGY USE (including BTX)				**400**

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-21. Butadiene Chain Production, Processing Energy, and Associated Processes

	% of Butadiene	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES/PRODUCTS Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
1,3-Butadiene 4.1 billion lbs byproduct of ethylene production (95%) **(95 Btu/lb)** dehydrogenation of butane or butene (5%) **(14,500 Btu/lb)** **Annual Energy Use: 22 Trillion Btu**	30	Styrene Butadiene Rubber (SBR) 2.3 billion lbs **(2,271 Btu/lb)** *Addition Polymerization*	Tires, footwear, coatings, adhesives, carpet backing	5
	20	Polybutadiene 1.6 billion lbs **(11,300 Btu/lb)** *Solution Polymerization*	Tires, blends with SBR	18
	50	Other products: adiponitrile, neoprene rubber, nitrile rubber,styrene butadiene latex		
TOTAL ENERGY USE (including butadiene)				**45**

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-22. Agricultural Fertilizers Chain Production, Processing Energy, and Associated Processes

	% of Feedstock	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
Ammonia 28.4 billion lbs **(12,150 Btu/lb)** *- Steam Reforming* **Annual Energy Use:** **345 Trillion Btu**	50	Urea 11.8 billion lbs **(843 Btu/lb)** *Pressurized Reactor*	Fertilizer (84%)	10
	26	Nitric Acid 13.5 billion lbs **(267 Btu/lb)** *2-Stage Catalytic Oxidation of Ammonia*	Ammonium Nitrate (80%*) → Fertilizer 12.3 billion lbs **(341 Btu/lb)** *Non-catalyzed Reactor Crystallizer*	8
	4	Ammonium Sulfate 4.1 billion lbs **(4,000 Btu/lb)** *Byproduct of Caprolactam Production, Evaporation*	Fertilizer (90%)	16
	4	Ammonium Phosphates 18.9 million lbs **(323 Btu/lb)**	Fertilizer (98%)	6
	2	Superphosphates 3.4 billion lbs **(690 Btu/lb)**	Fertilizer (100%)	3
Sulfuric Acid 71.4 billion lbs **(-900 Btu/lb)** *- Catalytic Sulfur Oxidation* *- Absorption* **Net Energy Producer**	65	Phosphoric Acid Wet Process Fertilizer Grade 19.8 billion lbs **(4,300 Btu/lb)**	Fertilizer (92%)	36
	35	Petroleum Refining (5%) Ore Processing (5%) Other Uses (25%)		-
	TOTAL ENERGY USE (including ammonia and sulfuric acid)			**424**

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

Table 1-23. Chlor-Alkali/Caustics Chain Production, Processing Energy, and Associated Processes

	% of Feedstock	PRIMARY INTERMEDIATE Annual Production (Process Energy) Primary Process(es)	SECONDARY INTERMEDIATES Annual Production (Process Energy) Primary Process(es)	ESTIMATED ANNUAL PROCESS ENERGY (Trillion Btu)
Sodium Chloride (NaCl salt) 17 billion lbs	50	Sodium Hydroxide (Caustic Soda) 22.7 billion lbs **(3,765 Btu/lb)** *Electrolytic Cell*, *Steam Concentration*	Chemical manufacturing, pulp and paper production, soaps and detergents, textiles	86
	50	Chlorine 26 billion lbs **(4,800 Btu/lb)** *Electrolytic Cell*, *Drying and Compression*	Ethylene dichloride/vinyl chloride (38%), polyurethanes (14%), pulp and paper (6%), other uses	125
Trona Ore (sesqui-carbonate) 42.7 billion lbs	~100%	Sodium Carbonate (Soda Ash) 23.7 billion lbs **(3,393 Btu/lb)** Heating of Trona ore	Sodium silicate, sodium tripolyphosphate (for soaps and detergents) Flue gas desulfurization, water treatment, pulp and paper production	80
	TOTAL ENERGY USE (does not include salt or Trona ore mining/production)			**291**

Table 1-24. Comparison of Process Use among Various Chemical Production Chains

Chemical Chain	Processes							
	Distill-ation	Steam Cracking/ Reforming	Electro-lysis	Catalytic Oxidation	Other Catalytic Reactions	Evapor-ation/Hy-dration	Polymeri-zation Reactions	Hydroly-sis
Ethylene	●●	●		●	●●		●●●	●
Propylene	●●	●	●	●●●	●	●●	●●●●	
BTX	●●	●			●●		●●	
Butadiene		●			●		●	
Agricultural Chemicals		●		●●		●		
Caustics			●●					

Key: ● Indicates number of product lines where process is used.

Sources: Sittig 1977, Boustead 1979, ANL 1980, BIO 1988, EEA 1983, PNNL 1994, Brown 1996, Enviro-Chem 1999a-d, HP 1999.

for only about 8 percent of the energy use attributed to the ethylene chain. The ethylene chain accounts for nearly 25 percent of the processing energy represented by the six chains.

The **propylene chain**, on the other hand, accounts for a large amount of annual chemical production but relatively little energy consumption (see Table 1-19). With 73 percent of the chain's products analyzed, overall energy use attributed to this chain is 80 trillion Btu per year, or about 5 percent of total energy use for the six chains.

The **BTX chain**, whose primary products are benzene, toluene, and xylene, is the third largest energy consumer among the six chains, using about 24 percent of the total (see Table 1-20). The production of ethylbenzene and styrene accounts for the largest amount of the energy consumed within this chain, 228 trillion Btu per year. Most of this is attributed to the production of styrene, a very energy-intensive process.

The caustics chain is associated with co-production of **chlorine and sodium hydroxide** (see Table 1-23). This is also an energy-intensive process, and large quantities of these chemicals are produced each year, accounting for a significant portion of the total annual energy use for the six chains, about 13 percent. Production of **sodium carbonate** (soda ash) is less energy-intensive but still consumes a considerable amount of energy because nearly 24 billion pounds are produced annually. Overall the caustics chain accounts for about 18 percent of energy consumed by the six chains.

Over 95 percent of **butadiene** is produced as a co-product of ethylene. The butadiene chain consumes the least amount of energy among the six chains under discussion (see Table 1-21).

Among the chains, energy consumption is roughly split between chemicals that are organic in nature (ethylene, propylene, BTX, butadiene) and those that are inorganic (agricultural chemicals [see Table 1-22], caustics). Processes involving organic chemicals consume about 57 percent of the total energy use represented.

Table 1-24 examines the processes in which the six chemical chains are involved, including processes common to one or more of the chains. Distillation, steam cracking, catalytic oxidation and other catalytic reactions, and various polymerization reactions are common to 60 percent of the chains.

In general, these tables provide another means for identifying targets of opportunity for improving production and energy efficiency. The remainder of this study will examine in more detail the six chemical chains identified, with a focus on their most economically important and energy-intensive products.

1.4 Environmental Overview

The Chemical Industry's Pollutant Emissions Are Decreasing

In recent years the industry has made major advances in protecting the environment as well as the health and safety of its workers. The development of new technologies and investments in new equipment, processes, and practices have contributed in large part to these advances. The industry has also instituted initiatives like Responsible Care®, an industry-wide program that promotes continuous improvements in health, safety, and environmental performance. An additional contributing factor is the myriad of federal and state laws and regulations that have set environmentally strict standards for government, industry, and consumers.

The total amount of toxic releases from the chemical industry declined significantly between 1988 and 1994. The Chemical Manufacturers Association reports that toxic releases of over 300 pollutants by its member companies fell 55 percent between 1988 and 1996, while industrial production during the same period rose by more than 23 percent. Moreover, this improved environmental performance was not achieved by shipping larger quantities off-site for treatment; transfers to treatment facilities also fell 42 percent during the same time period (CMA 1998).

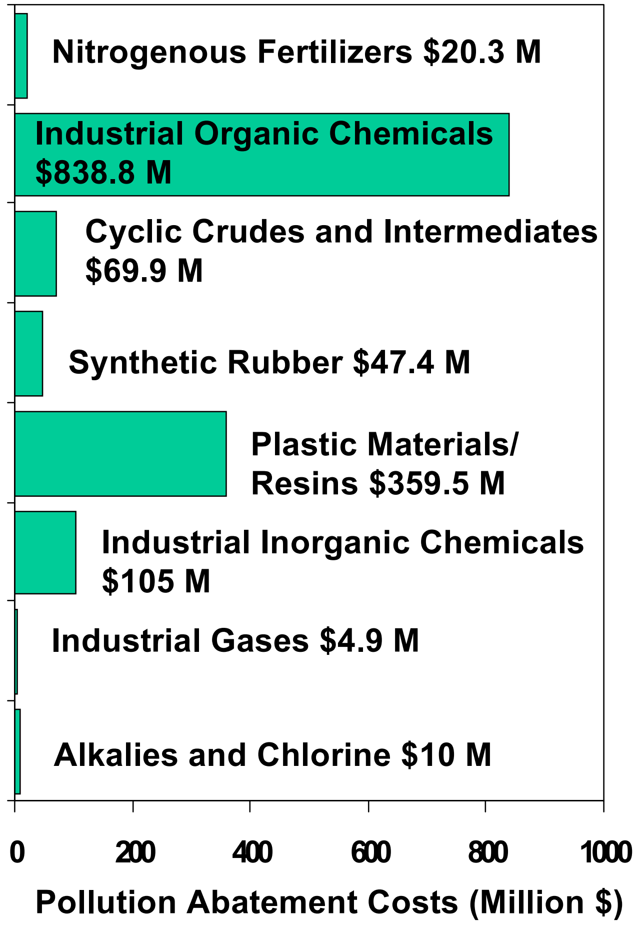
Many firms also participate in EPA's 33/50 Program, a voluntary effort targeting a reduction in emissions of 17 priority chemicals by 33 percent from 1988 to 1992, and by 50 percent by the end of 1995. CMA reports that its member companies met the 50 percent reduction goal in 1994, one year ahead of schedule (CMA 1996). Despite these gains in resource efficiency, however, the industry continues to face considerable challenges in the management of emissions.

The Industry Makes Substantial Investments in Pollution Control

Since 1973, the industry has acted to lessen the environmental impacts of chemical production by investing more than $25 billion in capital expenditures for pollution abatement and control. In 1997, the industry's pollution-related capital expenditures totaled about $2.1 billion, and were equivalent to about 1.1 percent of sales. These expenditures represent nearly 26 percent of total capital expenditures for pollution abatement and control by all U.S. manufacturers.

Operating costs for carrying out pollution abatement and control at chemical manufacturing facilities cover depreciation, labor, material and supplies, and services, and these costs are substantial. In 1997, these costs represented about 1.6 percent of sales, worth about $3.1 billion. Chemical companies also spend about $1.2 billion annually on Superfund and other hazardous waste site remediation (CMA 1998).

Overall, gross annual costs for pollution abatement and control in the chemical industry topped $5.4 billion in 1997, about 1.7 times the costs incurred in 1987 (CMA 1998). Four segments of the industry bear the bulk of expenditures for pollution abatement and control: SIC 2869, 2821, 2819, and 2865 (see Figure 1-13). Of these four, pollution abatement costs are greatest for SIC 2869, Industrial Organic Chemicals, nec, which is also the largest energy consumer (EPA 1995c).



Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA) provide a mechanism for the cleanup of contaminated waste sites. To fund these activities, the legislation allowed specific taxes to be imposed on petroleum refineries and chemical facilities. The mandate to impose taxes expired several years ago, however, and the fund is expected to be depleted of cash sometime in early 2000.

Title III of SARA also established “right to know” standards that require chemical plants and other industries to provide information to the public about stored toxic substances and annual release of substances into the environment (known as the Toxic Release Inventory or TRI). EPA is preparing a proposal to add persistent, bioaccumulative, and toxic pollutants (PBTs) to the TRI, and to lower threshold reporting for these compounds.

Re-authorization of CERCLA is currently underway, although regulators are not optimistic about resolving the long-standing dispute about which parties should be exempt from Superfund liability. In addition, most Superfund clean-up activities are slated to be completed within five years (CHEMWK 1999).

The Industry Is Subject to a Growing Number of Environmental Laws

Industry operations are controlled by a growing number of **state and federal laws** regulating the effects of chemicals production on the environment (EPA 1995b, EPA 1995a, CMA 1998). Major legislation includes the following:

Toxic Substances Control Act (TSCA) of 1976 regulates any chemical substance whose manufacture, processing, distribution in commerce, use, or disposal may present an unreasonable risk of injury to health or the environment. Under TSCA, the EPA can prohibit, limit, or ban the manufacture and use of chemicals. For example, under TSCA, the EPA has banned most uses of asbestos.

Resource Conservation and Recovery Act (RCRA) of 1976 establishes standards and regulations for management of solid and hazardous wastes. The law also calls for the establishment of programs at individual companies to reduce the volume and toxicity of hazardous wastes. Efforts to re-authorize and amend RCRA began in 1990. These efforts have lost some momentum, however, since EPA’s final regulation that exempts certain clean-up wastes from RCRA (December 1998). Although it appears the rule will result in faster and less-costly clean-ups, it does not meet industry’s desire for broad delegation of authority to state regulators (CHEMWK 1999).

The Clean Air Act, first passed in 1970 and later amended in 1990, regulates criteria air pollutants from automobiles, electric power plants, and all industrial sources, including chemical plants. The 1990 amendments established emission standards for industrial sources of 41 air pollutants (air toxics) to be met by 1995, and for 148 other air toxics to be met by 2003. The Act promulgates maximum achievable control technology (MACT) standards for relevant chemical industry segments. It also contains a provision to phase out the use of ozone-depleting chemicals, such as chlorofluorocarbons (CFCs). This provision continues to significantly impact chemical segments that previously produced and used CFCs and other ozone depleters (CHEMWK 1999). Under the *Amendments of 1990,* several major rules have not yet been promulgated.

The Clean Water Act, first passed in 1972 and later amended in 1977 and 1987, regulates effluents from sewage treatment plants, chemical plants, and other industrial sites. Specific guidelines are included for individual segments of the chemical industry. The act sets "best available technology" (BAT) standards for direct and indirect discharges to publicly owned water treatment works (POWTs). There are currently proposals in Congress to re-authorize this act, but they face opposition from the current administration because of fears that restrictions on wetlands will be eased (CHEMWK 1999).

The Hazardous Materials Transportation Act (HMTA) authorizes the Department of Transportation (DOT) to regulate the movement of hazardous materials. Chemical manufacturers must comply with regulations governing all aspects of transportation, including shipping documentation and labeling, loading and unloading of cargoes, emergency and security planning, incident notification, and liability insurance. Substances covered by the act include RCRA hazardous wastes as well as those designated by the DOT as hazardous. Re-authorization of the HMTA is now underway.

Pollution Prevention Act establishes a national policy to reduce or eliminate the generation of waste at the source wherever feasible, and directs EPA to establish a comprehensive pollution-prevention program.

EPA Initiatives coming in the near future include a voluntary testing program for high volume chemicals (greater than 1 million lbs/year) that was negotiated by the Chemical Manufacturers Association, EPA, and the Environmental Defense Fund in November 1998. Chemical companies must also complete risk management plans for EPA, including worst-case scenarios, by June 1999. Under this program the plans will be shared with local communities and made available to the public (CHEMWK 1999).

Chemical Producers Manage Large Quantities of Hazardous and Toxic Wastes

The U.S. chemical industry generates considerable amounts of hazardous and non-hazardous wastes every year.   One report (EPA 1993b) indicates that the industry produced about 450 million short tons of **hazardous waste** in 1989, which represents over 90 percent of the total amount of hazardous waste generated by the U.S. manufacturing segment. A survey of 627 chemical production facilities conducted in 1989 (CMA 1991) revealed that

Toxic Release Inventory Definitions

Toxic release - an on-site discharge of a toxic chemical to the environment. This includes emissions to the air, discharges to bodies of water, and releases at the facility to land and underground injection wells.

Point source air emissions - occur from controlled air streams, such as stacks, vents, ducts, or pipes.

Fugitive air emissions - equipment leaks, evaporative losses from surface impoundments, and releases from ventilation systems.

Releases to water - discharges to stream, rivers, lakes, oceans, and other bodies of water, including storm run-off.

Releases to land - occur within the boundaries of a facility, including disposal of chemicals in a landfill, land treatment, and surface impoundment.

Underground injection - disposal of waste fluids by subsurface placement in a well by injection.

Off-site transfers - transfer of toxic chemicals in wastes to a geographically or physically separated facility, for energy recovery, treatment, recycling, or disposal. Except for disposal, these quantities do not represent entry of the chemical into the environment.

Transfers to POTW - transfer of wastewater to publicly owned treatment works (POTW) for water treatment. Not all chemicals can be treated by a POTW ; those not removed are released to surface waters.

the vast majority of this hazardous waste, 97 percent, was contaminated wastewater. Hazardous waste generation is assigned to specific industry segments in Figure 1-14. Of the segments shown, Industrial Organic Chemicals accounts for the largest portion of hazardous waste generation.

Some hazardous waste is also considered "toxic," as defined by the **Toxic Chemical Release Inventory (TRI)** Reporting Program, which began collecting data on toxic releases in 1987 (see sidebar for TRI definitions). In 1996, the U.S. chemical industry reported about 10 billion pounds of production-related toxic chemical waste through the TRI Reporting Program (EPA 1998). Currently, this data is reported under the SIC code system. In 1996, five chemical segments accounted for the majority of toxic releases (see Figure 1-15). However, in many cases firms are conducting more than one type of chemical manufacturing. (i.e., manufacturing products that are classified in separate categories). For example, a facility may manufacture both inorganic chemicals and agricultural chemicals. Others may produce both organic chemicals and plastics. Toxic-containing production wastes from these multiple-product facilities account for nearly 50 percent of wastes reported (see Table 1-25).

The largest **multiple-code reporting** category is the combination of plastics and organic chemicals. An example of this would be a facility producing ethylene primarily as a feedstock for the production of polyethylene, a major plastic produced at the same facility. The second largest multiple-code reporting category is the combination of organic chemicals (ethylene, propylene) with cyclic crudes and intermediates (aromatics such as benzene, xylene), many of which are co-produced in the same process.

The combination of alkalies and chlorine with inorganic chemicals production is also common, primarily because chlorine and caustic soda are common inputs for the production of many inorganic chemicals. Agricultural chemicals and fertilizers are also often produced in the same facilities because byproducts can be recycled as inputs. This is true in general for many multiple-code facilities, where byproducts are utilized to make useful products on-site rather than being sold off-site.

Table 1-25. Top Ranked Multiple-Code Toxic Waste Generators - 1996 (ranked in order) (million lbs)

SIC Code Combination[a]	Number Facilities Reporting	Total On- and Off-Site Releases	Total Other On-Site Waste Management	Total Transfers Off-site for Further Waste Management	Total Production-Related Waste
2821, 2869	1,194	54	1,148	106	1,306
2865, 2869	809	38	1,060	85	1,183
2812, 2819	190	10	257	98	267
2873, 2879	521	105	153	3	262
2821, 2865, 2869, 2879	448	16	214	11	239
2812, 2813, 2842	190	2	177	118	179
2819, 2873	194	68	79	25	176

[a] SIC Codes: 2812 Alkalies & Chlorine, 2813 Industrial Gases, 2819 Industrial Inorganic Chemicals nec, 2821 Plastic Materials & Resins, 2842 Polishes & Sanitation Goods, 2865 Cyclic Crudes & Intermediates, SIC 2869 Industrial Organic Chemicals nec, SIC 2873 Nitrogenous Fertilizers, SIC 2879 Agricultural Chemicals nec; Source: EPA 1998.

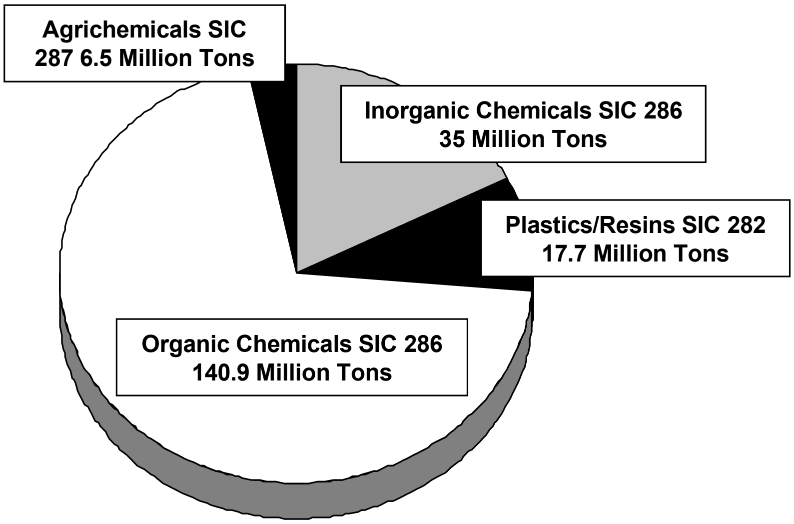


Figure 1-14. Hazardous Waste Generation in Selected Chemical Segments, 1989 (CMA 1991)

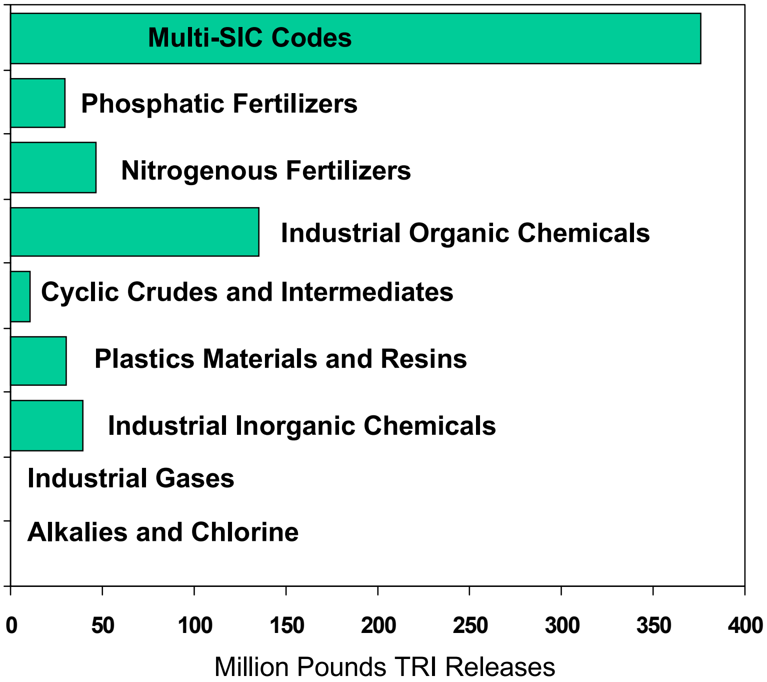


Figure 1-15. Toxic Releases in Selected Chemical Segments, 1996 (EPA 1998)

Table 1-26 summarizes the chemical industry's release and transfer activity for toxic wastes between 1995 and 1996. Total production of toxic wastes decreased by about 2 percent, and about 6 billion pounds were ultimately recovered through recycling or energy recovery (EPA 1998). On-site recycling increased by over 12 percent, while energy recovery increased by nearly 6 percent.

Table 1-26. Summary of Toxics Release and Transfer[a] Activity for SIC 28 - 1995-96 (million pounds)

Activity	1995	1996	Percent Change 95/96
RELEASES			
Releases and On-site Land Disposal	**814.6**	**754.3**	-7.4
Total Air	421.9	392.4	
Fugitive Air	98.6	93.4	
Point Air	323.3	299.1	
Water Discharges	88.2	90.4	
Underground Injection	235.1	200.5	
On-site Land Disposal	69.4	71.0	
ON-SITE WASTE MANAGEMENT			
Recycling	**3324.7**	**3731.3**	12.2
Energy Recovery	**1277.6**	**1348.4**	5.5
Treatment	**3829.4**	**3254.5**	-15
OFF-SITE TRANSFERS			
Transfers	**950.0**	**929.7**	-2.1
POTW Discharge	114.8	109.5	
Disposal	29.7	30.8	
Recycling	236.1	256.6	
Treatment	159.0	154.3	
Energy Recovery	410.3	378.4	
Other Transfers	0.1	0.1	
TOTAL	**10196.3**	**10018.2**	-1.8

[a] Releases are defined as an on-site discharger to the environment, including emissions to air, discharges to water, releases to land, and contained underground disposal. Transfers are defined as the transfer of the toxic chemical to a facility that is geographically or physically separate from the reporting facility, and do not necessarily represent entry of the chemical into the environment.

Source: EPA 1993a.

The 15 toxic chemicals released in greatest quantity by the chemical industry are shown in Table1-27 (EPA 1998). The "top two" chemicals in terms of amount released both originate in large part from the manufacture of agricultural chemicals.

The two largest generators of toxic waste (SIC 286, Industrial Organic Chemicals and SIC 281, Industrial Inorganic Chemicals) manage most of their wastes on-site through recycling, energy recovery, or treatment. The Pollution Prevention Act of 1990 requires facilities to report information about the management of TRI chemicals and efforts made to reduce or eliminate those chemicals. The data is useful for assessing trends in source reduction within industries and facilities.

Data collected for the organic chemical segment, for example, indicates that this industry managed about 2.3 billion pounds of production-related wastes in 1997, with about 90 percent of those managed on-site. The inorganic chemical segment managed about 2 billion pounds of production-related waste, with over 95 percent managed on-site.

The organic chemicals segment recycles about 25 percent of wastes. In the inorganic chemicals segment, the percentage of recycled wastes is much larger–close to 80 percent. Table 1-28 provides an accounting of waste management activities for these industrial segments in 1997 (EPA 1997c). Major toxic and hazardous pollutants from the processing of inorganic chemicals include chlorine gas emissions (both fugitive and point source), impurities removed from electrolytic cell effluents, and pollutants originating from electrolytic cell materials and other parts. The top five toxic chemicals in the amount released include the following:

- hydrochloric acid
- chromium and chromium compounds
- carbonyl sulfide
- manganese and manganese compounds
- ammonia

Major toxic and hazardous pollutants from organic chemicals processing include fugitive emissions, liquid wastes, solid wastes, and contamination in ground water. Fugitive emissions arise from pumps, valves, flanges, and other sources. Liquid wastes include wash solvents, surplus chemicals, product washes/purifications, scrubber blowdown, cooling water, steam jets, leaks, spills, and waste oils/lubricants.

Table 1-27. Releases and Transfers, Top 15 Toxic Chemicals (1994)

Chemical	Toxic Releases by Chemical SICs (million lbs)	Major Chemical Manufacturing Sources
Ammonia	108	Alkalies, chlorine, industrial gases, inorganic chemicals, plastics, rubber, cyclic crudes, organic chemicals, fertilizers
Nitrate Compounds	94	Fertilizers, chemicals manufacture
Methanol	65	Inorganic chemicals, plastics, medicinals, pharmaceuticals, cyclic crudes, organic chemicals
Carbon Disulfide	60	Plastics, cellulose fibers, carbon black
Phosphoric Acid	55	Inorganic chemicals, fertilizers
Ethylene	32	Plastics, organic chemicals
Acetonitrile	24	Organic chemicals
Chromium compounds	22	Catalysts, organic chemicals, inorganic pigments
Propylene	20	Plastics, organic chemicals
Nitric Acid	19	Fertilizers, inorganic chemicals
Toluene	16	Inorganic chemicals, plastics, rubbers, medicinals, pharmaceuticals, paints, varnishes, organic chemicals
Manganese Compounds	15	Inorganic pigments
Ethylene Glycol	13	Organic chemicals
Formic Acid	13	Organic chemicals
Hydrochloric Acid	12	Alkalies, chlorine, inorganic chemicals, organic chemicals

Source: EPA 1998.

Table 1-28. Source Reduction and Recycling Activity for Organic and Inorganic Chemicals, 1997

Segment	Quantity of Production Related Waste (million lbs)	% Of Waste Handled On-Site			% of Waste Handled Off-Site			
		% Recycled	% Energy Recovery	% Treated	% Recycled	% Dis-posed	% Energy Recovery	% Treated
Organic Chemicals SIC 286	2,342	24	27	35	1	6	4	3
Inorganic Chemicals SIC 281	2,008	79	0	17	0	3	0	0

Source: EPA 1997c.

Solid wastes typically consist of spent catalysts, spent filters, sludges, biological sludge from wastewater treatment, contaminated soil, packaging materials, reaction by-products, spent resins, and drying materials. The top five toxic chemicals released include ammonia, nitric acid, methanol, ethylene glycol, and acetone.

Chemical manufacturers also generate and manage a diversity of non-hazardous wastes, from wastewaters and wastewater treatment sludges to process wastes, contaminated soil, and trash. Although limited data is collected on non-hazardous waste, an earlier report (CMA 1992) indicates that the chemical industry produced nearly 6 billion tons of non-hazardous waste in 1991,with 99.6 percent of that being wastewater. While currently not subject to the same stringent regulations as hazardous waste, handling and disposing of these non-hazardous wastes still create a large financial burden for the industry. It is anticipated that some of these wastes could eventually be subject to some form of regulatory control.

The Industry Generates a Number of Criteria Air Pollutants

Chemical manufacturing processes are a source of **criteria air pollutants** regulated under the Clean Air Act and its amendments. These pollutants are produced directly by chemical processing, and through the combustion of fossil fuels in boilers and other heating systems used in processing.

With the exception of volatile organic compounds (VOCs), U.S. industry generally emits only a small fraction of most air pollutants compared to those generated by the transportation and utility sectors. Industrial processes are responsible for nearly 50 percent of total U.S. VOC emissions, however, with the transportation sector generating most of the remainder of these pollutants.

Table 1-29 shows the relative contribution of the chemical industry to the national total air emissions for criteria pollutants. The industry's contributions range from about 1 percent to 7 percent when combustion-related emissions are included. Combustion-related emissions were calculated based on energy consumed by the industry in 1996, using the emission factors shown in Table 1-30 (EPA 1995b, CMA 1998).

Sulfur and nitrogen oxides represent the largest share of combustion-related emissions from the chemical industry. Carbon monoxide is the largest air pollutant from chemical processes, although this pollutant represents less than 2 percent of total U.S. air emissions.

Table 1-29. Criteria Pollutant Emissions From Chemical Processes, 1996 (Million Short Tons)

Air Pollutant	Total U.S. Emissions	Chemical Industry Process Emissions	Chemical Industry Combustion-Related Emissions[a]	Total Chemical Industry Emissions (% of U.S.)
Sulfur Oxides	19.1	0.3	0.98	1.26 (6.6)
Nitrogen Oxides	23.4	0.2	0.46	0.66 (2.8)
Volatile Organic Compounds	19.1	0.4	0.09	0.49 (2.6)
Carbon Monoxide	88.8	1.2	0.12	1.32 (1.5)
Particulates	31.3	0.07	0.21	0.28 (0.9)

[a] Calculated based on energy consumption by fuel type in 1996 (CMA1998), using conversion factors developed by the U.S. Environmental Protection Agency

Sources: EPA 1986, 1988, 1995b; CMA 1998.

Table 1-30. Combustion Emission Factors By Fuel Type (lbs/million Btu)

Fuel Type	SO_x	NO_x	CO	Particulates	VOCs[a]
Distillate Fuel	0.160	0.140	0.0361	0.010	0.002
Residual Fuel	1.700	0.370	0.0334	0.080	0.009
Other Oils	1.700	0.370	0.0334	0.080	0.009
Natural Gas	0.000	0.140	0.0351	0.003	0.006
LPG	0.000	0.208	0.0351	0.007	0.006
Propane	0.000	0.208	0.0351	0.003	0.006
Steam Coal	2.500	0.950	0.3044	0.720	0.005
Petroleum Coke	2.500	0.950	0.3044	0.720	0.005
Electricity	1.450	0.550	0.1760	0.400	0.004

[a] volatile organic compounds

Sources: EPA 1986, 1988, 1996.

Slowing Global Climate Change and Reducing Greenhouse Gases Emissions May Be Future Challenges

Global climate change refers to the myriad of environmental problems that are believed to be caused, in part, by the reaction of the world's climate (temperature, rainfall, cloud cover) to rapidly increasing human activities such as the combustion of fossil fuels, emission of pollutants to air and water, changes in the Earth's reflectivity (albedo) due to deforestation, and emission of ozone-depleting chemicals.

Greenhouse gases refer to gases that trap heat in the atmosphere. In particular, they are transparent to solar radiation that enters the Earth's atmosphere, but strongly absorb the infrared thermal radiation emitted by the Earth. The most common man-made and natural sources of greenhouse gases are shown in Table 1-31. The natural greenhouse effect permits life to exist on Earth. Without greenhouse gases in the atmosphere, ambient temperatures would be much colder–below the freezing temperature for water–and the Earth would be incapable of sustaining life.

The Earth's climate system adapts relatively well to small, slow changes in atmospheric greenhouse gas concentration. However, rapid changes in anthropogenic (man-made) greenhouse gases may constitute a major force for climate change. Larger environmental disruptions may result from climatic disequilibrium caused by a combination of climate change forces, i.e., increasing greenhouse gases, albedo changes, and stratospheric ozone depletion. When climate forces are disrupted, global weather patterns

Table 1-31. Sources of Greenhouse Gases

Greenhouse Gas	Anthropogenic Sources	Global Emissions of Anthropogenic Sources (MMTCE)	Natural Sources	Global Natural Emissions (MMTCE)
Carbon dioxide (CO_2)	Combustion of fossil fuels; calcination of limestone, soda ash manufacture and use; aluminum production.	7,100	Biological processes	150,000
Nitrous oxide (NO, NO_2)	Combustion of fossil fuels; nitrogen fertilizers, manufacture of adipic and nitric acid.	4-8	Biogenic processes in soil; lightning.	6-12
Methane (CH_4)	Coal mining; oil refining; gas drilling and transmission; chemical, iron and steel production.	300-450	Aerobic decay of vegetation; termites (tropics); ruminant animals; rice fields.	110-210
Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)	Release of engineered chemical refrigerants and solvents	0.2 (U.S. only)	No natural source.	—

Source: EIA 1994a.

become less predictable and may include an increase in the number of hurricanes and tornados, and in the amount of flooding. As greenhouse gases increase, the rate of change in global climate patterns may accelerate and limit the ability of ecosystems to adapt to these changes.
There is little doubt among the scientific community that global climate change could have significant impacts on the world as we know it. However, there is no scientific consensus that global climate change is actually occurring at the present time. NASA's satellite data fails to show net warming over the past 18 years, and actually indicates a slight cooling trend since the early 1900s. Surface temperature readings, however, show an increase of 1 Celsius degree over the past century, with most of the warming occurring before 1940 and before the majority of man-made emissions began to occur. These types of ambiguities in the available data have resulted in considerable disagreement among scientists over the potential for and extent of global warming.

A recent report of the Intergovernmental Panel on Climate Change stated that estimates of natural variability and uncertainties in key factors limit the ability of investigators to quantitatively determine the influence of humans on global climate. Scientists agree that extensive research is required, as well as long-term assessment of the impact of any temperature increase.

The Union of Concerned Scientists (UCS) is urging world leaders and the current U.S. administration to take immediate action and sign a global climate change treaty. At an international summit meeting in Kyoto, Japan, in late 1997, world leaders met to discuss and formulate an international agreement to reduce the generation of greenhouse gases. The resulting **Kyoto Protocol** calls for a significant reduction in greenhouse gases by the United States and European Nations by the year 2010 (CHEMWK 1999). The current Administration signed the agreement in November 1998, but had not yet submitted it for Senate ratification at the beginning of 2000. Pending the signing of the treaty, legislation is being proposed that would allow credit to companies for voluntarily reducing greenhouse gas emissions.

The Kyoto Protocol could have dramatic impacts on consumer prices and economic growth. Many industries are concerned that the economic impacts of such a treaty are not well understood, and are opposing proposed plans by the United States to sign the agreement. A recent study indicates that the economic cost would be high, and that mandatory emissions goals (holding emissions to 1990 levels) could result in a loss of gross domestic product of $227 billion (1992 dollars) in 2010 alone (WEFA 1997). According to the study, implementing the protocol would also mean sharply higher prices for energy, which could give developing nations (which are not required to reduce emissions) a competitive advantage over the United States and other developed countries. The study also indicates that energy-producing states would suffer the greatest amount of economic disruption.

Summary of the Kyoto Protocol

- United States to reduce greenhouse gas emissions by 7% below 1990 levels by 2010
- European Nations to reduce greenhouse gas emissions by 8% below 1990 levels by 2010
- No commitments from developing nations to reduce greenhouse gas emissions, and no agreement on a voluntary process for reducing/limiting their emissions
- Emissions trading for Annex I parties only (main sellers would be Russia and Ukraine)

Chemical Reactions and Combustion of Fuels in Chemical Processes Produce Some Greenhouse Gases

In the chemicals industry, greenhouse gases (carbon dioxide, methane, and nitrous oxide) are emitted during chemical reactions, from flue gas desulfurization processes, and from the combustion of fossil fuels.

The amount of carbon released when fossil fuels are burned is dependent on the carbon content, density, and gross heat of combustion for the particular fuel. The carbon coefficients and energy consumption data used to calculate **combustion-related emissions** of carbon dioxide are shown in Table 1-32 A detailed explanation of how carbon coefficients were derived can be found in *Emissions of Greenhouse Gases in the United States, 1987-1992* (EIA 1994a). Table 1-33 summarizes the emissions of greenhouse gases from both process and combustion-related sources in the chemical industry. Industrial carbon dioxide emissions represent only about 3 percent of the total U.S. emissions of carbon dioxide. Industrial emissions of nitrous oxide are larger, representing about 9 percent of the Nation's total emissions of nitrous oxides.

The production and use of soda ash (sodium carbonate) is another source of carbon dioxide in chemicals manufacture. As soda ash is processed into various products, additional carbon dioxide may also be emitted if the carbon is oxidized. Chemical products in this category include sodium silicate and sodium tripolyphosphate, which are manufactured from sodium carbonate and used as components in detergents. While soda ash has a number of uses outside the chemical industry in such areas as water treatment, glass manufacturing, and pulp and paper production, more than half the carbon dioxide emissions associated with soda ash originate in the chemical industry.

While emissions of methane are dwarfed by carbon dioxide emissions, methane is a more effective greenhouse gas. Considering just its heat-absorption potential, one molecule of

Table 1-32. Carbon Emissions from Combustion of Fossil Fuels in the Chemical Industry - 1997

Fuel Type	Carbon Coefficient (lbs CO_2/million Btu)	1997 Energy Use (Trillion Btu)	Carbon (MMTCE)	CO_2 (MMT)
Distillate Fuel	161.2	11	0.2	0.8
Residual Fuel	173.6	50	1.1	3.9
Natural Gas	116.9	1,927	27.9	102.3
Coal & Coke	207.5	250	6.4	23.6
Purchased Electricity	133.4	545	9.0	33.0
Electricity Losses	133.4	1132	18.7	68.5
Other Fuels	163.3	251	5.1	18.6
TOTALS	-	4,166	68.4	250.7

Note: MMTCE indicates million metric tons of carbon equivalents; MMT indicates million metric tons of carbon dioxide.
Source: EIA 1994b.

Table 1-33 Emissions of Greenhouse Gases From the Chemical Industry-1997 MMTCE

Greenhouse Gas	Total U.S. Emissions	Process Emissions	Combustion-Related Emissions	Total Chemical Industry Emissions (% of U.S.)
Carbon Dioxide	1,501	1.2[a]	49.7[b]	51 (3.4%)
Methane	168	0.4[c]	--	0.4 (0.3%)
Nitrous Oxide	86	7.4[d]	--	7.4 (8.5%)

Note: Carbon equivalents for gases other than carbon dioxide are calculated based on the global warming potentials of the individual gases (EIA1998).

[a] Based on estimated emissions from the manufacture of soda ash, sodium silicate, and sodium tripolyphosphate. Does not include consumption of soda ash in flue gas desulfurization, as this data is not available.

[b] Calculated based on energy consumption by fuel type in 1997 (CMA 1998), using conversion factors developed by the U.S. Department of Energy (EIA 1996). Includes losses for on-site and cogenerated electricity, but not purchased electricity.

[c] Based on emissions from production of ethylene, ethylene dichloride, styrene, methanol, and carbon black.

[d] Based on emissions from production of adipic acid and nitric acid.

Source: EIA1998

methane can have 24 times the heat-trapping effect of one molecule of carbon dioxide (EIA 1995). The primary source of methane emissions from chemical processing is the "cracking" of petrochemical feedstocks, which produces a number of chemical byproducts, including methane.

Emissions of nitrous oxide are much smaller than those of methane or carbon dioxide, but with a heat-trapping potential 310 times that of carbon dioxide, nitrous oxide can be a significant contributor to global warming. Chemical industry sources include the production of adipic acid, a fine, white powder used primarily in the manufacture of nylon fibers and plastics, and nitric acid, a primary ingredient in fertilizers (EIA 1998).

The relative heat-trapping potential of various gases has been studied extensively, which has led to the development of the global warming potential of various gases (IPCC 1995). Despite these studies, there are still many uncertainties about their effects, primarily due to the complex way in which these gases react in the atmosphere. Having precise information about how various gases contribute to the greenhouse effect would be very useful, particularly in helping policy-makers determine where to concentrate efforts in controlling emissions of these gases.

1.5 Targets of Opportunity for Improved Energy and Resource Efficiency

The chemical industry has reduced its energy intensity over the last decade and made significant progress in reducing the environmental impacts of chemicals production. However, to remain at the forefront in global markets and to maintain its competitive position, the industry will have to continue to takes steps to strengthen market share, such as increased development of markets where the United States has a technological advantage.

Improvements to energy and resource efficiency will also play an important role in the future competitiveness of the industry. Such improvements can increase productivity, lower production costs, and increase profits while enhancing the public image of the industry and reducing the depletion of the Nation's limited energy resources. Using the energy, materials, and waste data presented so far, a profile of the chemical industry’s energy use, waste generation, and other factors is shown in Table 1-34. This data provides an initial means for identifying and ranking targets for improving energy and materials efficiency.

The profile shown in Table 1-34 reveals a number of major chemical products that rank high in four or five categories. These include ethylene, ammonia, propylene, sodium hydroxide, chlorine, and a few others. These chemicals are also feedstocks for many of the other chemicals ranking in the top 15. They can be categorized into the cohesive chemical

Table 1-34. The Top 15 Chemicals Ranked as Targets of Opportunity for Improved Energy and Materials Efficiency

Rank	Chemical	Production	Process Energy	Savings/ Theoretical	Savings/ Catalysts
1/3	Nitrogen/Oxygen	77,776	11/14	3	
2	Sulfuric Acid	35,707		6	
4	Ethylene	24,125	1	2	
5	Lime	21,175	4	5	
6	Propylene	14,350	2	10	
7	Ammonia	14,204		4	1
8/10	Chlorine/Sodium Hydroxide	24,835	5/6	1	2
9	Sodium Carbonate (Soda Ash)	11,838	8		
11	Ethylene Dichloride	10,088	10		13
12	Phosphoric Acid	9,909	7	11	
13	MTBE	9,038			
14	Vinyl Chloride	8,763	12	8	5
15/25/26	BTX (Benzene-toluene-xylene)		15	12	3
16	Ethylbenzene	6,950			
17	Nitric Acid	6,765		7	
18	Ammonium Nitrate	6,147			
19	Methanol	6,013			6
20	Urea	5,918			
21	Styrene	5,700	3	9	9
22	Terephthalic Acid	5,000			15
23	Hydrochloric Acid	4,219	9		
24	Formaldehyde	4,188		13	
27	Ethylene Oxide	3,550		15	7

Table 1-34. The Top 15 Chemicals Ranked as Targets of Opportunity for Improved Energy and Materials Efficiency (continued)

Rank	Chemical	Production	Process Energy	Savings/ Theoretical	Savings/ Catalysts
28	Cumene	2,913			
29	Ethylene Glycol	2,813			
30	Acetic Acid	2,425			
31	Phenol	2,175	13		12
32	Ammonium Sulfate	2,045			
33	Butadiene (1,3-)	2,038			4
34	Propylene Oxide	1,963			11
35	Carbon Black	1,750			
36	Acrylonitrile	1,663			8
37	Vinyl Acetate	1,500			10
38	Titanium Dioxide	1,478			
39	Acetone	1,463			14
30	Aluminum Sulfate	1,181			
41	Sodium Silicate	1,155			
42	Cyclohexane	1,100			
43	Bisphenol A	863			
44	Caprolactam	825			
45	Aniline	713			9
46	Isopropyl Alcohol	700		14	
47	Sodium Sulfate	639			
48	Methyl Chloride	563			
49	Propylene Glycol	538			
50	Methyl Methacrylate	313			

TOTAL PRODUCTION 1997 364,171,000 tons

"chains" that show how each major feedstock is used to produce a variety of downstream products. Rather than focusing individually on the most energy- or waste-intensive chemicals, it is more revealing to examine how the major constituents relate to the products they are used to create in terms of energy use, production quantities, and processes used.

2

The Ethylene Chain

2.1 Overview of the Ethylene Chain

Ethylene is a Feedstock for the Production of Polymers

Ethylene ranks fourth among chemicals produced in large volumes in the United States with about 48 billion pounds produced in 1997. It is a principal building block for the petrochemicals industry, with almost all of the ethylene produced being used as a feedstock in the manufacture of plastics and chemicals.

Ethylene is used as a raw material in the production of the most widely used plastic in the world, polyethylene (PE), and of many other important derivatives (see Figure 2-1). PE is used to manufacture plastic films, packaging materials, moldings (e.g., toys, chairs, automotive parts, beverage containers), wire and cable insulation, pipes, and coatings. Production of polyethylene in 1997 was about 27 billion pounds.

Ethylene dichloride is another important ethylene derivative, ranking eleventh in U.S. chemicals production in 1997 with over 20 billion pounds produced. Essentially all ethylene dichloride is used to manufacture **poly vinyl chloride (PVC)**, another important and widely used plastic. The largest use for PVC is the construction industry, which accounts for more than 50 percent of production. Construction-related uses include drainage and sewer pipes, electrical conduits, industrial pipes, wire and cable coatings, wall panels, siding, doors, flooring, gutters, downspouts, and insulation. A variety of household items and consumer goods are also made from PVC (e.g., shower curtains, rain coats, ice cube trays, credit cards). U.S. production of PVC was about 14 billion pounds in 1997.

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

Ethylene (48.3 billion lbs)
Polyethylene (27 billion lbs)
Ethylene Dichloride (20.2 billion lbs)
Poly Vinyl Chloride (14.1 billion lbs)
Ethylene Oxide (7.1 billion lbs)
Ethylene Glycol (5.6 billion lbs)
Polyester (5.9 billion lbs)

Source: CMA 1998, SPI 1998.

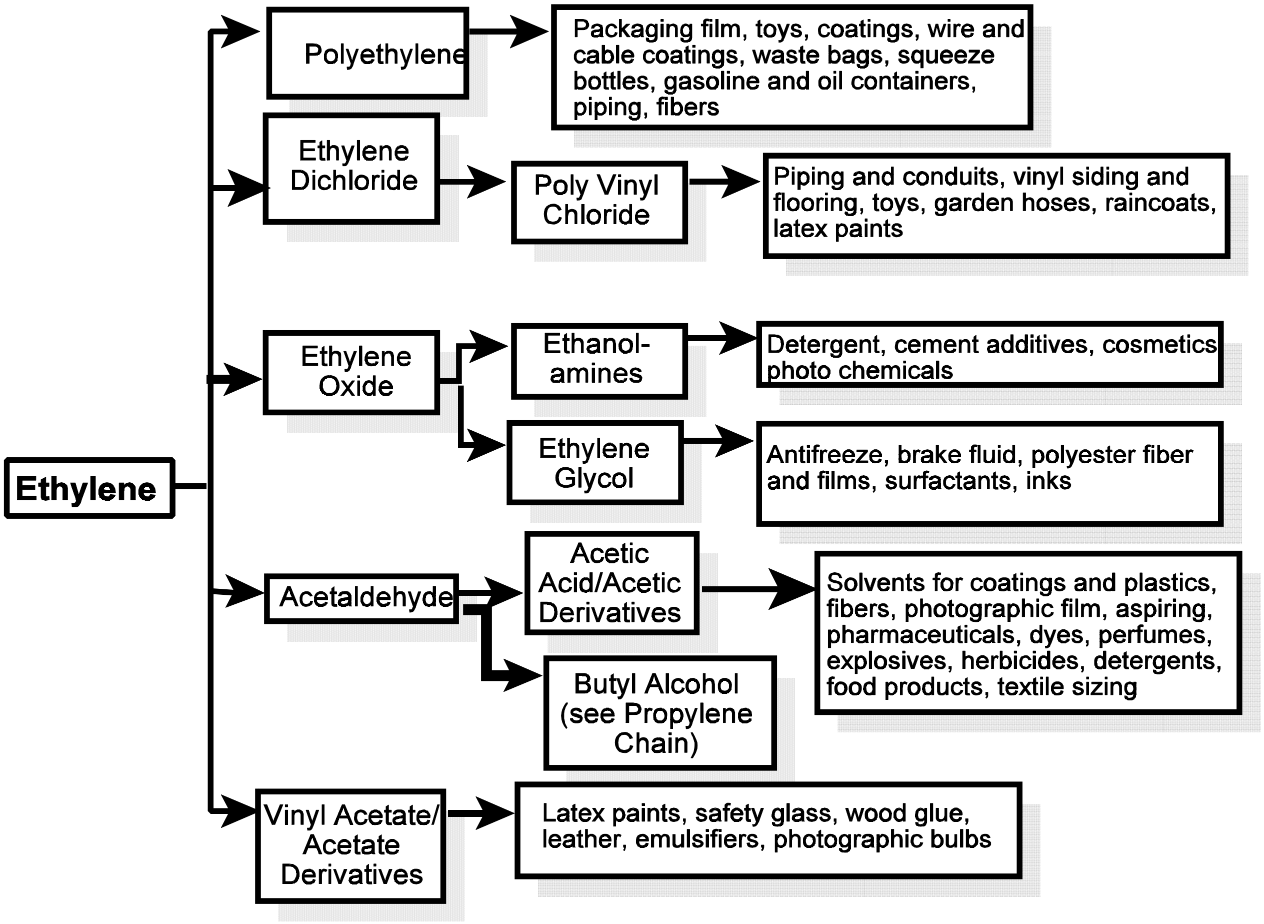


Figure 2-1. The Ethylene Products Chain (CMA 1998)

Ethylene oxide is another important ethylene derivative, used primarily for the production of **ethylene glycol**, a commonly used antifreeze. Ethylene glycol also serves as a raw material in the production of **polyester**, a fiber widely used for manufacturing textiles. Ethylene oxide and ethylene glycol are both listed among the top fifty chemicals produced in the United States, with ethylene oxide ranking twenty-seventh (7.1 billion pounds in 1997) and ethylene glycol ranking twenty-ninth (5.6 billion pounds in 1997) (CMA 1998).

Worldwide Demand for Ethylene and Its Derivatives is Strong and Growing

As the building block for so many plastics and important chemical derivatives, the **demand for ethylene** has nearly doubled over the last fifteen years (HP 1997a, OGJ 1998). A large part of this growth has been due to rapid increases in demand for petrochemicals in the Asia-Pacific region. The recent Asian financial crises has weakened this demand somewhat, but average annual growth in ethylene production is expected to remain strong at more than 5 percent. Predictions are that by 2005, Asia will consume more ethylene than any other region in the world, demanding 31 percent of the market.

Good margins since 1995 have resulted in additional capacity, with capacity now over-reaching demand. The gap between supply and demand is expected to widen until 2002-2003, and is likely to create steadily decreasing prices and weaker margins.

World demand for ethylene was about 180 billion pounds in 1998, and is predicted to reach 250 billion pounds by 2005. The United States is currently the largest ethylene-producing country in the world, with the Western European countries close behind in second place (OGJ 1998).

Demand for ethylene is directly related to the demand for its major derivatives, especially PE and PVC. Worldwide the polyethylene industry is a 100 billion pound market with over 150 producers. **Demand for polyethylene** has nearly doubled over the last decade, with the strongest growth markets in Asia and Eastern Europe (HP 1997b, HP 1997c). The U.S. is currently the largest producer of polyethylene in the world, followed by Western Europe and the Asia-Pacific region. Demand for polyethylene is expected to remain strong, although oversupply may become an issue as additional capacity comes on-line in the U.S. and Asia (OGJ 1998).

There is also a large global market for poly vinyl chloride, with worldwide capacity currently estimated at about 7.5 billion pounds. The Asia-Pacific region is keeping **demand for poly vinyl chloride** strong. In China alone, the vinyl market is predicted to be almost 5 billion pounds by the year 2000. About 25 percent of this demand will be met by imports.

2.1.1 Ethylene Manufacture

Ethylene Production Is Closely Tied To the Availability of Petroleum Feedstocks

The petroleum refining industry is the major supplier of raw materials for ethylene production, and a large percentage of ethylene capacity is located at petroleum refineries that are in close proximity to petrochemical plants. Currently about 20 percent of ethylene is produced from naphtha (a light petroleum fraction) and 10 percent from gas oil from refinery processing units (see Figure 2-2).

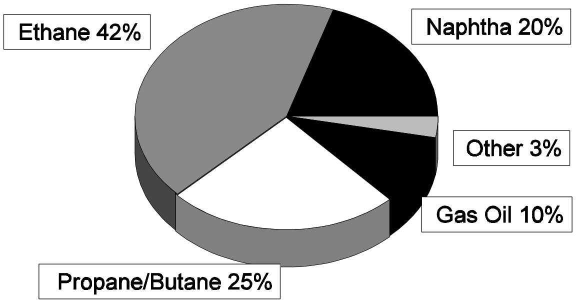


Figure 2-2. Ethylene Feedstocks

In Western Europe, as well as in some Asian countries (South Korea, Taiwan, Japan), naptha and gas oil account for 80 to 100 percent of feed to ethylene crackers. Overall, more than 50 percent of ethylene production capacity is currently located at refineries (CHEMX 1999, OGJ 1998).

Thus, ethylene production and ethylene's performance in the marketplace affect not only petrochemical and consumer product markets, but also the petroleum refining industry. This interdependence between petroleum feedstocks, petrochemicals, and widely used consumer goods make the ethylene chain one of the most important in the chemical industry.

Virtually all Ethylene is Produced by Pyrolysis of Hydrocarbons

Pyrolysis of hydrocarbon feedstocks is the process used to produce virtually all ethylene worldwide. Hydrocarbon feedstocks most often include ethane, naphtha, and gas oil, although propane and other hydrocarbons may be used. The same process is used regardless of the feedstock employed, although capital and energy requirements will differ depending on both the feedstock and the desired product slate.

% Products from Cracking Various Feedstocks
(Chenier 1992)

Product	Ethane	Propane	Naphtha	Gas Oil
Ethylene	76	42	31	23
Propylene	3	16	16	14
C4	2	5	9	9
Hydrogen	9	2	2	1
Methane	6	28	17	11

While there are a number of configurations available to accomplish pyrolysis, essentially all begin with the introduction of hydrocarbon feed and steam into a tubular pyrolysis furnace (see Figure 2-3). In the pyrolysis furnace the feed and steam are heated to a cracking temperature

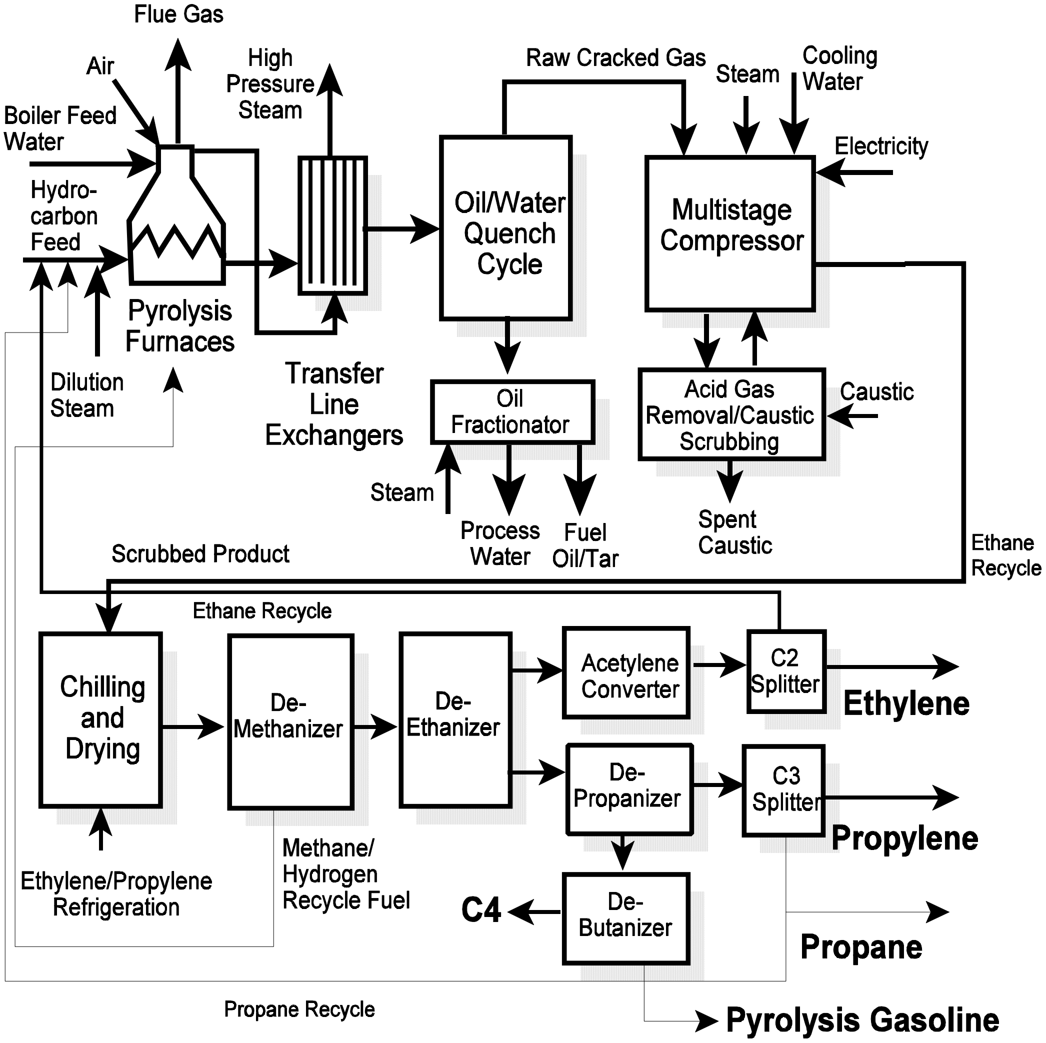


Figure 2-3. Ethylene Manufacture (Orica 1999, HP 1999)

Key Energy and Environmental Facts - Ethylene Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process: 8,197 Btu/lb* *Feedstock ΔHc: 31,414 Btu/lb* *Energy Recovered: 6,071 Btu/lb* *Slight import of energy typical of ethane crackers - other feeds (propane, naphtha) are balanced or energy exporters.*	*Largest source - fugitive emissions of volatile hydrocarbons, and furnace emissions (quantified estimates are not available)*	*Largest source - spent caustic solution and dilution stream blowdown*	*Spent catalyst (alumina, noble metals) from acetylene converters; spent drying dessicant.*

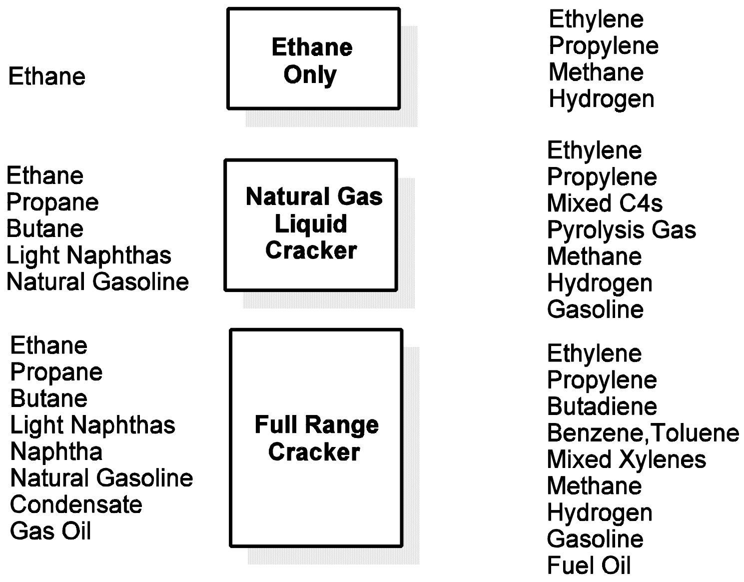


Figure 2-4. Feedstocks and Associated Products from Pyrolysis

of about 1400ºF- 1600ºF (760ºC-870ºC). Temperature requirements for cracking ethane will be higher than for heavier feedstocks. Lower molecular weight feedstocks (e.g., ethane) will give a high percentage of ethylene (see Figure 2-4); yields of propylene will increase with higher molecular weight feedstocks (e.g., naphtha).

The principal reactions occurring during pyrolysis include dehydrogenation and demethylation. The exact reactions that occur for liquid feeds such as naphtha and gas oil are difficult to predict because of the diversity of chemical species present in the feed. For example, the composition of one naphtha may differ drastically from another naphtha, and will produce a different product slate during pyrolysis. Figure 2-4 illustrates the feedstocks and products of pyrolysis. In today's chemical plants ethylene manufacture is a high efficiency process, in many cases generating all the energy required and often providing excess energy that can be exported for use in various process operations. The energy necessary to heat the feed to temperatures where pyrolysis occurs usually comes from burning the hydrogen and methane that are produced with the ethylene. With ethane as a feedstock, small amounts of energy must be imported; when other feeds are used, particularly propane and naphtha, the process is energy-balanced or provides export energy.

Pyrolysis/Cracking Reactions

Dehyrogenation

$C_2H_6 \longrightarrow CH2 = CH_2 + H_2$

Ethane Ethylene

Demethylation

$C_n\text{-Alkane} \longrightarrow C_{n-1}\text{ - Olefin} + CH_4$

Steam is added to the feed to reduce the partial pressure of the feed in the furnace and to slow the build-up of coke (carbon) on furnace surfaces. Reducing the partial pressure drives the reaction of the feed toward ethylene and inhibits secondary reactions that may occur (e.g., polymerization, cyclization), producing undesired co-products. Coke formation is slowed as the steam reacts with coke to form carbon monoxide. The tendency for coke build-up is greater with heavier feedstocks (e.g., naphtha, gas oil) and the amount of steam needed per weight of feedstock can increase by as much as 3 to 1. Steam to hydrocarbon ratios range from 0.3/1 for ethane to 3/1 for gas oil. Heavier feedstocks also provide less yield of ethylene, so that more feed must be cracked to provide a given ethylene yield. For example, the amount of feed required can increase by as much as a factor of four when comparing ethane feed with gas oil.

The effluent gas from the furnace is cooled rapidly in transfer line exchangers, and the heat removed from the cracked gas is used to raise high-pressure steam. Rapid cooling of the products is employed to minimize the occurrence of additional reactions. After this rapid cooling stage the furnace effluent is direct-quenched (cooled) with oil in a quench tower, then passes to a fractionator where fuel oil is separated (only if a naphtha or gas oil feed is employed) by steam stripping. Final cooling is generally accomplished by a direct-water quench tower. Whether water or oil is used, the operation of quench towers usually consists of the hot gases entering the bottom of the tower and rising where they come into direct contact with the quenching oil or water.

After final quenching, the furnace gas mixture is compressed and cooled using multistage centrifugal compressors with interstage cooling so that it can be separated into pure products. Acid gases (hydrogen sulfide and carbon dioxide) and water are removed using a caustic scrubber. This is necessary to prevent freezing in cryogenic components and to meet purity requirements for polymer-grade products.

After acid gases have been removed, the product gases must be dried to prevent ice formation and blocking of lines in cryogenic equipment. Drying is accomplished by chilling with propane or propylene refrigeration to remove most of the water, and then passing the gases through a tower for drying by absorption of water on a solid dessicant (e.g., activated alumina).

After drying the vapors are cooled using refrigeration equipment for the separation of the gas mixture into products. The refrigeration system is a highly integrated process designed to be energy- and capital-efficient. Cooled products then pass to a de-methanizer, a de-ethanizer, and through a series of fractionation (distillation) columns for distillation into final product streams. Polymer-grade ethylene and propylene are the major final products of this process. Ethane is usually recycled back to the pyrolysis furnace.

Acetylene is removed because of the purity requirements for polyethylene production. It can be carried out before hydrogen is removed from the gas mixture (front end reactor) or after hydrogen is removed (tail end reactor). Removal is usually accomplished by selective hydrogenation of acetylene over a noble-metal catalyst (e.g., palladium, nickel/cobalt/chromium) in a packed-bed reactor. This can take place before de-methanizing, or more commonly, after de-propanization at the tail end of the process.

Operating conditions and feedstocks can be varied to obtain the product slate desired by an individual producer. Temperature and residence time in the radiative part of the furnace can be moderated to adjust the relative product yields. For example, the highly severe conditions of high temperature and short residence time will maximize the production of ethylene. A producer desiring more propylene for on-site use, however, might utilize less severe conditions to increase production of propylene. (Process Description: ANL 1980, HP 1999, HP 1997d, Orica 1999).

2.1.2 Polyethylene Manufacture

Polyethylene, a Polymer of Ethylene, Can be Produced by High- or Low-Pressure Processes

Polyethylene is an odorless, translucent solid that is usually sold in pellet form so that it can be converted into a variety of derivative products. It is one of the most stable and inert polymers, and is highly resistant to chemical attack. Its versatile properties have contributed to the wide use of polyethylene in many products, the most common being packaging films.

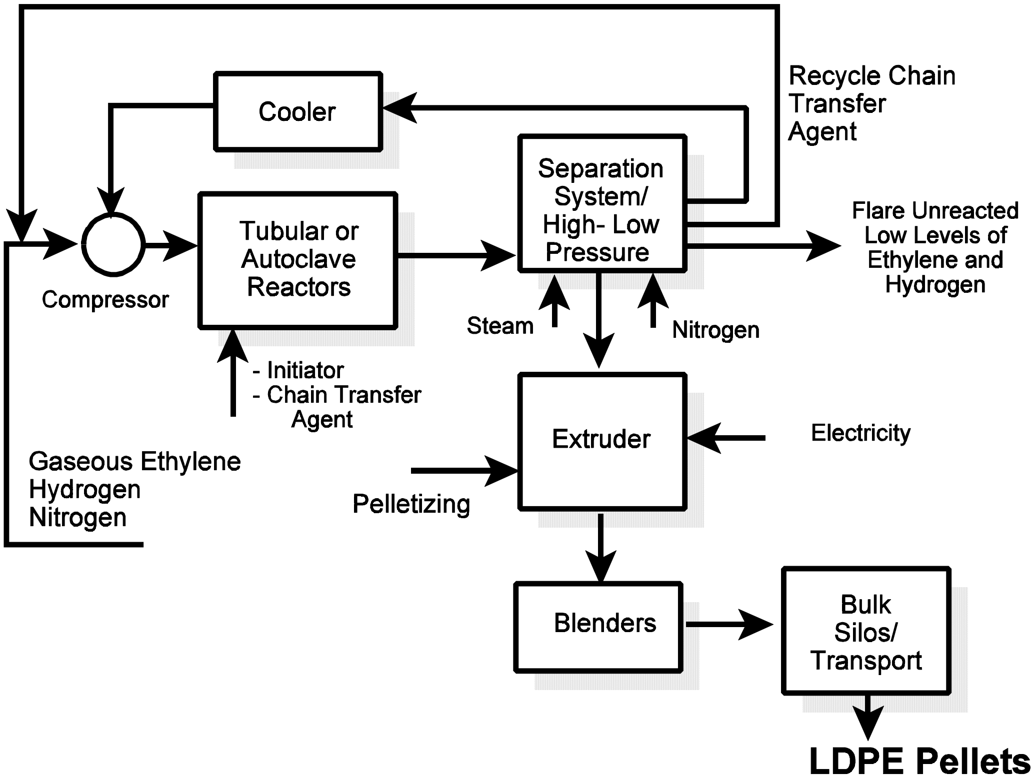


Figure 2-5. High Pressure Manufacture of LDPE (Orica 1999, HP 1999, HP 1997d)

Key Energy and Environmental Facts - LDPE Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 1,520 Btu/lb* *Feedstock ΔHc: 21,625 Btu/lb* *Low Pressure Steam Generated: 0.5 lb steam/lb product*	*Largest source - fugitive emissions (e.g., ethylene)*	*Largest source - process water*	*Off-grade or contaminated polymer scraps*

The types of polyethylene used most frequently include **low density polyethylene (LDPE)**, **linear low density polyethylene (LLDPE)**, and **high density polyethylene (HDPE)**. The specific gravity of LDPE, sometimes referred to as high-pressure polyethylene because of its method of manufacture, is specified to be less than 0.925. Figure 2-5 is a flow diagram of the most common process for producing LDPE. LLDPE has a specific density between 0.917 and 0.945, and its resins show certain enhanced properties such as a higher impact, tear, and tensile strength compared to conventional LDPE with the same melt index and density. HDPE has a specific gravity greater than 0.94, and is often referred to as low-pressure polyethylene.

The **high-pressure production** of LDPE was first developed in 1933 at ICI's (now Orica's) research laboratory in the United Kingdom through experiments on ethylene gas at very high pressures (Orica 1999). It was commercialized in the United States in 1943 and remained the process of use until 1953, when two researchers (Zeigler and Natta) found that ethylene could be polymerized in the presence of specific transition metal catalysts at relatively low pressures to form HDPE. LLDPE was subsequently introduced in

1977 by Union Carbide as a low-cost, high- volume polymer with improved properties (ANL 1980, Orica 1999).

With the commercialization of metallocene catalysts in 1991, the plastics industry has moved into a new era with the production of entirely new types of polymers. Metallocene catalysts allow exact control of molecular weight distribution, comonomer[1] distribution and content, and tacticity (structural organization). With these controlled structures, extremely uniform homo- or co-polymers can be produced with the desired physical properties. Poly-ethylenes produced with these catalysts can compete in completely different markets than those currently produced. Dow Plastics, DuPont and Exxon Chemical are now using metallocene technology to produce ethylene-based polymers, and capacity for their production is growing (C&E 1995).

Two types of processes are used to manufacture polyethylene: high-pressure processes for LDPE, and low-pressure processes for LLDPE and/or HDPE. In many facilities some low-pressure units are used as "swing" operations that can be used to alternate between production of LLDPE and HDPE, according to the demand.

The high-pressure technologies used most often to produce **LDPE** are either a stirred autoclave or a tubular reactor. Figure 2-5 presents a flow diagram for production of LDPE using the autoclave process. In this process, ethylene is pressurized through a two-stage compression process to reach high pressures of 1000 to 3400 atmospheres. The high pressure promotes the addition-polymerization reaction of ethylene. The compressed ethylene is sent to a stirred autoclave or tubular reactor, where it is mixed with a free-radical initiator (oxygen, benzoyl peroxide) to initiate the polymerization reaction. The molecular weight of the polymer is controlled by the addition of a chain-transfer agent such as propane or another alkane. The polymerization reaction is highly exothermic (heat evolving) and process temperature must be carefully monitored to avoid decomposition of ethylene to carbon, hydrogen, and methane.

Typical tubular reactors have tubes with an inner diameter of about 1 inch, and may be as long as 2000 feet. A reactor of this type would have a residence time of up to 45 seconds. Ethylene usually enters the reactor below the reaction temperature and is subsequently heated from 200 to 390°F (93^{oC} to 199°C) through heat exchange with hot fluid in the reactor jacket. The temperature increases as the reaction proceeds (up to 570°F) (299°C) and cooling must be incorporated in the jacket. Conversions of as high as 25 percent have been reported for each pass, with yields greater than 95 percent. Ethylene that is not converted during a single pass is separated in a series of separators by pressure reduction, cooled, and where appropriate, re-pressurized for recycling through the reactor. If the polyethylene plant is co-located with an ethylene plant, the ethylene may be sent back through ethylene fractionation.

Large stirred autoclave reactors have much larger internal diameters (up to 2 feet), with the outer diameter three times that size. Residence time can range from 30 seconds to 2 minutes, and reactions may be carried out in a zoned vessel to modify the molecular structure.

Following polymerization, the molten polymer is pelletized by forcing it through a screw extruder, cooling with a water bath, and cutting it into pellets with a rotating knife. The pellets are dried with hot air and the water is recycled. Off-grade polymer that is generated during irregular reactor conditions is blended and sometimes re-extruded and sold as "non-prime" product at a lower cost. Any of this material that is contaminated is sold to scrap buyers. Finished pellets are shipped in lots that range from 50-pound bags to railroad cars filled with 200,000 pounds. (Process Description: ANL 1980, Orica 1999, HP 1999.)

There are four low-pressure processes that can be used to produce **HDPE:**

- Ssolution polymerization
- Gas phase fluidized bed
- Slurry polymerization
- Modified high pressure :

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[1] Monomers are basic building blocks that combine to make polymers. For example, ethylene is the monomer used to make polyethylene. When two or more compounds combine to make a polymer, they are called comonomers.

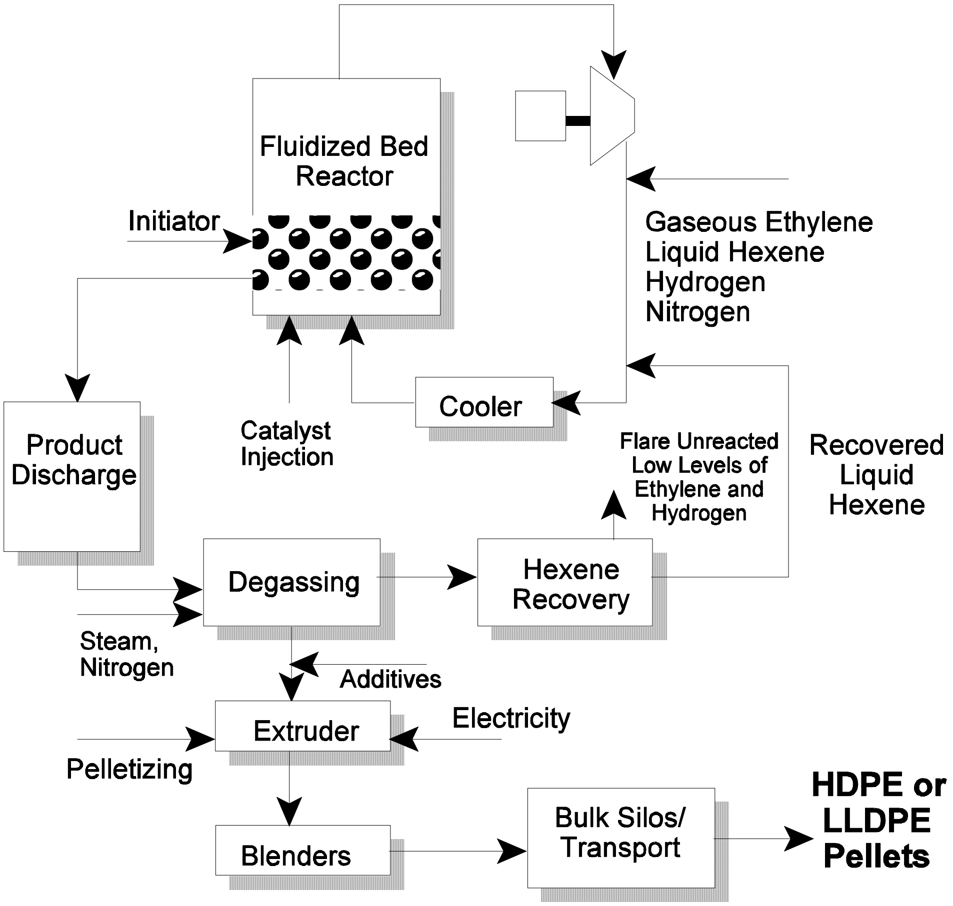

Figure 2-6. Low Pressure Manufacture of HDPE or LLDPE: Gas Phase Fluidized Bed Polymerization (HP 1999, HP 1997d, Orica 1999)

Key Energy and Environmental Facts - Low Pressure HDPE or LLDPE (Gas Phase or Slurry)			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process: 832 Btu/lb* *Feedstock: 21,625 Btu/lb*	*Largest source - fugitive emissions (e.g., ethylene)*	*Largest source - process water*	*Off-grade or contaminated polymer scrap*

Gas phase fluidized bed units based on the operation developed in the 1950s by Zeigler-Natta are one of the most commonly used processes (see Figure 2-6). This process operates at pressures of less than 20 atmospheres, and uses the Zeigler-Natta type of transition metal catalysts (titanium tetrachloride partially reduced and activated by an aluminum alkyl) or chromium on silica or silica/alumina.

The Ziegler-Natta catalyst is prepared in two stages from titanium tetrachloride and diethyl aluminum chloride, with a hydrocarbon diluent. This catalyst slurry is then fed into an agitated polymerization reactor or fluidized bed reactor along with ethylene and hydrogen. Chromium catalysts are usually injected into the reactor after activation because they produce broader molecular weight products than the Ziegler-Natta catalysts.

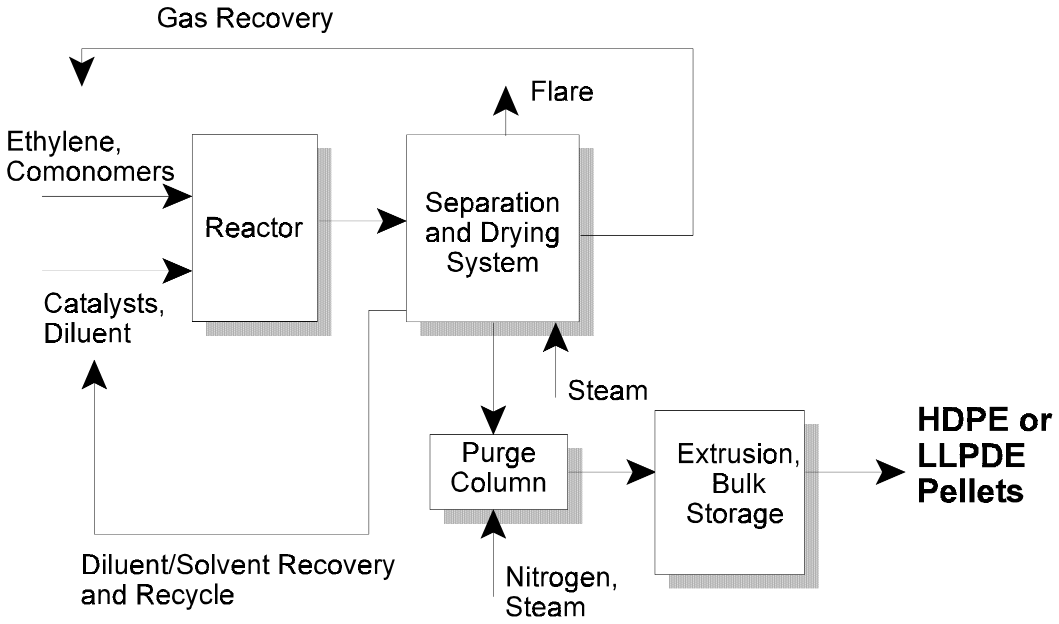

Figure 2-7. Low Pressure Manufacture of HDPE or LLDPE: Slurry Polymerization (HP 1999, HP 1997d)

After catalyst injection a polymeric suspension forms, and flows continuously into a second, much smaller reactor. The ethylene undergoes nearly 100 percent complete conversion to HDPE. The polymer molecule grows by insertion of ethylene at the interface between the polymer and the transition metal catalyst surface. The polymer is removed from the reactor through a sequential let-down system and is purged and degassed to strip any residual unreacted hydrocarbons. The granular or powdery reactor product is sent to a finishing section where additives are incorporated prior to pelletization and storage. Pelletization is accomplished by extrusion using high-capacity screw extruders. Pellets are then bagged for shipment to end-users. (Process Description: ANL 1980, Orica 1997, HP 1997d.)

Slurry polymerization is also commonly used for production of LLDPE and HDPE (see Figure 2-7). In this process, ethylene, comonomer, catalyst, and a diluent (solvent) are fed continuously into a reactor where polymerization occurs at temperatures lower than 212ºF (100ºC). Polymerization occurs in a slurry using very high-activity catalysts, which eliminate the need for catalyst removal. Comonomers are used to control density, and can include butene-1, hexene-1, 4-methyl-1, pentene, and octene-1. Reactor effluent is flashed or sent to a drying system to separate the solid resin. Most of the solvent (diluent) from the slurry can be directly recycled to the reactors without any treatment.

The polyethylene powder is purged with nitrogen to remove traces of hydrocarbons. It is then pneumatically conveyed to extruders for stablization and pelletizing. (Process Description: HP 1999, HP 1997d)

Additives Are Used To Achieve Specific Polymer Properties

Most types of polyethylene include **additives** that are incorporated to obtain specific properties. Stabilization additives are used when other additives are present to protect the polymer during conversion into a finished product. Its purpose is primarily to prevent the formation of gels and lumps in the product.

A slip additive is used in grades of polyethylene for flexible packaging film to reduce the coefficient of friction and prevent the film from sticking on metal surfaces during manufacturing. Anti-block additives are used to make it easier to open films, particularly bags. Other additives include UV stabilizers that protect the polymer during long-term outdoor exposure. When polymers are used in applications where they contact food, the additives must comply with world-wide food and drug standards.

2.1.3 Ethylene Dichloride and Poly Vinyl Chloride

Essentially all Ethylene Dichloride Is Used To Manufacture Poly Vinyl Chloride (PVC)

Poly vinyl chloride (PVC) is similar in structure to polyethylene, but substitutes a chlorine atom for every fourth hydrogen in the hydrocarbon chain. This means that chlorine is about 57 percent by weight of the vinyl chloride monomer molecule. PVC is produced as a rigid, relatively tough material (with a specific gravity of 1.4) but becomes a more flexible material if plasticizers are added. It is chemically inert to acids, salts, and petroleum products, but may react with aromatic hydrocarbons, chlorinated chemicals, and other organic compounds. It resists the growth of fungi, is more impermeable to air than polyethylene, and can be produced in a variety of colors.

The uses for PVC are extremely diverse — no other plastic can be used in a comparable variety of applications because PVC can be compounded to meet the specific requirements of the end-product. It is found most frequently, however, in construction materials (ANL 1980, Orica 1999).

The production of PVC is accomplished by the dehydrochlorination of ethylene dichloride (1,2-dichloroethane) to vinyl chloride monomer (VCM) and subsequent polymerization of the monomer to PVC. Virtually all of the ethylene dichloride produced in the United States is used in this manner to produce PVC.

The production of PVC from vinyl monomer was first patented in 1912, but the polymer produced was unstable and tended to decompose too readily. In the 1930s, materials were developed that could be compounded with the polymer to improve stability.

Hydrochlorination of acetylene (derived from coal via calcium carbide) was the main route to manufacturing vinyl chloride monomer until the 1950s, when the current process based on ethylene dichloride was developed (see Figure 2-8). Here **ethylene dichloride** is prepared by reaction of ethylene and chlorine gas in a pool of ethylene dichloride and cooled to remove the heat of reaction, which is exothermic. The reaction is usually catalyzed by the presence of a metallic chloride catalyst. The reactor product is washed to remove hydrochloric acid, which can corrode equipment, and the ethylene dichloride is distilled to a high purity of > 99 percent.

Ethylene dichloride can also be produced by oxyhydrochlorination of ethylene with air and hydrochloric acid, which is also an exothermic reaction. This is accomplished in a fixed copper catalytic reactor or fluidized bed. This process produces low-pressure steam as a side-product, and the ethylene dichloride produced is less pure than in the previous process.

Ethylene dichloride is then thermally cracked to produce vinyl chloride, hydrochloric acid, and some unconverted ethylene dichloride. These products are separated through quenching and distillation operations. The vinyl chloride monomer is washed with a caustic soda solution and charged to the polymerization unit. Hydrochloric acid is recycled to the oxyhydrochlorination reactor for the production of ethylene dichloride. Any unconverted ethylene dichloride is also purified and recycled.

The most widely used technique for polymerization of vinyl chloride monomer is **suspension polymerization**. During this process vinyl chloride droplets are polymerized while suspended in water in the presence of an initiator and other additives. A typical

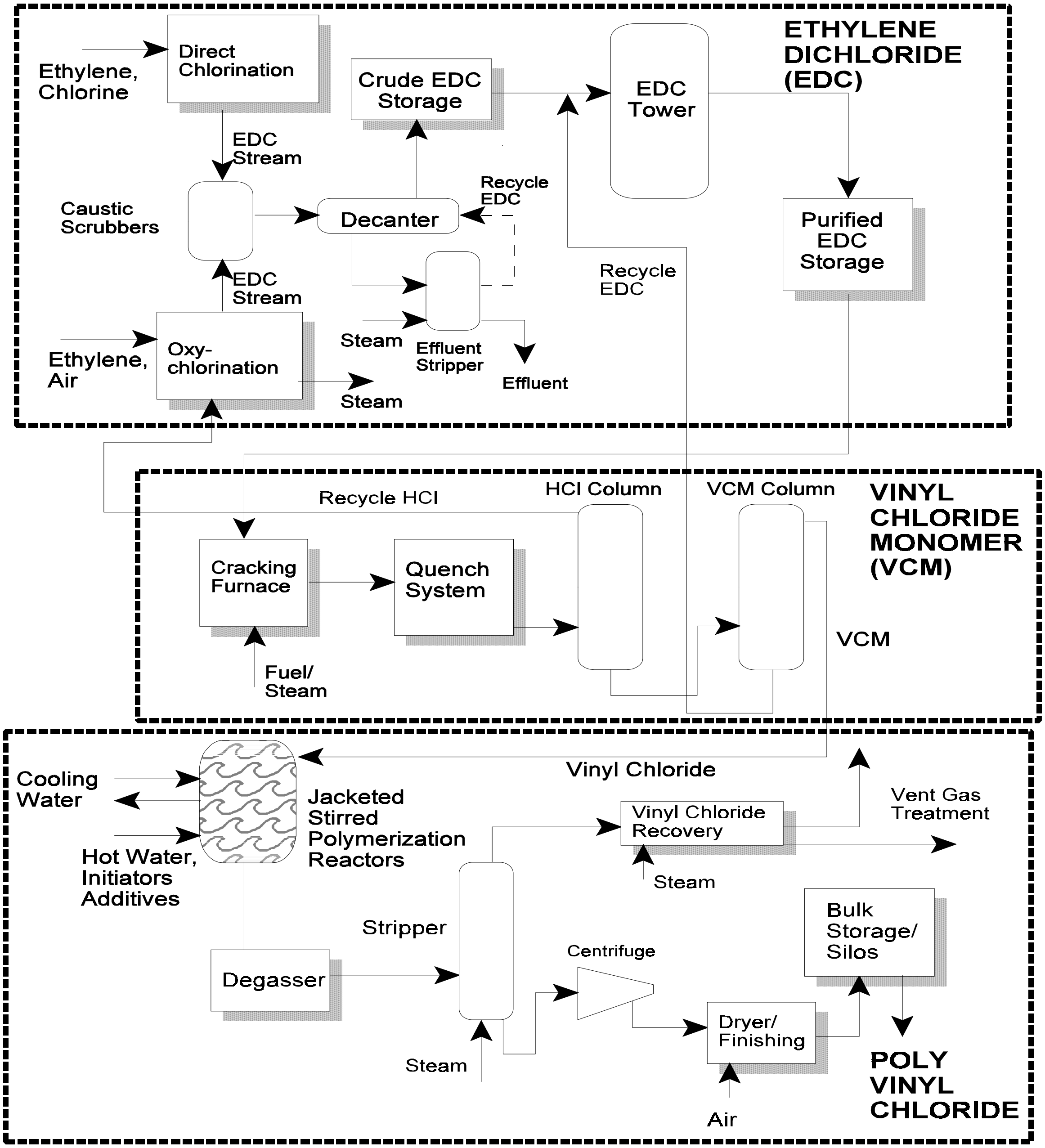

Figure 2-8. Ethylene Dichloride and Poly Vinyl Chloride Manufacture
(ANL 1980, EPA 1991, Orica 1999, HP 1999)

Key Energy and Environmental Facts - Ethylene Dichloride and Poly Vinyl Chloride Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Energy use: *Process: 4,656 Btu/lb* *Feedstock ΔHc: 20,095 Btu/lb*	*Largest sources - fugitive emissions (vinyl chloride monomer, solvents, other volatiles)*	*Largest source - process water, steam stripper water*	*Scrap or off-grade polymer*

configuration is a batchwise operation carried out in a number of parallel reaction trains consisting of stirred, jacketed reactors (see Figure 2-8).

The reaction takes place in the sealed, stirred reactor, under pressure and elevated temperature. Demineralized water containing the suspending agent (gelatin, methyl cellulose, poly vinyl alcohol, sodium lauryl sulfate) is sent to the reactor, followed by the vinyl chloride monomer and initiator (peroxide or persulfate free-radical initiator). The temperature is raised to about 160ºF (70ºC) by hot water coursing through the reactor jacket.

The vessel is cooled during the 10 to 12 hour reaction time to maintain a constant reaction temperature during the exothermic reaction. The reaction is terminated at about 90 percent conversion, since beyond that yield, resin color and porosity may be impacted. When the reaction is complete the vinyl will have formed a slurry of small powder particles floating in water, which must be continually stirred to prevent settling.

Slurry from the reactor is collected in a let-down vessel; unused vinyl chloride monomer is vented to a gas holder and re-liquefied for re-use in subsequent reactions. The slurry is steam-stripped and/or agitated to reduce the level of vinyl chloride to less than one part per million. This is critical because vinyl chloride monomer has been identified as a human carcinogen, and residual monomer must be removed from the polymer to low levels to ensure that it complies with standards for human health and safety.

After the polymer slurry has been stripped it is collected in stirred slurry tanks, centrifuged, and dried. The dry powder is screened and packed for transportation in sizes ranging from 10-pound sacks to tonnage road tankers. (Process Description: ANL 1980, EPA 1991c, HP 1999, Orica 1999).

2.1.4 Ethylene Oxide, Ethylene Glycol and Polyester

Ethylene Oxide Is a Feedstock in the Manufacture of Ethylene Glycol and Polyester

Oxides in general are very unstable compounds because they contain a strained epoxy group[2] and are used almost entirely as intermediates to produce other chemicals. **Ethylene oxide**, however, can be used as an intermediate or directly as a sterilant and fumigant, an anti-acid, or as rocket fuel. It is currently used as an intermediate in the production of ethylene glycol (antifreeze), surfactants, glycol ethers, and other chemicals.

The most important of these is **ethylene glycol**, which is used primarily as antifreeze and in aircraft deicing fluids because of its high boiling point and non-corrosive properties. Another important application of ethylene glycol is in the production of polyester fiber.

Polyester fibers are strong, and resistant to bacteria, insects, mildew, many organic solvents, weak acids, and bases. At elevated temperatures they are degraded by strong alkalies and acids. Polyester fabrics do not retain body heat so are not useful in cold weather materials, and they do not "breathe," which makes them uncomfortable in hot weather. However, they are very compatible with natural fibers and are often blended with cotton to improve moisture absorption and opacity.

Over half of the polyester produced is used in manufacturing garments. Other uses include the production of plastic bottles, tire cords, belts, and stuffing in quilts, pillows, and sleeping bags.

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[2] The epoxy group contains -C-C- triangulated with oxygen (O).

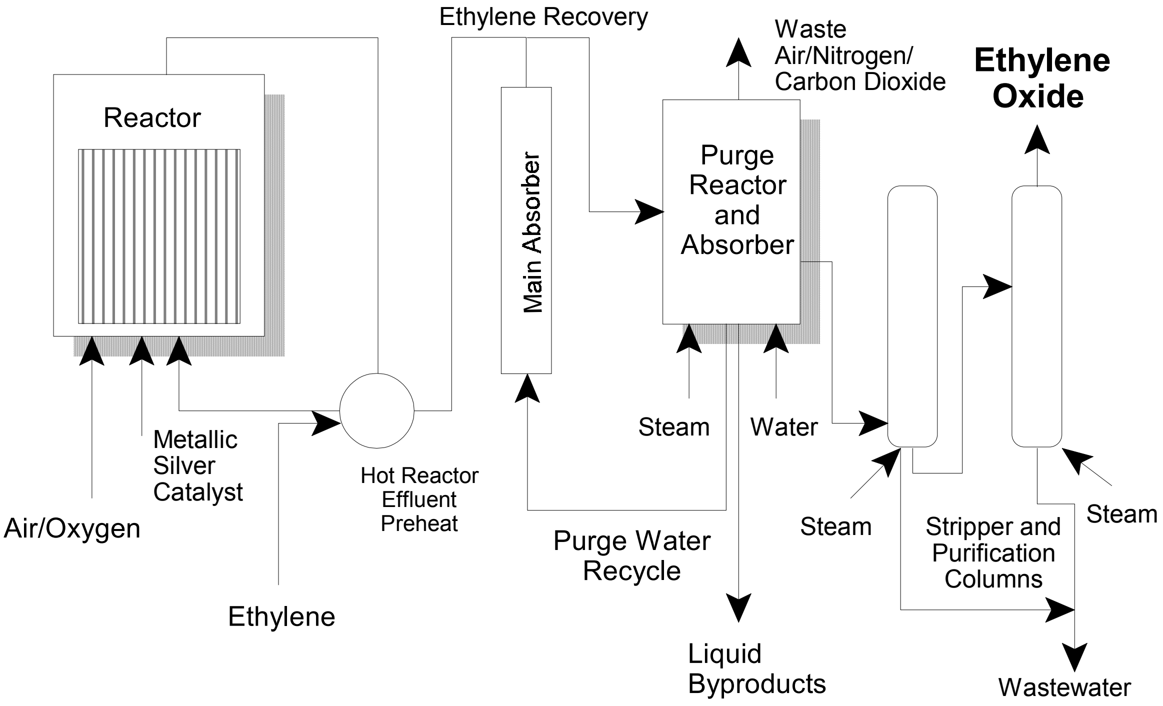

Figure 2-9. Ethylene Oxide Manufacture (ANL 1980, Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Ethylene Oxide Manufacture			
Energy	***Emissions***	***Effluents***	***Waste/Byproducts***
Net Energy use: *Process: 1,711 Btu/lb* *Feedstock ΔHc: 19,463 Btu/lb*	*Largest sources - fugitive emissions (e.g., ethylene, ethylene oxide)*	*Largest source -wastewater from stripper and absorber (recycled)*	*Byproduct gases*

All Ethylene Oxide Is Made by Direct Oxidation

For many years ethylene oxide was made by a chlorohydrin route. Today, however, virtually all ethylene oxide is produced by the **direct oxidation of ethylene** over a silver oxide catalyst (see Figure 2-9). While this process has a lower yield, using air as an oxidant provides greatly improved economics.

In the direct-oxidation process, ethylene and air (or oxygen) are preheated to 500-550ºF (260ºC-288ºC) by hot effluent from the reactor, which contains the silver oxide catalyst. The reactor contains several thousand reactor tubes of 20 mm-50 mm diameter. Although metallic silver is placed directly in the reactor, the actual catalyst is silver oxide that precipitates under reaction conditions. The reaction is exothermic and heat is removed by a coolant (water, organic liquid) that surrounds the reactor tubes.

Control of the temperature in the reactor is critical to ensure that combustion of ethylene to carbon dioxide and water is kept to a minimum. The combustion reaction, which competes with the oxidation reaction, increases as the temperature increases. Combustion produces about 15 times more energy than oxidation, so

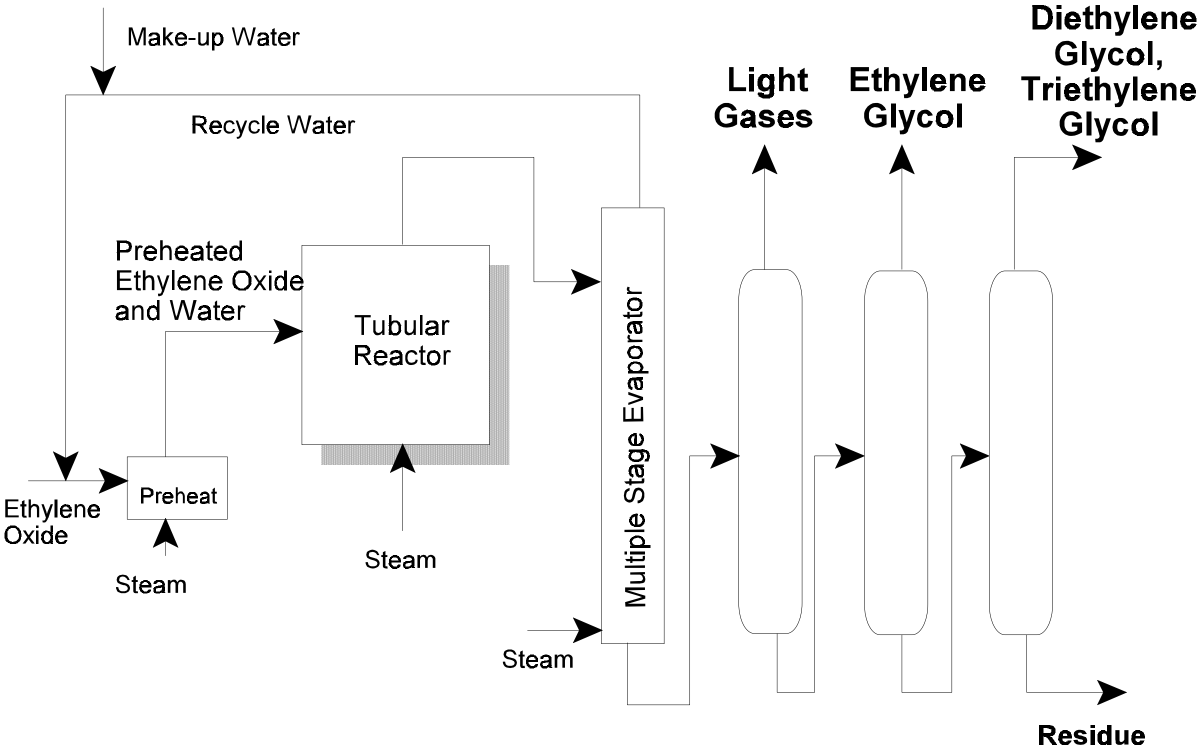

Figure 2-10. Ethylene Glycol Manufacture By Direct Hydration
(ANL 1980, Chenier 1992, HP 1999)

Key Energy and Environmental Facts - Ethylene Glycol Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes or Byproducts***
Energy use: *Process: 2,045 Btu/lb* *Feedstock ΔHc: 14,651 Btu/lb*	*Largest sources - fugitive emissions (e.g., ethylene oxide, ethylene glycol, byproducts)*	*Largest source - process water*	*Diethylene and triethylene glycol; residues.*

control of the combustion reaction is essential to prevent a runaway effect.

Gases from the reactor are cooled and sent to a counter-current absorber where water dissolves the ethylene oxide and small amounts of carbon dioxide, nitrogen, and aldehydes. The oxide-rich water is recycled, and the ethylene oxide is sent to a stripper to remove light gases. Distillation is then used to obtain the desired purity.
The per-pass conversion to ethylene oxide is low, and the subsequent gases from the water absorber contain large quantities of ethylene. The value of this ethylene is significant, and effective recycling of gases is essential to improve yield and keep costs down.

If air is used (rather than oxygen), a purge reactor and absorber are needed to remove nitrogen as it builds up. If oxygen is used, the purge reactor and the absorber are not needed, which lowers plant costs. (Process Description: ANL 1980, Chenier 1992, HP 1999).

Virtually All Ethylene Glycol Is Made by Hydration of Ethylene Oxide

Since 1978 virtually all ethylene glycol has been produced by **acid- or thermally-catalyzed hydration of ethylene oxide**. The yield of glycol from this process is usually better than 95 percent.

In this process (see Figure 2-10), refined ethylene oxide and pure water are mixed with recycled waters and sent to the hydration reactor after being preheated with hot water and steam.

The glycol unit is often part of a combined ethylene oxide/ethylene glycol plant, and in this case better economics are gained by incorporating bleed streams from the ethylene oxide unit as feed. Doing so, however, may affect product quality, and additional pretreatments may be necessary. The pure water adds to the oxide to yield a mono-glycol (e.g., ethylene glycol), which in turn reacts with the oxide to form higher glycols, such as diethylene glycol (DEG) and triethylene glycol (TEG).

Conditions of the reaction are dependent on whether or not an acid catalyst is used. Less severe reaction conditions are needed in the presence of a catalyst: atmospheric pressure, and temperatures of 120ºF-210ºF (49ºC-99ºC). The non-catalytic process requires higher pressures (over 190 psi) and temperatures of 300-390ºF (149ºC-199ºC). The non-catalytic process is generally preferred as it avoids dealing with corrosives and acid separation. The advantages of the acid-catalyzed process compared to standard conditions are lower pressures and temperatures.

The water-glycol mixture from the reactor is fed to the first stage of a multiple-stage evaporator, which is reboiled with high-pressure steam. Subsequent stages are operated at successively higher vacuum (and lower pressures) to remove excess water. The evaporated water is removed as condensate and recycled. The glycol solution exiting the evaporator is fractionated in a series of distillation towers to produce purified ethylene glycol and higher glycols such as DEG and TEG (Process Description: ANL 1980, Chenier 1992, HP 1999).

Polyester Is Made by a Condensation Reaction and Melt Spun into Fibers

The term polyester is used to describe any polymer with an ester group present in the chain. The most commercially important polyester is polyethylene terephthalate (PET), and is commonly know by trademarked products such as Dacron®, Terelene®, Fortrel® fibers and Mylar® film. Polyester is a thermoplastic (which means it can be melted and reformed), and can be classified as having high- or low-viscosity.

PET is made from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA) through a condensation polymerization route. During the DMT process methanol is produced which creates the need for methanol recovery and purification operations. Methanol can also produce significant emissions of volatiles. Since polymer grade TPA became available in 1963, newer plants use the TPA route, which is simpler and more energy efficient. The manufacture of TPA is discussed in more detail in Chapter 6 under the BTX chain.

In the TPA-based process (shown in Figure 2-11), the TPA and ethylene glycol are mixed along with a catalyst in a tank to form a paste. This is a simple way of introducing them to the process and allows control of feedstock density. The paste is then introduced to an esterification reactor (or several) where the monomer (di-ester bishydroxyethyl terephthalate) is produced along with some byproducts (dimers and trimers).

TPA slowly dissolves in ethylene glycol and undergoes esterification to yield the prepolymer. The process proceeds at moderately high temperatures and pressures: 390ºF-400ºF (199ºC to 204ºC) and 30-150 psi. The liquid product, termed prepolymer, is purified by filtration before entering the polymerizer.

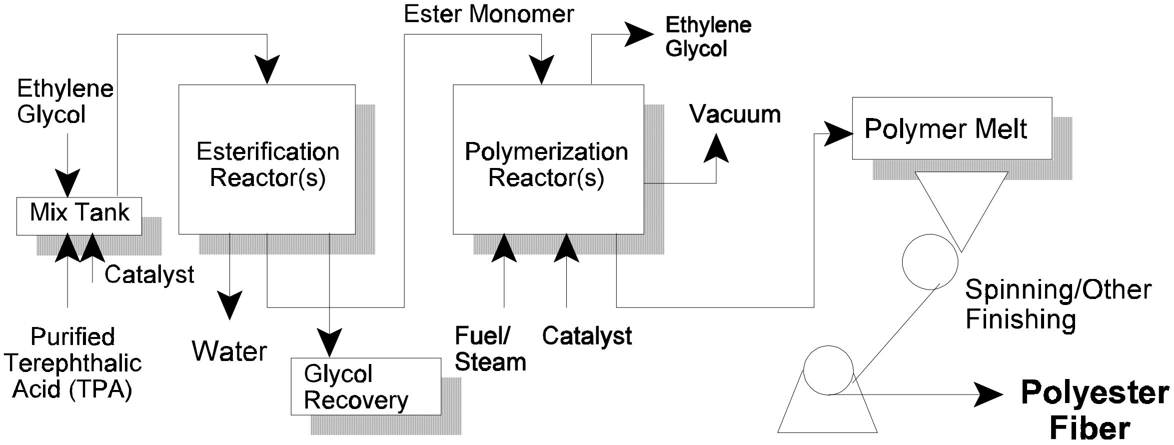

Figure 2-11. Polyester Manufacture Using TPA (ANL 1980, Chenier 1992)

Key Energy and Environmental Facts - Polyester Manufacture Using TPA			
Energy	***Emissions***	***Effluents***	***Wastes or Byproducts***
Energy use: *Process: 12,128 Btu/lb* *Feedstock: 22,448 Btu/lb*	*Largest sources - fugitive emissions*	*Largest source - process water and produced water from esterification*	*Spent catalyst, off-grade polymer*

After purification, the prepolymer is sent to stirred reactors where polymerization takes place in the presence of a catalyst (e.g., antimony trioxide). Typically there are two polymerization reaction vessels in series (low and high polymerization). The temperature is relatively high in the reactor (500ºF-570ºF), (260ºC-299ºC) but pressures are reduced to vacuum conditions (about 0.015 psi) to drive the reaction toward polymerization. Pressures and temperatures are varied to obtain either a high- or low-density product. A vacuum is maintained by steam jets with barometric intercondensers. A recirculation system provides cooling water to the intercondensers.

During the reaction ethylene glycol is produced and is continuously distilled off and recovered. The reaction proceeds for four to six hours until the right molecular weight is obtained (about 80 rings per chain).

The product is a clear, pale-yellow molten polymer, which is further processed by spinning or by quenching and cutting into small pieces that can later be reheated and melt-spun. The polymer's melting temperature is about 520ºF (270ºC).

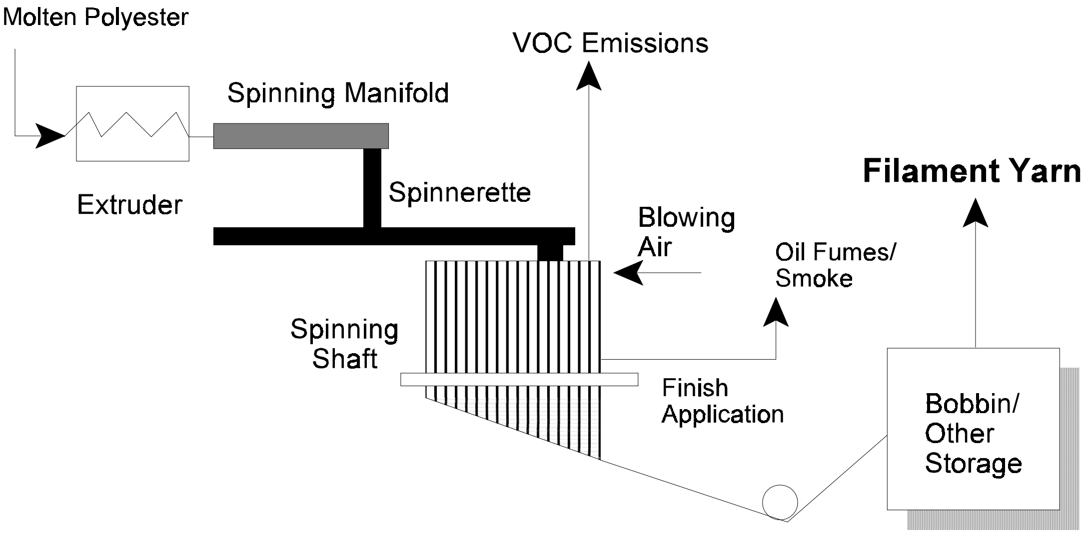

Figure 2-12. Melt Spinning of Polyester Fiber (ANL 1980, Chenier 1992, Brown 1996)

Key Energy and Environmental Facts - Polyester Melt Spinning			
Energy	***Emissions***	***Effluents***	***Wastes or Byproducts***
Energy use: *Process: 2,602 Btu/ton of spun fiber*	*Largest sources - fugitive emissions of volatiles, polymer dust, lubricant/oil fumes or smoke, burned polymer and combustion products*	*Negligible*	*Off-grade polymer*

In many plants molten PET is pumped at high pressure directly through an extruder spinerette, forming polyester filaments, in a process called melt spinning (see Figure 2-12). Melt spinning uses heat to melt the polymer to a viscosity that is appropriate for extrusion. Filament solidification is accomplished by blowing the filaments with cold air.

A thread guide converges the individual filaments to produce a continuous filament yarn, or spun yarn, that usually consists of between 15 to 100 filaments. The filament yarn is wound onto bobbins or further treated to obtain certain characteristics. Post-spinning operations may include lubricants and finishing oils that are applied to the fibers.

The process for manufacturing polyester that is based on DMT is quite similar to the process described above, except that methanol instead of water is produced in the esterification reactors. The methanol must be recovered and stored, adding complexity and cost to the process. (Process Description: ANL 1980, EPA 1991b, Chenier 1992)

2.2 Summary of Inputs/Outputs

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

Ethylene Manufacture

Inputs:	Outputs:.
Hydrocarbons	Ethylene
- Ethane	Propylene
- Propane	Butadiene
- Butane	Ethane
- Naphtha	Hydrogen
- Gas Oils	Fuel Oil
Electricity	Fuel Gas
Fuel/Steam	Pyrolysis Gasoline
Cooling Water	Steam
Boiler Feed Water	Process Water
Catalyst (acetylene conversion)	Spent Caustic
Caustics	Spent Catalyst

Polyethylene

Inputs:	Outputs:.
Ethylene	LDPE Pellets
Hydrogen	LLDPE Pellets
Catalysts	HDPE Pellets
Initiators	Purge Gas
Nitrogen	Process Water
Comonomers	Off-grade Polymer
Additives	
Steam/Fuel	
Electricity	
Cooling Water	
Boiler Feed Water	

Ethylene Dichloride/Vinyl Chloride

Inputs:	Outputs:
Ethylene	Ethylene Dichloride
Chlorine Gas	Vinyl Chloride Monomer
Caustics	Stripper Effluent
Air/Oxygen	Caustic Wastewater
Hydrochloric Acid	Hydrochloric Acid
Steam/Fuel	
Process Water	
Electricity	

Poly Vinyl Chloride

Inputs:	Output:
Vinyl Monomer	Poly Vinyl Chloride
Initiators	Recycle Monomer
Additives	Off-grade Polymer
Suspension Agent	Wash Water
Process Water	Process Water
Steam/Fuel	Vent Gases
Electricity	

Ethylene Oxide

Inputs:	Outputs:
Ethylene	Ethylene Oxide
Air/Oxygen	Liquid Byproducts
Metallic Silver Catalyst	Waste Air/Nitrogen
Cooling Water	Waste CO_2
Fuel/Steam	Wastewater
Electricity	

Ethylene Glycol

Inputs:	Outputs:
Ethylene Oxide	Ethylene Glycol
Pure Water	Diethylene Glycol
Acid Catalyst (optional)	Triethylene Glycol
Fuel/Steam	Light Gases
Electricity	Residue
Boiler Feed Water	Recycle Water

Polyester

Inputs:	Outputs:
Terephthalic Acid or Dimethyl Terephthalate	Polyester Fiber/Film
Ethylene Glycol	Spent Catalyst
Fuel/Steam	Ethylene Glycol
Electricity	Off-grade Polymer
Catalyst (antimony trioxide)	Wastewater
Cooling Water	Methanol (DMT only)
Boiler Feed Water	

2.3 Energy Requirements

The **process and feedstock energy** used for the production of ethylene, polyethylene, poly vinyl chloride, ethylene oxide, ethylene glycol, and polyester is shown in Tables 2-1 through 2-8 (HP 1997d). 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 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.

Total net energy inputs include processing energy for the final product, plus the heat of combustion of the feedstocks, minus any steam

Table 2-1. Estimated Energy Use in Ethylene Manufacture- 1997

Energy	Specific Energy[e] (Btu/lb)	Average Specific Energy (Btu/lb)	Total Energy Use [f] (10^{12} Btu/lb)	Estimated Chemical Industry Use [g] (10^{12} Btu/lb)
Net Electricity[a]	270 - 540	405	19.6	9.8
Energy for Steam/Process Heat [f]				
Fuel Oil and LPG[b]	154 - 308	231	11.2	5.6
Natural Gas	3,954 - 7,907	5,931	287.0	143.5
Coal and Coke	514 - 1,027	770	37.3	18.6
Other[c]	514 - 1,027	770	37.3	18.6
NET PROCESS ENERGY	**5,405 - 10,809**	**8,107**	**392.4**	**196.2**
Electricity Losses	561 - 1,121	841	40.7	20.4
Energy Export	(3,927 - 8,215)	(6,071)	(293.8)	(146.9)
TOTAL PROCESS ENERGY	**2,039 - 3,715**	**2,877**	**139.3**	**69.6**
Heat of Feedstock (ΔHc) [d]	31,414	31,414	1,520.4	760.2
TOTAL PRIMARY ENERGY	**33,453 - 35,129**	**34,291**	**1,659.7**	**829.8**
Feedstock Process Energy	329.00	329	15.9	8.0
TOTAL ENERGY EMBODIED IN ETHYLENE MFG	**33,782 - 35,458**	**34,620**	**1,675.6**	**837.8**

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 ethane (Perry 1984).
e Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity use for licensed technologies, including ABB Lummus Global SRT Furnace, Linde AG Pyrocrack Furnace, Stone & Webster Ultra Selective Cracking Furnace (Source: ANL 1980, Brown 1996, HP 1999).
f Based on 1997 production values (48.3 billion lbs) (CMA 1998).
g Assumes 50 percent of ethylene is produced at chemical plants (24.2 billion lbs) (CHEMX 1997).

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: fuel oil and LPG - 3%; natural gas - 77%; coal and coke - 10%; other - 10% (CMA 1998). The “other” category includes any other fuel source (e.g., byproduct fuel gases).

Ethylene manufacture is an energy-intensive process (see Table 2-1). The largest energy input is embodied in the feedstocks, (ethane, naphtha, gas oils) which are hydrocarbon fuels or fuel precursors. Processing energy in the form of fuels or steam accounts for about 82 percent of the total energy input for ethylene manufacture. Much of this energy is consumed in the ethylene cracking furnace. However, ethylene plants are largely energy self-sufficient and often net exporters of fuel.

Energy sources such as process byproducts (e.g., fuel oil, fuel gas), flue gases, and waste heat sources are utilized to supply as much as 95 percent of energy demand in modern ethylene furnaces (DOW 1999). Primary sources of energy include hot flue gases, transfer line heat exchangers (where the first stage of quenching is accomplished), and the primary fractionator. Combined heat recovery from hot flue gases and the transfer line exchangers supplies a large share of energy demand.

Heat is also recovered from quench towers in the form of low- or medium-pressure steam or low-temperature heat for downstream reboilers. Heavy fuel oil from these towers can be recovered as a byproduct but is also sometimes burned to generate process steam.

A methane-hydrogen gas stream is recovered in the methane separation tower, and is used to meet furnace fuel requirements. In some cases this stream also provides fuel for energy export to other processes.

The radiative zone of the pyrolysis furnace consumes more energy than any other single area. Energy requirements for this area of the furnace are greater for heavier feedstocks, although nearly all of this energy can be recovered from hot flue gases and hot products.

Steam is used primarily for compression and refrigeration, and is also added to the feedstock as a diluent to lower partial pressure and slow the build-up of coke. Combined energy requirements for compression and refrigeration account for 30 to 40 percent of energy demand (ANL 1980, Brown 1996). In most cases all the steam required for compression and refrigeration is supplied by the transfer line exchangers.

In the refrigeration system, streams are cascaded to take the greatest advantage of energy recovery. For example, propylene is cooled with cooling water, and ethylene is cooled with the coldest propylene stream. Each part of the system has different temperature levels to maximum thermodynamic efficiency. Process streams are thus cooled to minimize the amount of work lost, and reflux can be performed by refrigeration at an appropriate constant temperature. A complex system of heat exchangers is employed to recover refrigeration from exiting cold streams.

Imported (purchased) electricity comprises a very small share of energy use (DOW 1999). Electricity is used primarily for running cooling water, quench water, quench oil pumps, and sometimes small methane compressors.

As shown in Table 2-1, the total amount of process energy consumed during the industrial production of ethylene was about 70 trillion Btus in 1997 (including electricity losses and accounting for export energy). When electricity losses (incurred during the generation and transmission of electricity) are not considered, energy consumption in 1997 was about 50 trillion Btus. Note that the process

Table 2-2. Estimated Energy Use in Polyethylene Manufacture - 1997

Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	473 - 1,278	876	23.6
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	5 - 13	9	0.3
Natural Gas	127 - 339	233	6.3
Coal and Coke	17 - 44	30	0.8
Other[c]	17 - 44	30	0.8
NET PROCESS ENERGY	**638 - 1,718**	**1,178**	**31.8**
Electricity Losses	982 - 2,654	1,818	49.1
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**1,620**	**2,996**	**80.9**
Heat of Feedstock (ΔHc) [d]	21,625	21,625	583.9
TOTAL PRIMARY ENERGY	**23,245 - 25,997**	**24,621**	**664.8**
Feedstock Process Energy[e]	8,649	8,649	233.5
TOTAL ENERGY EMBODIED IN POLYETHYLENE MFG	**31,894 - 34,646**	**33,270**	**898.3**

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 ethylene (Perry 1984).
e Energy used to manufacture ethylene 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 Elenac GmbH/Hoechst AG stirred tank diluent HDPE, ENICHEM/Snamprogetti high pressure autoclave LDPE/EVA, Exxon Chemical high pressure LDPE, Mitsui Petrochemical low pressure slurry HDPE, Philips Petroleum slurry LPE, and Stamicarbon high pressure tubular LDPE/EVA (Source: HP 1999, HP 1997d).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (27 billion lbs) (SPI 1998).

energy for the hydrocarbon feedstocks used to produce ethylene is not shown – it is assumed to be produced off-site (e.g., in a petroleum refinery).

Production of **polyethylene** by addition polymerization is also an energy-intensive process in terms of feedstock requirements. Processing energy in this case constitutes less than 5 percent of total energy inputs. The more energy-intensive processes are those used to produce LDPE and EVA, due to higher the electricity requirements. However, these high-pressure processes (autoclave, tubular reactor) also generate low-pressure steam that can be used to provide process heat in other parts of the plant. (Note: Due to the variable data available for steam produced a credit is not shown in Table 2-2). Values for steam generated range from 0.3 to 0.7 pounds of steam per pound of product. Electricity accounts for the largest share of process energy use in polyethylene manufacture, about 75 percent of the total. Electricity is used primarily for compression and cooling of ethylene feedstock, and centrifuging, blending, extruding, and pelletizing of the polymer product.

Table 2-3. Estimated Energy Use in Ethylene Dichloride Manufacture - 1997

Energy	Average Specific [f] Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	341	6.9
Energy for Steam/Process Heat [f]		
Fuel Oil and LPG[b]	92	1.9
Natural Gas	2,363	47.7
Coal and Coke	307	6.2
Other[c]	307	6.2
NET PROCESS ENERGY	**3,140**	**68.9**
Electricity Losses	708	14.3
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**4,118**	**83.2**
Heat of Feedstock (ΔHc) [d]	9,948	201.0
TOTAL PRIMARY ENERGY	**14,066**	**284.1**
Feedstock Process Energy[e]	72,066	145.6
TOTAL ENERGY EMBODIED IN ETHYLENE DICHLORIDE MFG	**21,272**	**429.7**

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 (Perry 1984).
e Energy used to manufacture feedstock ethylene (see Table 2-1), chlorine, and oxygen (ANL 1980). Stoichiometric ratios are: 0.46 lbs ethylene, 0.58 lbs chlorine, and 0.31 lbs oxygen for every lb of vinyl chloride monomer.
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 (20.2 billion lbs), and assuming all ethylene dichloride is used to make poly vinyl chloride (SPI 1998).

Energy consumed in the production of **ethylene dichloride, vinyl chloride monomer (VCM), and poly vinyl chloride (PVC)** is shown in Tables 2-3 and 2-4. All ethylene dichloride is used to produce vinyl chloride monomer, which is then polymerized to form poly vinyl chloride. Steam accounts for most of the process energy consumed in the production of both VCM and PVC (80 to 90 percent of total energy use). Steam is used to drive the oxychlorination, dehydro-chlorination, and polymerization reactions, and for separation, melting and drying processes. Electricity is used primarily for mixing, blending, melting, pelletizing, and packaging.

Process energy required for the production of **ethylene oxide** constitutes about 8 percent of total energy use (excluding electricity losses). The reaction is very exothermic, and hot product is used to provide effluent heating. Table 2-5 reflects energy consumption for a process using air rather than oxygen for the oxidation of ethylene. When air is used for oxidation, a purge reactor and absorber are needed to removed nitrogen, which adds to energy costs and utility requirements. Most of the steam

Table 2-4. Estimated Energy Use in Poly Vinyl Chloride Manufacture - 1997

Energy	Average Specific [f] Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	256	3.6
Energy for Steam/Process Heat [f]		
Fuel Oil and LPG[b]	30	0.4
Natural Gas	762	10.8
Coal and Coke	99	1.4
Other[c]	99	1.4
NET PROCESS ENERGY	**1,246**	**17.6**
Electricity Losses	532	7.5
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**1,778**	**25.1**
Heat of Feedstock (ΔHc) [d]	10,147	143.1
TOTAL PRIMARY ENERGY	**11,925**	**168.1**
Feedstock Process Energy[e]	7,350	103.6
TOTAL ENERGY EMBODIED IN POLY VINYL CHLORIDE MFG	**19,275**	**271.8**

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 ethylene dichloride (Perry 1984). Stoichiometric ratio: 1.02 lbs VCM for every lb of PVC.
e Energy used to manufacture feedstock ethylene dichloride and vinyl chloride monomer (see Table 2-4). Stoichiometric ratio: 1.02 lbs VCM for every lb of PVC (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 the technology licensed by EVC International, currently used in 80 percent of PVC manufacture (HP 1999)).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (14.1 billion lbs) (SPI 1998).

requirements are for distillation and steam stripping to purify the product. Electricity accounts for about 30 percent of energy use, and is used primarily in the pumping and compression of feedstock and recycled water and gases.

In the production of **ethylene glycol,** large amounts of water are evaporated, and the liquids distilled are of low volatility. To ensure the process remains economical under these conditions, careful energy conservation is critical. Steam is required for multiple stage evaporators and stripping towers. Electricity requirements are relatively high (about 38 percent) and most electricity is used for pumping and compression, particularly for non-catalytic processes that require higher pressures and temperatures.

Production of **polyester**, particularly **polyethylene terephthalate (PET)** is very energy-intensive. Processing energy requirements to produce the raw polymer are high (about 35 percent of total energy use, excluding losses). These are expended mostly in the esterification reactor and during polymerization. Significant processing energy

Table 2-5. Estimated Energy Use in Ethylene Oxide Manufacture - 1997

Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	360 -627	494	3.5
Energy for Steam//Process Heat [f]			
Fuel Oil and LPG[b]	27 - 46	37	0.3
Natural Gas	693 - 1,182	937	6.7
Coal and Coke	90 - 154	122	0.9
Other[c]	90 - 154	122	0.9
NET PROCESS ENERGY	**1,260 - 2,162**	**1,711**	**12.2**
Electricity Losses	748 - 1,302	1,025	7.3
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**2,008 - 3,464**	**2,736**	**19.4**
Heat of Feedstock (ΔHc) [d]	19,463	19,463	138.2
TOTAL PRIMARY ENERGY	**21,471 - 22,927**	**22,199**	**157.6**
Feedstock Process Energy[e]	8,891	8,891	63.1
TOTAL ENERGY EMBODIED IN ETHYLENE OXIDE MFG	**30,362 - 31,818**	**31,090**	**220.7**

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 (Perry 1984). Stoichiometric ratio: 0.9 lbs ethylene and 1.14 lbs oxygen for every lb of ethylene oxide.
e Energy used to manufacture ethylene and oxygen feedstocks (see Table 2-1). Stoichiometric ratio: 0.9 lbs ethylene and 1.14 lbs oxygen for every lb of ethylene oxide.
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 technology used in a U.S. Gulf Coast plant using oxygen (rather than air) for oxidation (Source: CEH 1999). Assumes 29 percent electricity, 71 percent steam/fuels (ANL 1980).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (7.1 billion lbs) (CMA 1998).

is also expended in the production of the feedstocks (ethylene glycol and terephthalic acid), as well as in the melt spinning and drawing process that produces finished fibers.

Electricity is required primarily for filtering, crystallization, and various equipment used in spinning. Spinning requires a number of steps such as crimping, drawing, cutting, and baling that use relatively large amounts of electricity. Overall electricity use, however, constitutes only about 5 percent of total energy requirements (excluding electricity losses).

Table 2-6. Estimated Energy Use in Ethylene Glycol Manufacture - 1997			
Energy	**Specific Energy [f] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Chemical Industry Energy Use [g] (10^{12} Btu)**
Electricity[a]	377 - 689	533	3.0
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	34 - 57	45	0.3
Natural Gas	865 - 1,463	1,164	6.5
Coal and Coke	112 - 190	151	0.9
Other[c]	112 - 190	151	0.9
NET PROCESS ENERGY	**1,501 - 2,589**	**2,045**	**11.5**
Electricity Losses	783 - 1,431	1,107	6.2
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**2,284 - 4,020**	**3,152**	**17.7**
Heat of Feedstock (ΔHc) [d]	14,597 - 14,705	14,651	82.1
TOTAL PRIMARY ENERGY	**16,881 - 18,725**	**17,803**	**99.7**
Feedstock Process Energy[e]	6,668	6,668	37.3
TOTAL ENERGY EMBODIED IN ETHYLENE GLYCOL MFG	**23,549 - 25,393**	**24,471**	**137.0**

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 for two processes: direct hydration of ethylene oxide, and ethylene oxidation followed by hydrolysis (Perry 1984). Stoichiometric ratio for direct hydration: 0.75 lbs ethylene oxide for every lb of ethylene glycol. Stoichiometric ratio for oxidation of ethylene: 0.68 lbs ethylene and 0.79 lbs of oxygen for every lb of ethylene glycol.

e Energy used to manufacture ethylene, ethylene oxide, and oxygen feedstocks (see Table 2-1). Stoichiometric ratio for direct hydration: 0.75 lbs ethylene oxide for every lb of ethylene glycol. Stoichiometric ratio for oxidation of ethylene: 0.68 lbs ethylene and 0.79 lbs of oxygen for every lb of ethylene glycol.

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 technology for direct hydration (Source: CEH 1999) and for oxidation of ethylene (ANL 1980). Assumes 38 percent for electricity use.

g Calculated by multiplying average energy use (Btu/lb) by1997 production values (5.6 billion lbs) (CMA 1998).

Table 2-7. Estimated Energy Use in Polyester Manufacture - 1997

Energy	Specific Energy [f] (Btu/lb)	Average Specific Energy (Btu/lb)	Chemical Industry Energy Use [g] (10^{12} Btu)
Electricity[a]	1,022 - 1,244	1,133	6.7
Energy for Steam/Process Heat [f]			
Fuel Oil and LPG[b]	298 - 362	330	2.0
Natural Gas	7,636 - 9,259	8,466	50.0
Coal and Coke	992 - 1,207	1,099	6.5
Other[c]	992 - 1,207	1,099	6.5
NET PROCESS ENERGY	**10,939 - 13,316**	**12,128**	**71.6**
Electricity Losses	21,222 - 2,583	2,353	13.9
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**13,061 - 15,899**	**14,480**	**85.4**
Heat of Feedstock (ΔHc) [d]	22,448	22,448	132.4
TOTAL PRIMARY ENERGY	**35,509 - 38,347**	**36,928**	**217.9**
Feedstock Process Energy[e]	4,863	4,863	28.7
TOTAL ENERGY EMBODIED IN POLYESTER MFG	**40,327 - 43,210**	**41,791**	**246.6**

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 p-xylene, methanol and ethylene glycol feedstocks (Perry 1984). Stoichiometric ratio : 0.63 lbs p-xylene, 0.05 lbs methanol, and 0.7 lbs ethylene glycol for every lb of polyester fiber.
e Energy used to manufacture p-xylene (used to manufacture purified terephthalic acid), methanol, and ethylene glycol. Stoichiometric ratio: 0.63 lbs p-xylene, 0.05 lbs methanol, and 0.7 lbs ethylene glycol for every lb of polyester fiber.
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 technology (Source: Brown 1996, ANL 1980). Does not include melt spinning and drawing (see Table 2-9).
g Calculated by multiplying average energy use (Btu/lb) by1997 production values (5.9 billion lbs) (SPI 1998).

Table 2-8 Estimated Energy Use in Polyester Fiber Melt Spinning and Drawing - 1997

Energy	Average Specific [c] Energy (Btu/lb)	Chemical Industry Energy Use [d] (10^{12} Btu)
Electricity[a]	826	4.9
Steam[b]	1,776	10.6
NET PROCESS ENERGY	**2,602**	**15.5**
Electricity Losses	1,715	10.1
TOTAL PRIMARY ENERGY	4,317	25.6

a Does not includes losses incurred during the generation and transmission of electricity.
b Includes all fuels used to produce steam..
c Values are based on published fuel use and electricity requirements for licensed technology (Source: Brown 1996).
d Calculated by multiplying average energy use (Btu/lb) by1997 production values (5.9 billion lbs) (SPI 1998).

2.4 Air Emissions

Fugitive and Point Source Emissions Are the Primary Source of Air Contaminants in the Ethylene Chain

The primary sources of emissions in the ethylene chain are fugitive and point air source emissions of volatile compounds emitted from equipment and during process reactions. Fugitive emissions of volatile compounds escape from leaks in valves, pumps, tanks, flanges, and similar sources. While individual leaks may be minor, the combined amount of fugitive emissions from various sources can be substantial. In 1996, nearly 60 million pounds of toxic fugitive emissions were reportedly released by chemical producers. (EPA 1998).

The primary toxic air emissions from production of **ethylene** and its derivatives include ethylene glycol, ethylene, ethylene oxide, methanol, and vinyl chloride. Air emissions of these compounds are reported annually in the Toxic Release Inventory (EPA 1998; see also EPA 1994a, 1994b). Ethylene and ethylene glycol are among the top reported toxic air emissions from organic chemicals production. In 1996, reported emissions of ethylene from fugitive and point sources amounted to 31.4 million pounds. That same year, fugitive emissions of ethylene glycol were about 3.0 million pounds. Emissions of ethylene oxide and vinyl chloride, both known or suspected carcinogens, were also significant (0.2 million pounds and 0.07 million pounds, respectively, in 1995) (EPA 1997c).

Air emissions from manufacture of **poly vinyl chloride** include fugitive and point source emissions of raw materials or monomers, solvents, or other volatile liquids emitted during the reaction; sublimed solids (e.g., phthalic anhydride); and solvents lost during storage and handling of thinned resins. Emission factors for the manufacture of poly vinyl chloride are shown in Table 2-9.

Table 2-9 Air Emission Factors for Polyvinyl Chloride Manufacture

Type of Plastic	Particulate Emissions (lb/ton)	Gases (lb/ton)
PVC	35	17

Source: EPA 1991c.

The manufacture of polyester produces emissions of volatile organic compounds (VOCs) and particulates. Total VOC emissions will depend on the type of system used to recover ethylene glycol, the primary volatile source. The largest point of origin is the cooling tower, and emissions from this source depend on glycol concentration as well as windage rate. Many plants recover the glycol using a spray scrubber condenser directly off the process vessel and before the stream passes through the vacuum system. This type of recovery results in low concentrations of glycol in the cooling water, which lowers emission rates overall.

The methanol recovery system in DMT polyester processes is the second largest source of VOCs. Estimated emission factors for non-methane sources of volatiles for both processes are shown in Table 2-10. Emissions from raw material storage include losses from storage and transfer of ethylene glycol. Particulate emissions originate from TPA dust and other sources.

During the **melt spinning of polyester** a number of emissions are created. These include polymer dust from drying operations, volatilized residual monomer, fiber lubricants (fumes or smoke), and burned polymer and combustion products from cleaning the spinning equipment. Emission factors for melt spinning operations are shown in Table 2-11.

Table 2-10 Air Emission Factors for Polyester Manufacture

Emission Stream	Nonmethane VOCs[a] (grams/kg)		Particulate Emissions (grams/kg)	
	DMT Process	TPA Process	DMT Process	TPA Process
Raw Material Storage	0.1	0.1	0.165	ND
Mix Tanks	N	N	ND	ND
Methanol Recovery System	0.3	NA	ND	NA
Recovered Methanol Storage[b]	0.09	NA	ND	NA
Esterification[c]	NA	0.04	ND	ND
Prepolymerization Vacuum System	0.009	0.009	ND	ND
Polymerization Reactor Vacuum System	0.005	0.005	ND	ND
Cooling Tower[d]	0.2 3.4	0.2 3.4	ND	ND
Ethylene Glycol Process Tanks	0.0009	0.0009	ND	ND
Ethylene Glycol Recovery Condenser	0.01	NA	ND	NA
Ethylene Glycol Recovery Vacuum System	0.0005	0.0005	ND	ND
Product Storage[e]	ND	ND	0.0003	0.0003
Sludge Storage and Loading	0.02		ND	NA
TOTAL PLANT[d]	0.73 3.9	0.36 3.6	0.17	NED

Source: EPA 1991a.

Notes: N= negligible; ND= no data; NA = not applicable; NED = not enough data.

[a] Rates reflect extensive use of condensers and other recovery equipment as part of normal industry practice.

[b] Reflects control by refrigerated condensers

[c] Reflects control with primary and secondary condensers

[d] Lower value indicates the use of spray condensers on all prepolymerizers and polymerization reactors, which greatly affects the amount of volatiles present in cooling water entering the cooling tower.

[e] Reflects control of product storage emissions. Without controls, emission rate is about 0.4 grams/kilogram of product.

Table 2-11. Air Emission Factors for Melt Spinning of Polyester (lbs/1000 lbs fiber spun, including waste fiber)

Type of Fiber	Nonmethane Volatile Organics	Particulates
Staple	0.6[a]	252[c]
Yarn[b]	0.05[a]	0.03[d]

Source: EPA 1990.

[a] Emitted in aerosol form, and uncontrolled
[b] Factors for high viscosity industrial and tire yarm are 0.18 lb VOC and 3.85 lb particulate
[c] After control on extrusion parts cleaning operations, and contains some aerosol
[d] Uncontrolled, and contains some aerosol

Lubricants and oils are sometimes vaporized, then condense and coalesce as aerosols. This occurs mostly in the spinning, and sometimes in the post-spinning operations. In some instances these are vented to demisters, which remove some of the oil, or to catalytic incinerators, which oxidize the volatile hydrocarbons. Finish oils that do not volatilize are recovered and re-circulated (EPA 1990).

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. 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 (incomplete combustion), heaters can be a significant source of emissions. Current emission factors for process heaters and boilers are discussed in Section 7, Supporting Processes.

2.5 Effluents

Liquid Wastes Are Comprised Primarily of Stripper or Equipment Wash Water

Effluents emitted during the production of ethylene and its derivatives consist primarily of product wash or purification process wastewaters, equipment wash water, and cooling water. In general, much of the water used in chemicals manufacture is recycled for reuse in the process wherever possible.

Limitations 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 originally promulgated in 1974 and has been revised several times since then. The chemicals in the ethylene chain are covered under Subparts C, D, F, and G in Part 414. Because these Subparts also cover numerous other chemicals, the limitations are presented as a whole in Section 7, Supporting Processes, where general water treatment processes are covered.

2.6 Wastes, Residuals, and Byproducts

Hazardous Wastes Are Associated with Production of Ethylene Dichloride and Poly Vinyl Chloride

The EPA classifies a number of wastes associated with the production of ethylene and its derivatives as hazardous waste under Title 40 Code of Federal Regulations (CFR), Part 261, Section 32. These include waste associated with the production of ethylene dichloride as well as vinyl chloride monomers (see Table 2-12).

There are many options available for the management of these hazardous wastes, ranging from incineration (which destroys the hazardous components) to various treatment technologies (which convert hazardous to non-hazardous components). Some are operated on-site and integrated into the plant, with waste energy recovery options. A significant amount is sent off-site for treatment at external facilities. The management of hazardous wastes from chemical processing is in itself a large, diverse topic, and is outside the scope of this report. For more information, refer to one of the many sources published on this topic.

Table 2-12. Hazardous Wastes from Production of Ethylene Dichloride and Poly Vinyl Chloride

Waste Classification	Description	Hazardous Constituents
K018	Heavy ends from the fractionation column in ethyl chloride	1,2-dichloroethane, trichloroethylene, hexachlorobutadiene, hexachlorobenzene
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production	Ethylene dichloride, 1,1,1-trichloroethane, tetrachloroethanes, trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride
K020	Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production	Ethylene dichloride, 1,1,1-trichloroethane, tetrachloroethanes, trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride

Source: BNA 1995.

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

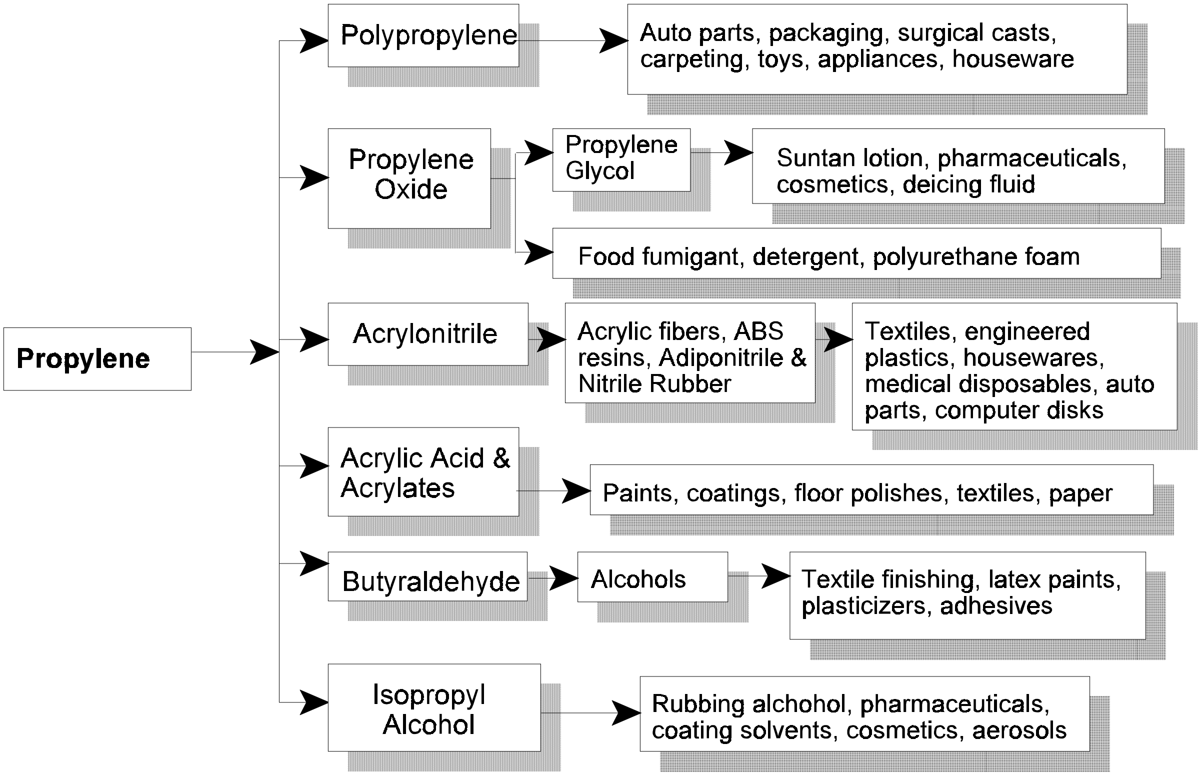

Figure 3-1. The Propylene Products Chain (CMA 1998)

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.

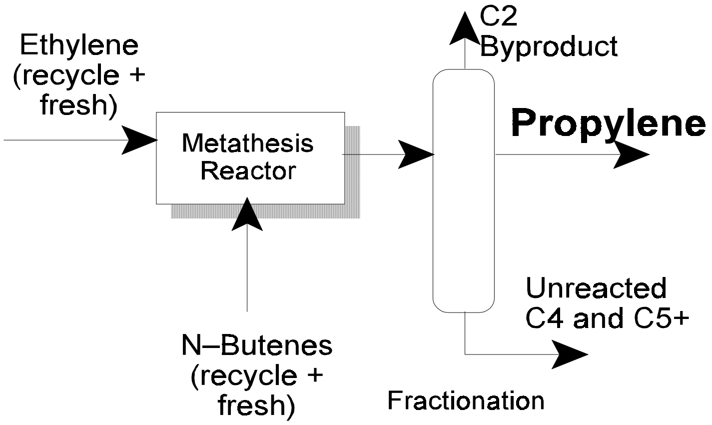

Figure 3-2. Propylene Production by Metathesis (HP 1999)

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*

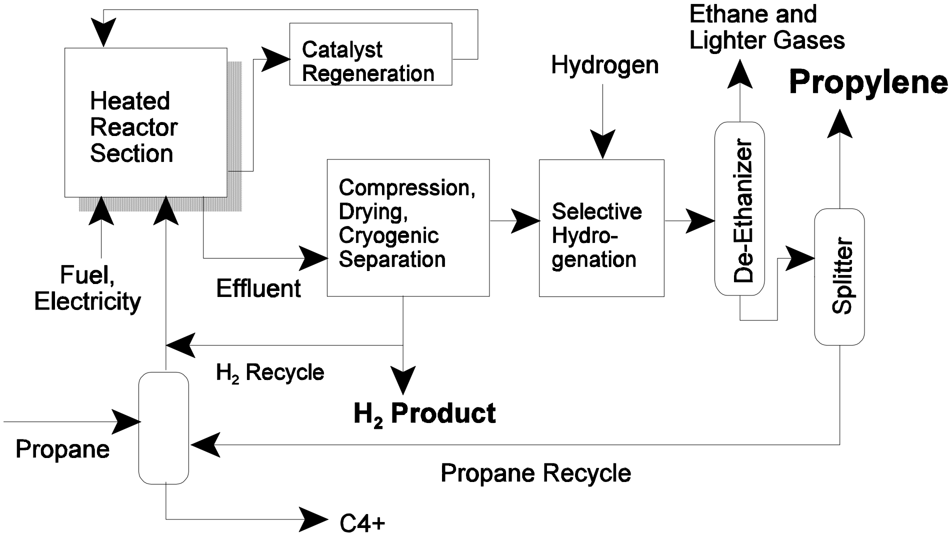

Figure 3-3. Dehydrogenation of Propane To Yield Propylene
(HP 1999)

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.

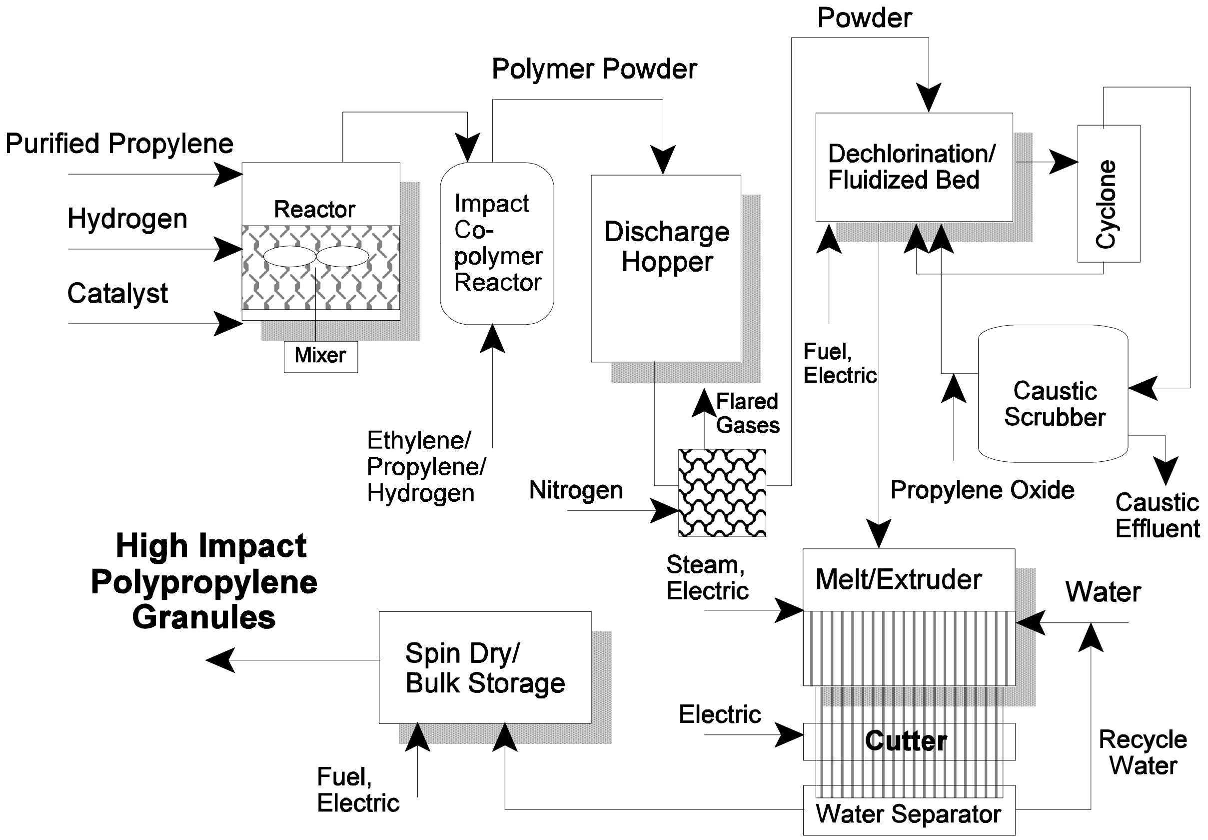

Figure 3-4. Polypropylene Manufacture
(ANL 1980, Brown 1996, HP 1999, Orica 1999)

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.

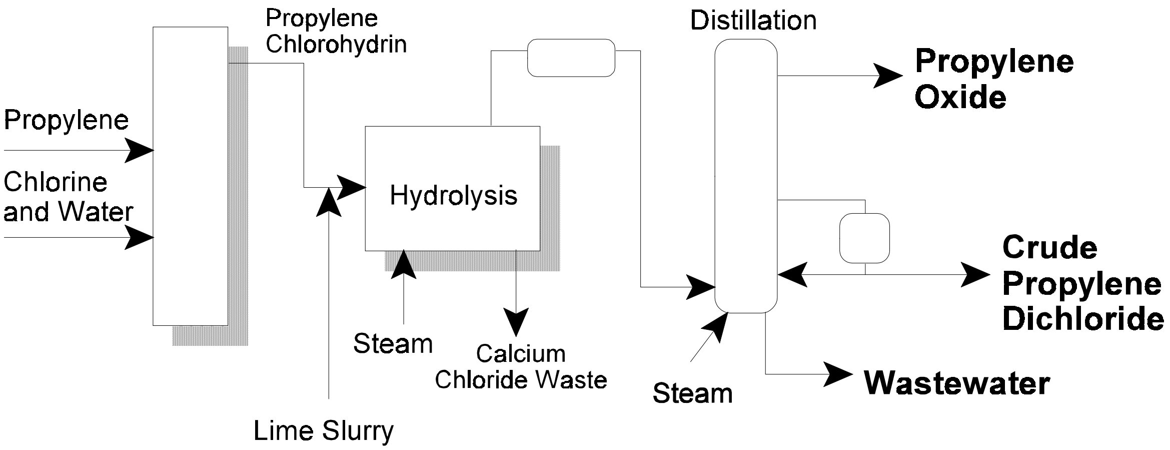

Figure 3-5. Manufacture of Propylene Oxide through Chlorohydrin Formation
(ANL 1980, Chenier 1992, HP 1999)

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*

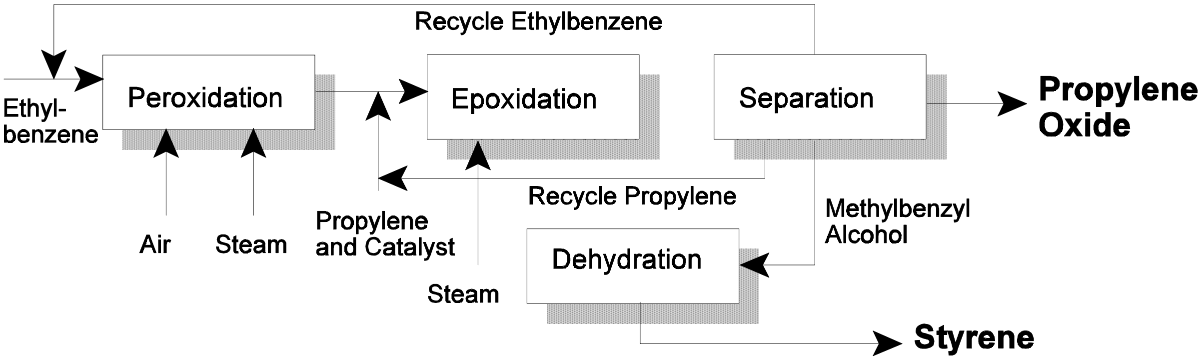

Figure 3-6. Manufacture of Propylene Oxide by Peroxidation
(ANL 1980, Chenier 1992)

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

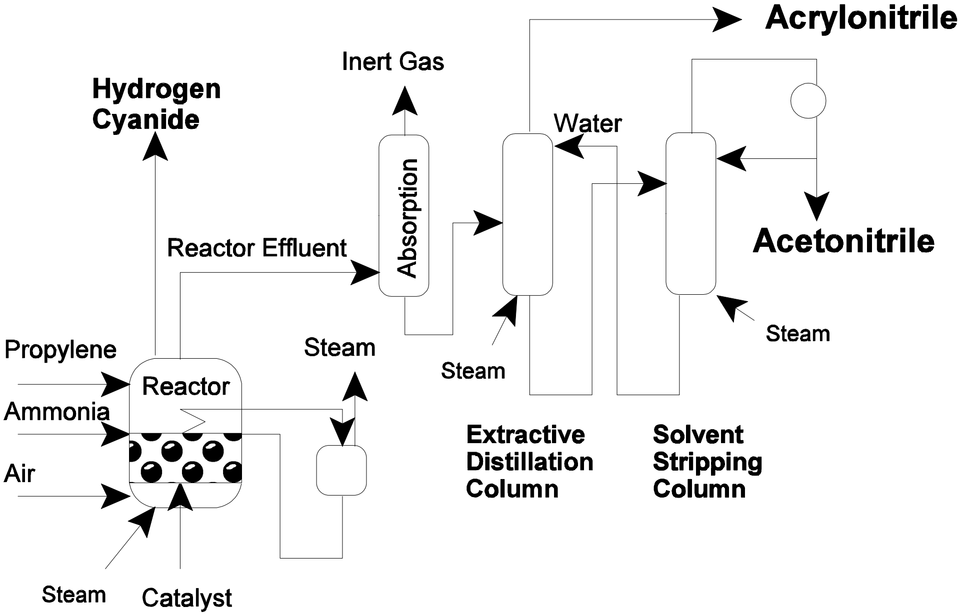

Figure 3-7. Acrylonitrile Manufacture from Propylene
(ANL 1980, Chenier 1992, ICETT 1997)

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.

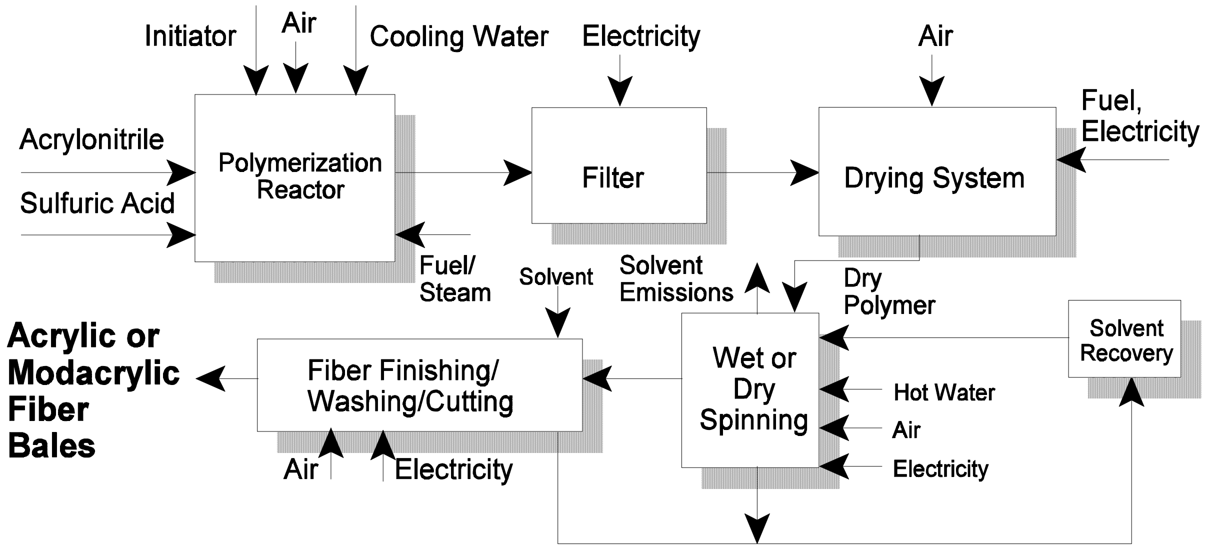

Figure 3-8. Acrylic/Modacrylic Fiber Production
(ANL 1980, EPA 1990)

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.

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

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.*

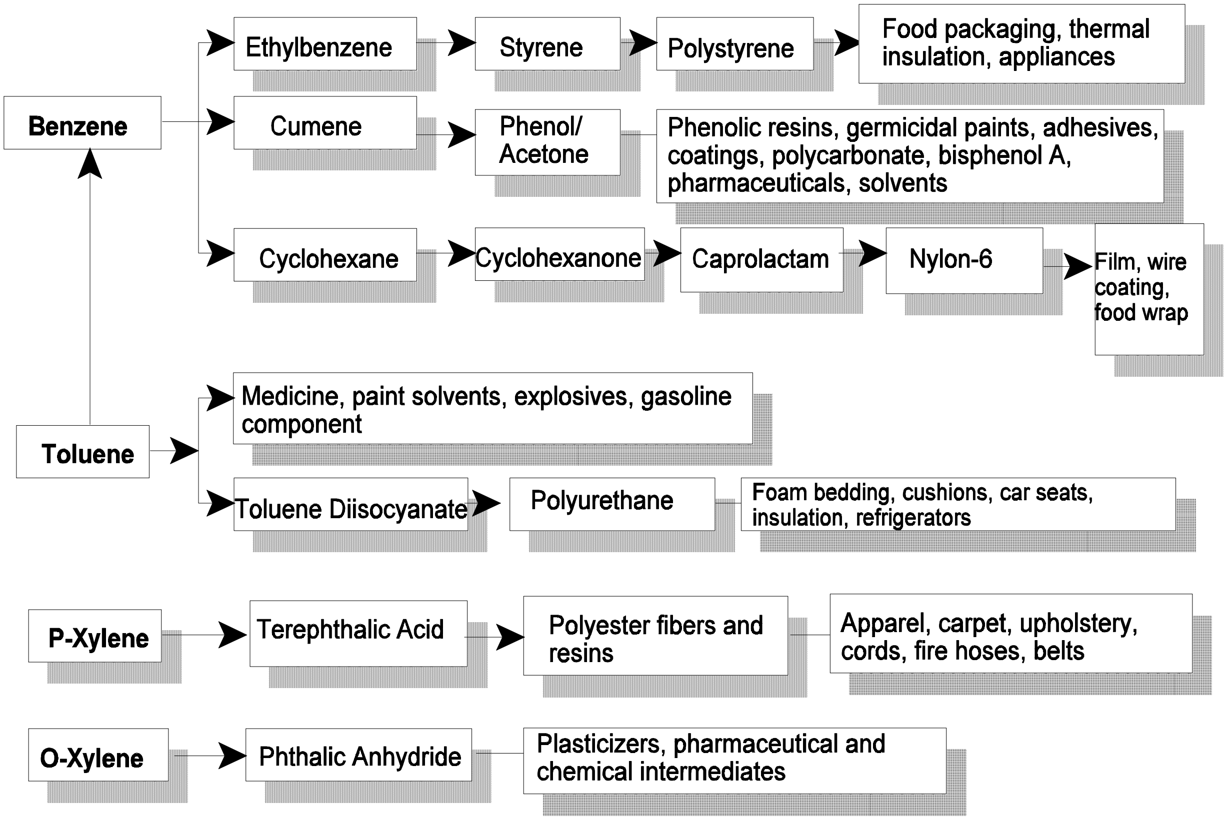

Figure 4-1. The BTX Chain (CMA 1998)

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.

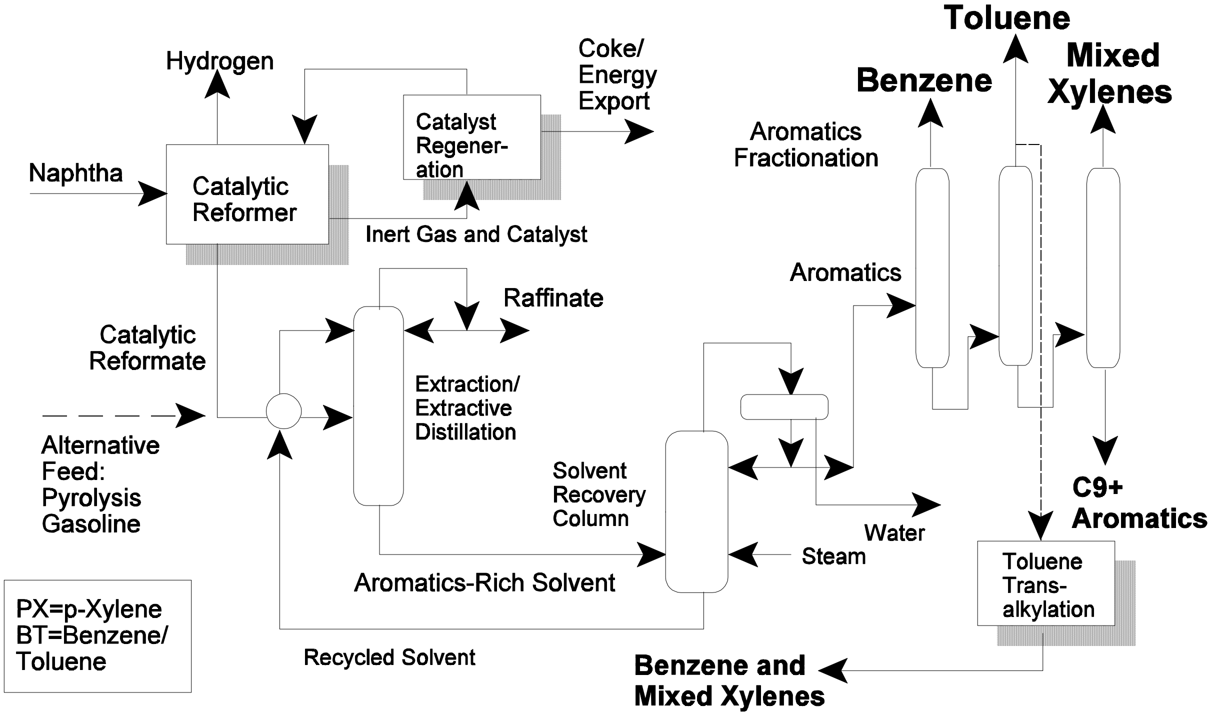

Figure 4-2. Possible Configuration for Reforming of Naphtha To Produce Benzene, Toluene, and Xylene (Chenier 1992, HP 1999, Orica 1999)

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

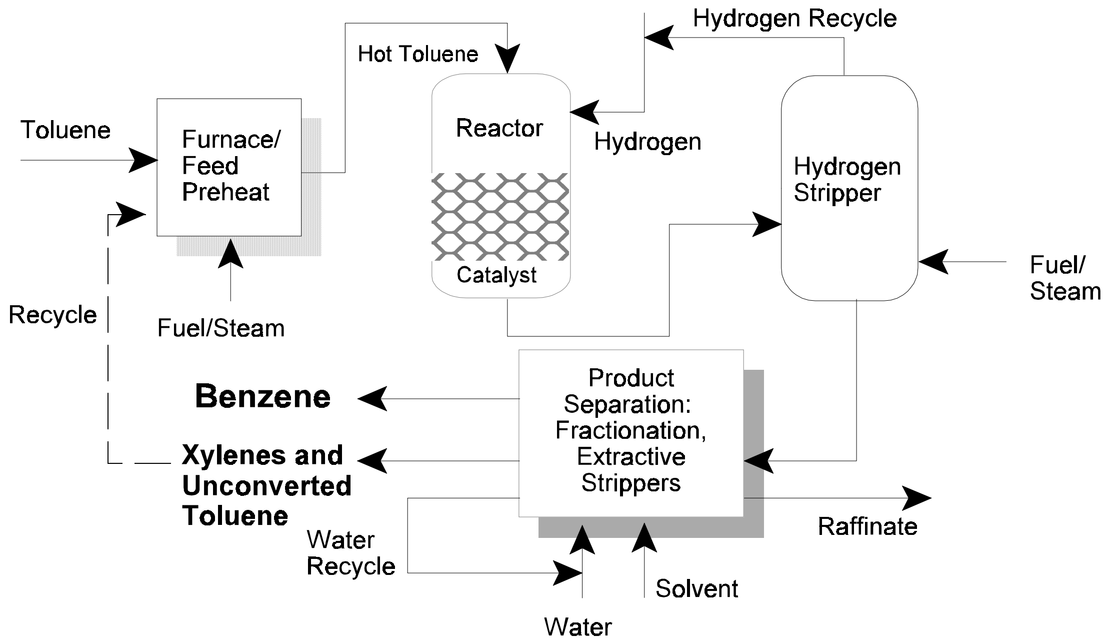

Figure 4-3. Toluene Hydrodealkylation to Produce Benzene (HP 1999, Orica 1999)

Key Energy and Environmental Facts - Toluene Hydrodealkylation			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 1,117 Btu/lb* *Feedstock ΔH_c: 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.

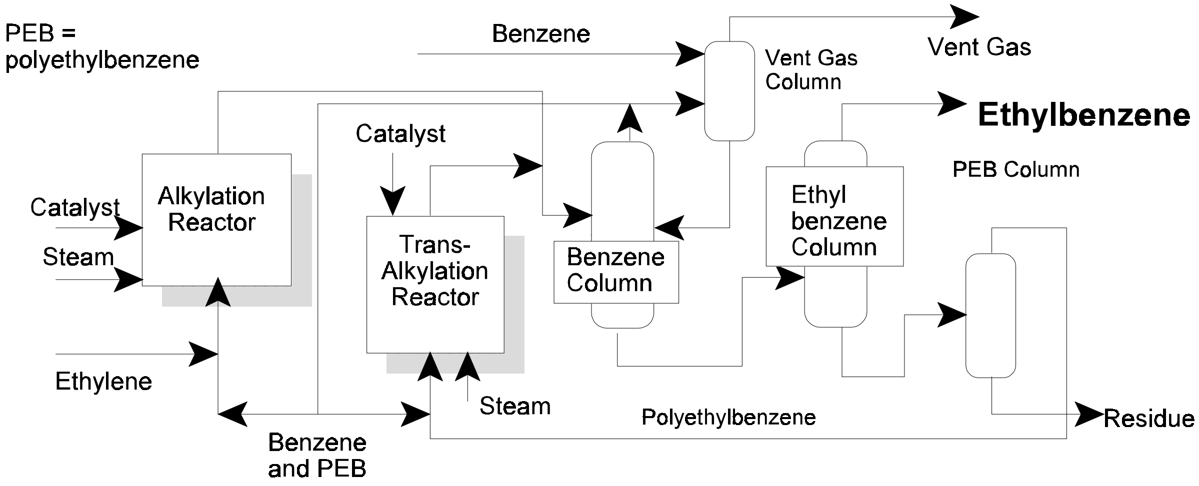

Figure 4-4. Ethylbenzene Manufacture (HP 1999)

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

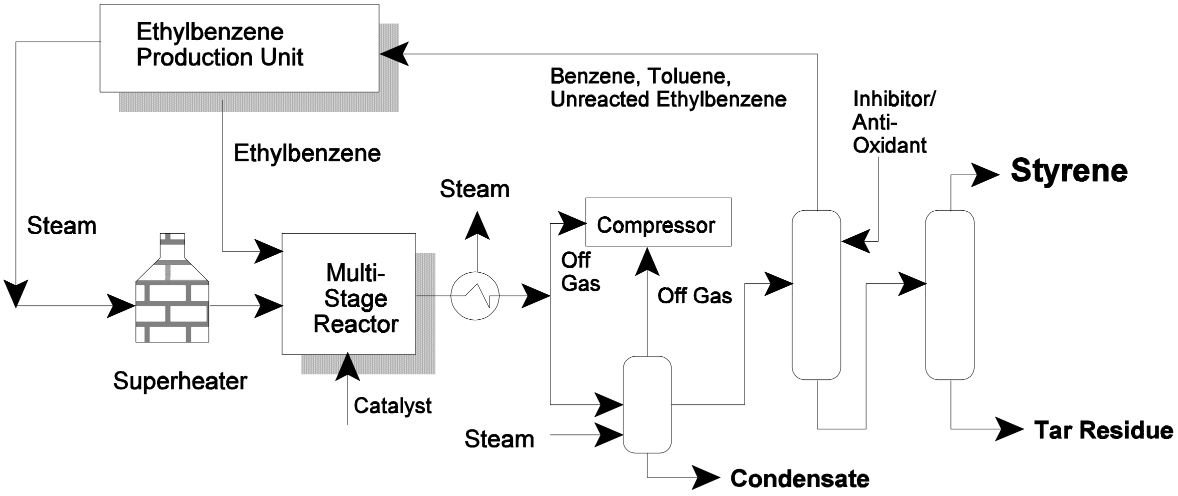

Figure 4-5. Styrene Manufacture (ANL 1980, HP 1999)

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

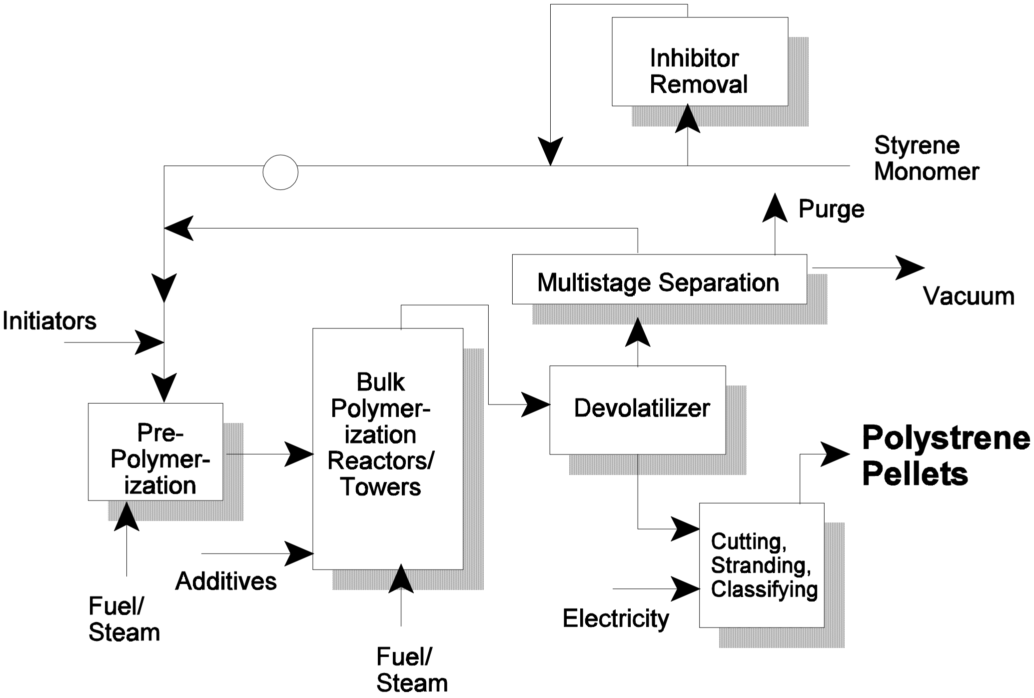

Figure 4-6. Polystyrene Manufacture (ANL 1980, HP 1999)

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 230°F to 350°F (110°C to 177°C) 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 500°F (260°C), 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

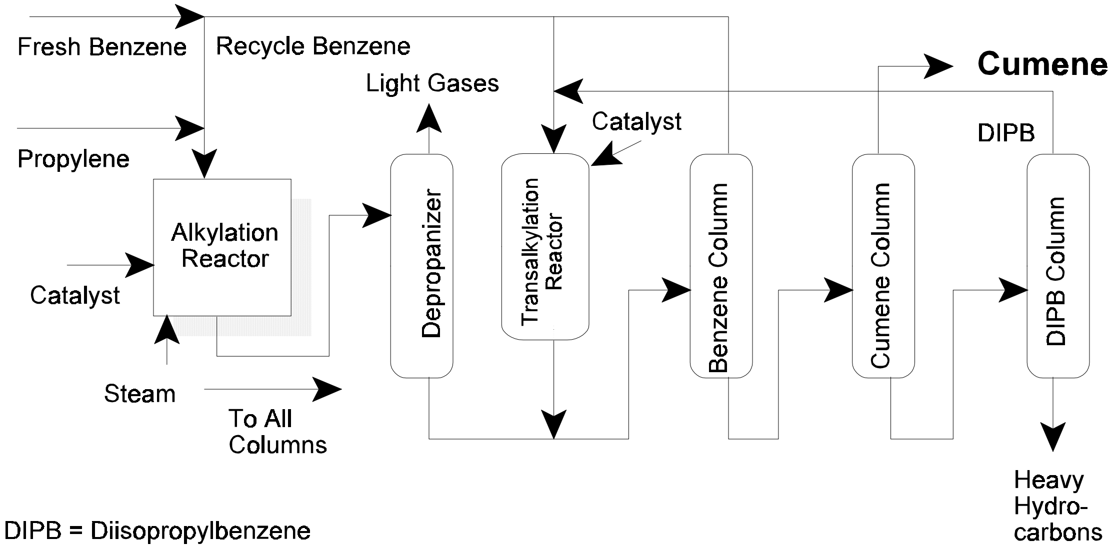

Figure 4-7. Cumene Manufacture (ANL 1980, HP 1999)

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

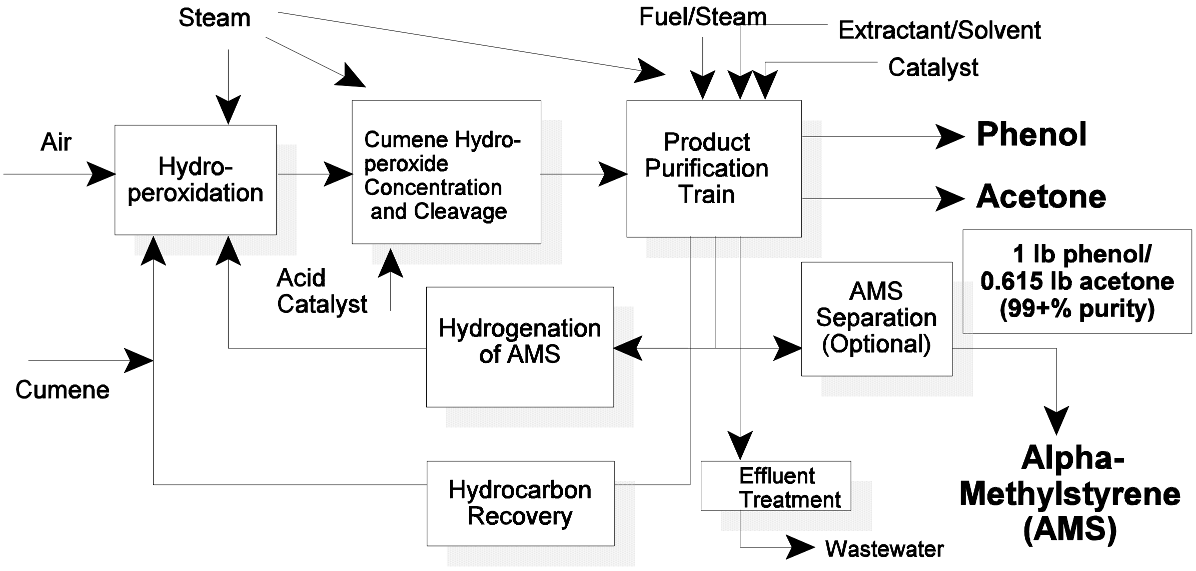

Figure 4-8. Phenol/Acetone Manufacture (Chenier 1992, HP 1999)

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).

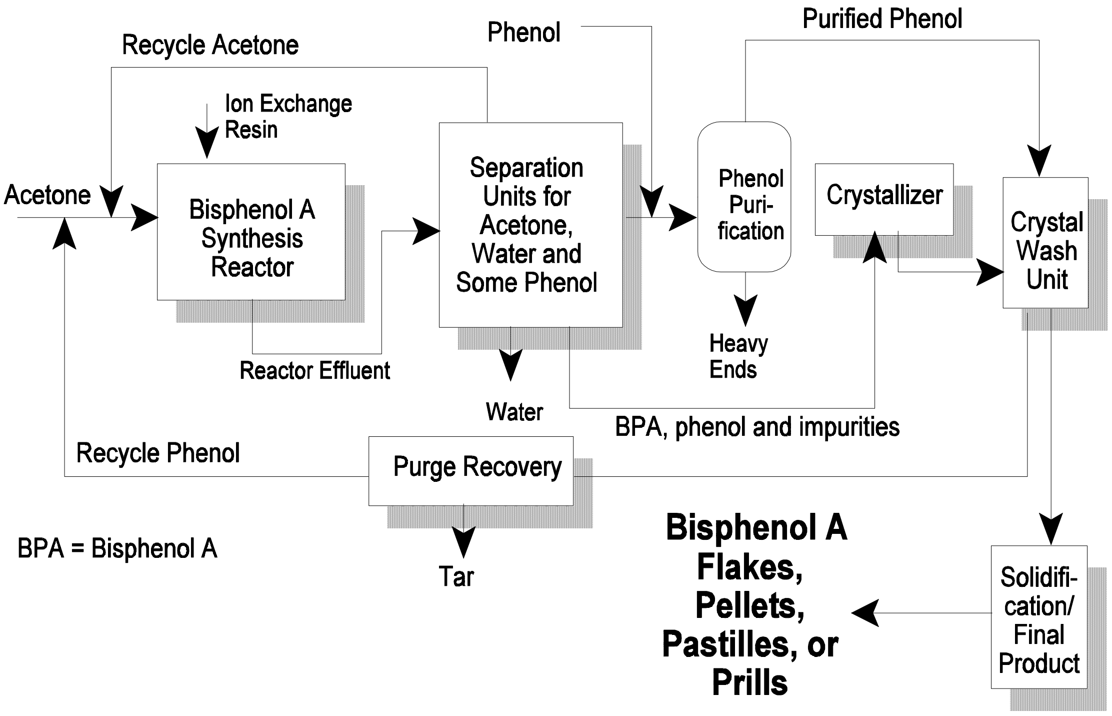

Figure 4-9. Bisphenol A Manufacture (Chenier 1992, HP 1999)

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

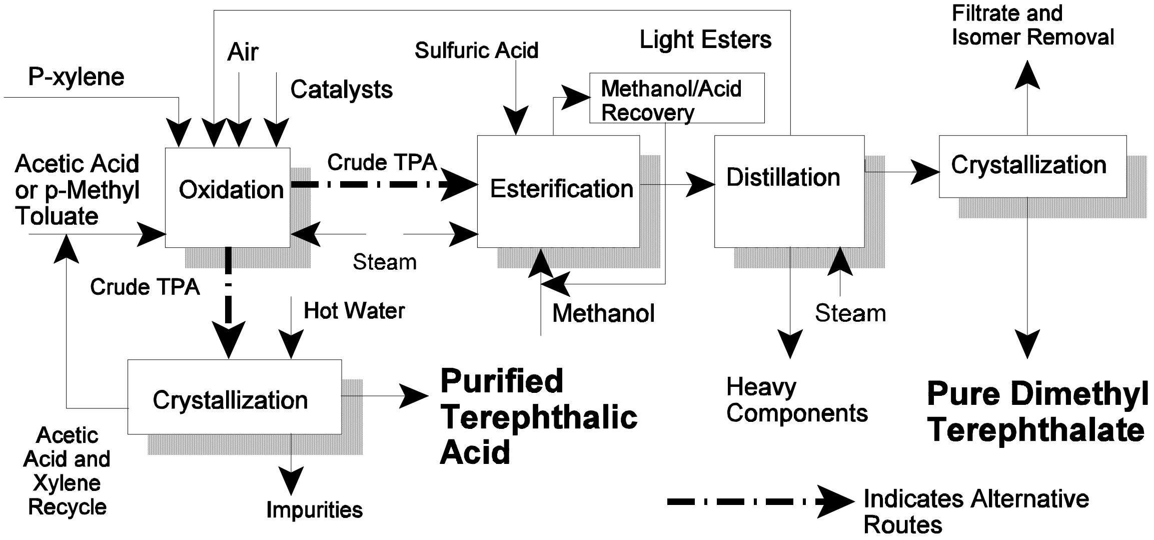

Figure 4-10. Manufacture of Terephthalic Acid and Dimethyl Terephthalate
(Chenier 1992, HP 1999)

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*

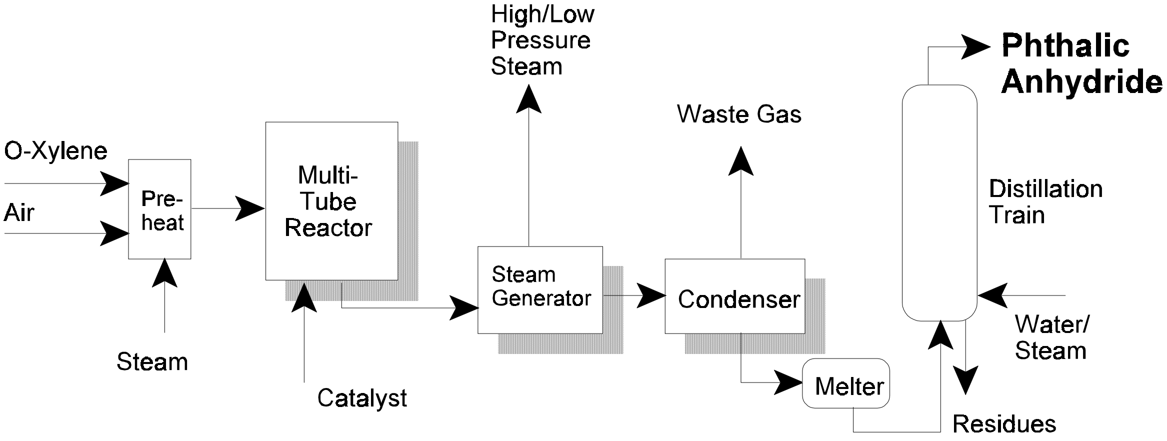

Figure 4-11. Manufacture of Phthalic Anhydride (Chenier 1992, HP 1999)

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.

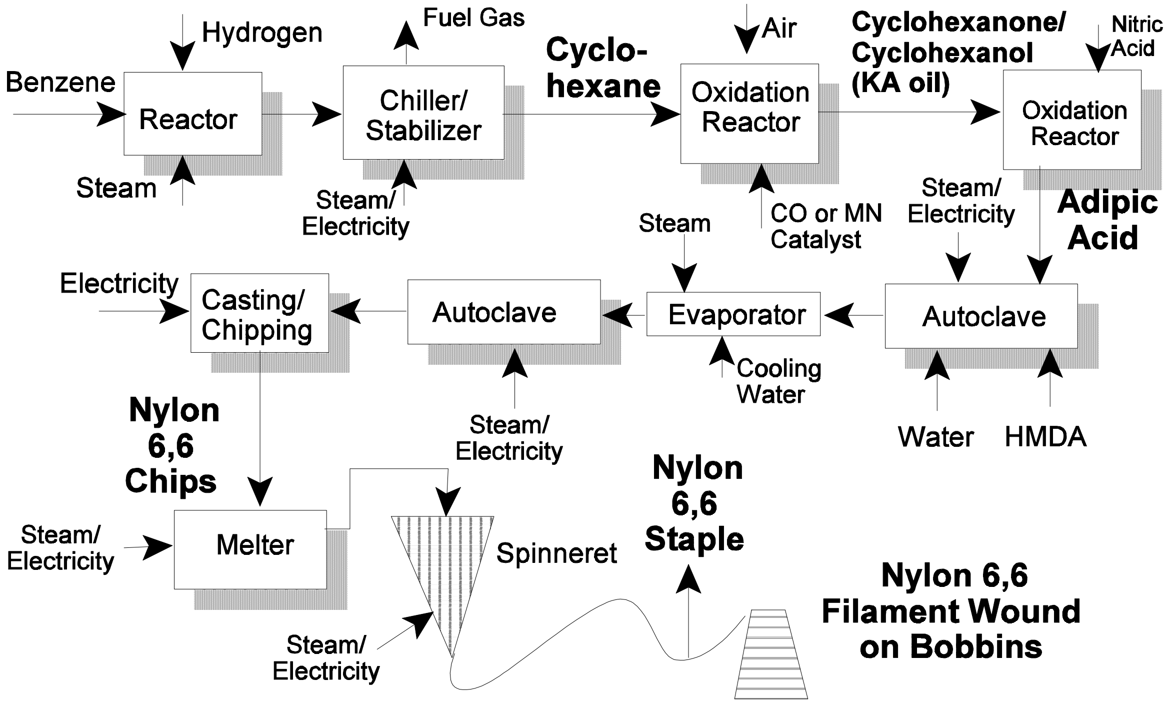

Figure 4-12. Nylon 6,6 Manufacture (EPA 1990, Chenier 1992, Brown 1996)

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*

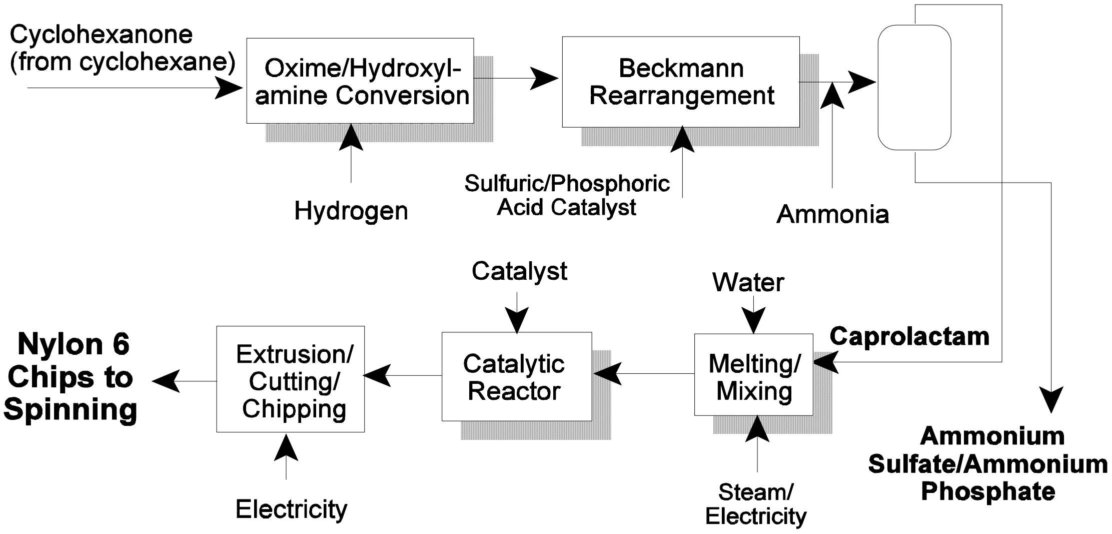

Figure 4-13. Nylon 6 Manufacture (EPA 1990, Chenier 1992, Brown 1996, HP 1999)

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	Benzene/Toluene/Xylene
Pyrolysis	Hydrogen
Gasoline	Water
Ethylbenzene	Coke/Energy Export
Solvent	Purge/Flared Gases
Inert Gas	Process Water
Catalyst	Extraction Raffinate
Water	Spent Catalyst
Steam/Fuel	
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:	Outputs:
Acetone	Bisphenol A Flakes, Pellets, Pastilles, or Prills
Phenol	Reaction-Produced Water
Ion Exchange Resin	Tar
Process Water	Heavy Components
Steam/Fuel	
Electricity	

Terephthalic Acid, Dimethyl Terephthalate

Inputs:	Outputs:
p-Xylene	Terephthalic Acid
Acetic Acid	Dimethyl Terephthalate
p-Methyl Toluate	Heavy Components
Sulfuric Acid	Filtrate
Methanol	Isomer Byproducts
Air	Process Water
Catalyst	Acid Byproducts
Process Water	
Steam/Fuel	
Electricity	

Phthalic Anhydride

Inputs:	Outputs:
o-Xylene	Phthalic Anhydride
Air	Heavy Components
Catalyst	High Pressure Steam
Process Water	Low Pressure Steam
Steam/Fuel	Spent Catalyst
Electricity	Waste Gases
	Process Water

Cyclohexane

Inputs:	Outputs:
Benzene	Cyclohexane
Hydrogen	Fuel Gas
Catalyst	Spent Catalyst
Steam/Fuel	
Electricity	

Adipic Acid

Inputs:	Outputs:
Cyclohexane	Adipic Acid
Air	Spent Catalyst
Catalyst	Vent Gases
Process Water	Wastewater

Caprolactam

Inputs:	Outputs:
Cyclohexane	Caprolactam
Hydrogen	Ammonium Sulfate
Acid Catalyst	Ammonium Phosphate
Ammonia	Wastewater
Process Water	Acid Waste
Steam/Fuel	
Electricity	

Nylon 6,6

Inputs:	Outputs:
Adipic Acid	Nylon 6,6 Filament or Staple
HMDA	Process Water
Process Water	
Steam/Fuel	
Electricity	

Nylon 6

Inputs:	Outputs:
Benzene	Cyclohexane
Hydrogen	Fuel Gas
Catalyst	Spent Catalyst
Steam/Fuel	
Electricity	

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	0.04[d]
Additives		
General Purpose	0.002	
High Impact	0.001	
Ethylbenzene Storage	0.001	
Dissolvers	0.008	
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.

5

Agricultural Chemicals: Fertilizers

5.1 Overview of Fertilizers

Ammonia and Sulfuric Acid Are Key Chemicals In Fertilizer Production

Approximately 85 percent of the **ammonia** produced worldwide is used to make agricultural fertilizers. While ammonia can be applied directly to the soil, it is usually first converted to a solid by reacting it with carbon dioxide or certain acids. Ammonia is also used as a raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products (see Figure 5-1).

Ammonia is ranked seventh among the top fifty chemicals, with an annual production of 28.4 billion pounds, and has ranked among the top ten chemicals for the last thirty years. Ammonia is derived from methane, an organic feedstock, but has traditionally been grouped with inorganic chemicals because its primary derivatives are inorganic. Many of its derivatives are also among the top fifty chemicals, including nitric acid, ammonium nitrate, ammonium sulfate, and urea (Chenier 1992, CMA 1998).

Nitric acid is a powerful oxidizing agent and is used primarily to manufacture ammonium nitrate. Its minor uses include the manufacture of adipic acid, nitroglycerin, trinitrotoluene (TNT), nitrobenzene, and other chemicals.

After World War II, the chief use of **ammonium nitrate** was as an explosive. Although it is still used in the manufacture of more than 75 percent of all explosives, its primary use today is as a fertilizer because of its high nitrogen content. Nitric acid and ammonium nitrate ranked

Production of Major Agricultural Chemicals (1997)

Ammonia (28.4 billion lbs)
Nitric Acid (13.5 billion lbs)
Ammonium Nitrate (12.3 billion lbs)
Urea (11.8 billion lbs)
Ammonium Sulfate (4.1 billion lbs)
Sulfuric Acid (71.4 billion lbs)
Phosphoric Acid (9.9 billion lbs)
Ammonium Phosphates (18.9 billion lbs)
Super Phosphates (3.4 billion lbs)

Source: CMA 1998, TFI 1999.

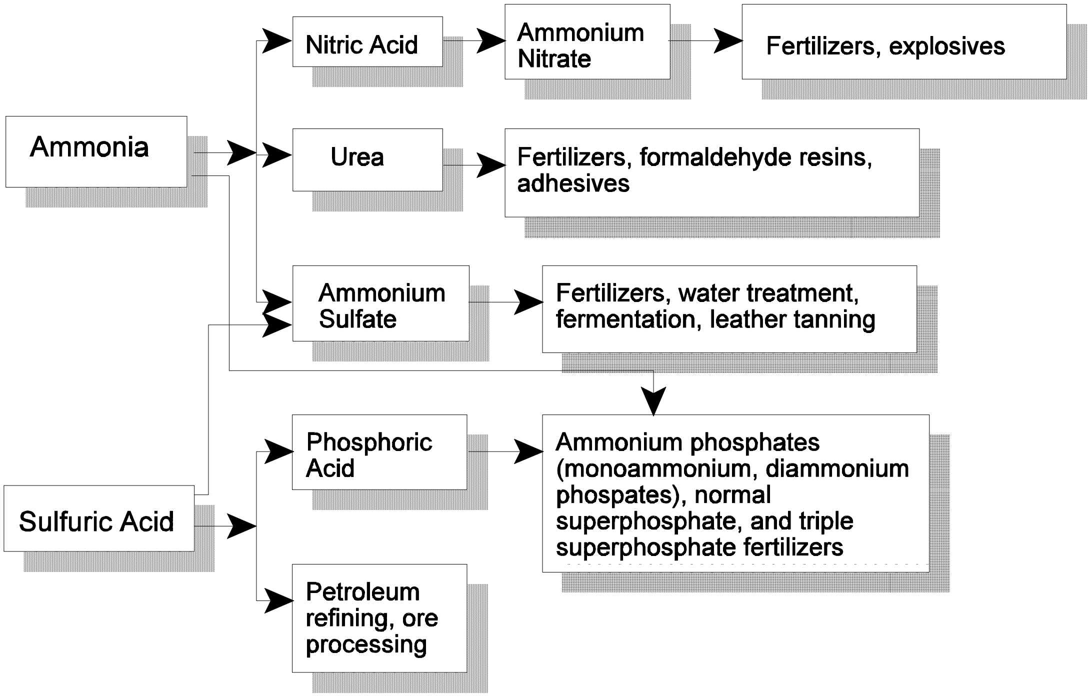

Figure 5-1. Agricultural Chemicals: The Fertilizer Chain

seventeenth and eighteenth, respectively, among the top fifty chemicals in 1997 (Chenier 1992, CMA 1998).

Although **urea** is considered an organic compound, it is usually grouped with other ammonia-derived synthetic nitrogen compounds because of its importance to the fertilizer industry. About 53 percent of the urea produced is used in solid fertilizers, 31 percent is used in liquid fertilizers, and the rest is found in other products, including animal feed, formaldehyde resins, and adhesives. Urea is often combined with other fertilizers, such as the commonly used urea-ammonium nitrate mixture. Formaldehyde resins made from urea are found in dinnerware and other consumer products (e.g., Formica®).

Ammonium sulfate, which ranked thirty-two on the top-fifty list in 1997, is used almost entirely as a fertilizer. Minor uses include water treatment, fermentation, and leather tanning (Chenier 1992).

Sulfuric acid is an essential input to the manufacture of agricultural chemicals. In 1997, it was the chemical produced in the second largest amount in the United States, at over 71 billion pounds annually. About 65 to 70 percent of the sulfuric acid produced is used to manufacture phosphoric acid. The remainder is used in chemical processing, petroleum refining (alkylation), pulp and paper production, plastics manufacture, and in non-chemical applications. Since its primary use is for fertilizer production, it is often grouped with agricultural chemicals (Chenier 1992, CMA 1998).

Phosphoric acid is the primary feedstock for producing phosphate fertilizers. Of the nearly 10 billion pounds of phosphoric acid produced in 1997, about 9 billion pounds were used to produce **ammonium phosphates**, **normal superphosphates**, and **triple superphosphates**. Ammonium phosphates contain both nitrogen and phosphorus, important fertilizer ingredients. The two most frequently used compounds are monoammonium phosphate and diammonium phosphate (EPA 1997f, CMA 1998).

Superphosphates are fertilizers containing relatively large amounts of phosphorus. **Normal superphosphates** contain up to 22 percent phosphorus; **triple superphosphates** contain over 40 percent phosphorus (EPA 1997f).

Demand for Fertilizers Is Closely Linked to Export Markets

The production of fertilizers and their precursor chemicals has declined significantly in recent years, showing, for example, a drop of 20 to 30 percent from 1996 to 1997. This is due in part to the growing capacity for manufacturing fertilizers in Third World countries such as Asia and Mexico, which have previously been major importers of U.S. products. Trends in U.S. exports of major products are shown below in Table 5-1.

China has affected the demand for **urea** by banning its importation beginning in mid-1997, although it is the world's largest consumer of this fertilizer. China is striving to become self-sufficient in fertilizer production and continues to bring new capacity on-line. India has also reduced its urea imports following government controls on selected fertilizers. The result has been weak prices in urea markets, which may not improve unless China resumes importing this product (CHEMWK 1999).The use of fertilizers in the United States has grown steadily over the last ten years and is now relatively stable. Rates of application range from about 140 to 270 pounds of fertilizer per acre (see Table 5-2).

Table 5-1. Export Trends of U.S. Fertilizers (1000 tons)

	1994	1995	1996	1997
Ammonia	288	426	584	561
Ammonium Sulfate	840	1011	909	957
Urea	1005	971	1621	1028
Phosphoric Acid	308	342	339	323
Super-phosphates	882	787	752	766
Di-ammonium Phosphate	10135	11088	8727	10405

Source: TFI 1999.

The United States is currently the largest exporter of **ammonium phosphates**, providing over 70 percent of the world's supply. New capacity additions in Morocco, Australia, and India will create an oversupply of this fertilizer, however, and may force reductions in U.S. production in the future (CHEMWK 1999). A number of firms have shut down high-cost capacity for **phosphoric acid** over the past few years, which should help improve margins for phosphorus and a number of its derivatives (CHEMX 1997).

Ammonia production is closely tied to agriculture and the demand for fertilizers. In the past, ammonia plants have sometimes operated at close to 100 percent capacity to meet demand. Today, oversupply and depressed margins are affecting this trend, and forcing producers to look for cheap ways to increase capacity. Some analysts predict there will be a 1.4 million ton/year surplus in ammonia supplies this year (CE 1996). Production decreased by a substantial 20 percent between 1996 and 1997, reflecting primarily decreased margins and changes in export demand for fertilizers.

Table 5-2. Percentage of U.S. Acres Receiving Fertilizer

Crop	Total lb/acre	Nitro-gen	Phos-pho-ic Acid	Potash
Corn	268	99	84	72
Cotton	202	90	67	58
Soybeans	163	20	28	33
Wheat	139	87	63	18

Source: TFI 1999.

Similar decreases of over 25 percent were noted for **sulfuric acid**, the primary input to phosphoric acid and phosphate fertilizer production. Future production trends will be quite dependent on export markets, particularly those in the Asia-Pacific region.

5.1.1 Ammonia Manufacture

Ammonia Is Still Produced by the Haber Process

Commercial synthesis and use of **ammonia** originated in Germany's need for nitrogen-rich compounds for explosives manufacture during World War I. In the early 1900s, German chemist Fritz Haber developed an ammonia synthesis process based on an iron catalyst that enabled large-scale production of ammonia. By1913, the German chemical company BASF[1] was making ammonia using this process at the rate of 30 metric tons per day. The new technology enabled greater, more rapid production of explosives and extended the war for many years. Haber, however, received the Nobel prize for his work in 1918, amidst objections from those who denounced his contributions to the war effort (Bristol 1999).

The **Haber process** is still the primary method for ammonia synthesis used today, and requires hydrogen, which can be produced from a variety of hydrocarbon sources, and nitrogen, which is supplied from air. The production of ammonia from coal-derived synthesis gas is considered one of the chemical engineering achievements of this century. Since the 1930s, however, the primary source of hydrogen for ammonia production in this country has been steam reforming of natural gas. About 2 percent of the hydrogen required for the Haber process is obtained from electrolysis of brine at chlorine plants.

Ammonia Formation

$$N_2 + 3H_2 \xrightarrow[\text{(Iron)}]{} 2NH_3$$

A typical process configuration for production of ammonia is shown in Figure 5-2. Natural gas is mixed with steam and charged to a primary reformer, where it is passed over a nickel catalyst. In the primary reformer, which operates at around 1300°F–1500°F (700°C–815°C), most of the gas is converted to hydrogen, carbon monoxide, and carbon dioxide. The exiting gas is mixed with air and charged to a secondary reformer operating at higher temperatures, 1650°F-1700°F (900°C–925°C), where the remaining natural gas is converted. The gas leaving the secondary reformer contains nitrogen, hydrogen, carbon monoxide, and carbon dioxide.

The reformed gas is cooled in a waste heat boiler where high-pressure, super-heated steam is generated. The cooled gas is then charged to high- and low-temperature shift converters containing different catalysts to convert the carbon monoxide into carbon dioxide to obtain additional hydrogen.

Shift Converter Reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

The mixture of gases is then charged to a carbon dioxide removal plant. Methods most commonly used for this purpose include absorption or wet scrubbing (e.g., with hot potassium carbonated or methyl diethanolamine). Outlet gas from the recovery plant is further purified through methanation and drying. The resulting pure synthesis gas is compressed and fed through heat exchangers to ammonia converters containing iron oxide catalysts (the Haber process). The gas stream is refrigerated to condense ammonia, and unreacted gases are recycled. The resulting product is anhydrous ammonia.

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[1] BASF, or Badashe Analine und Soda Fabrik

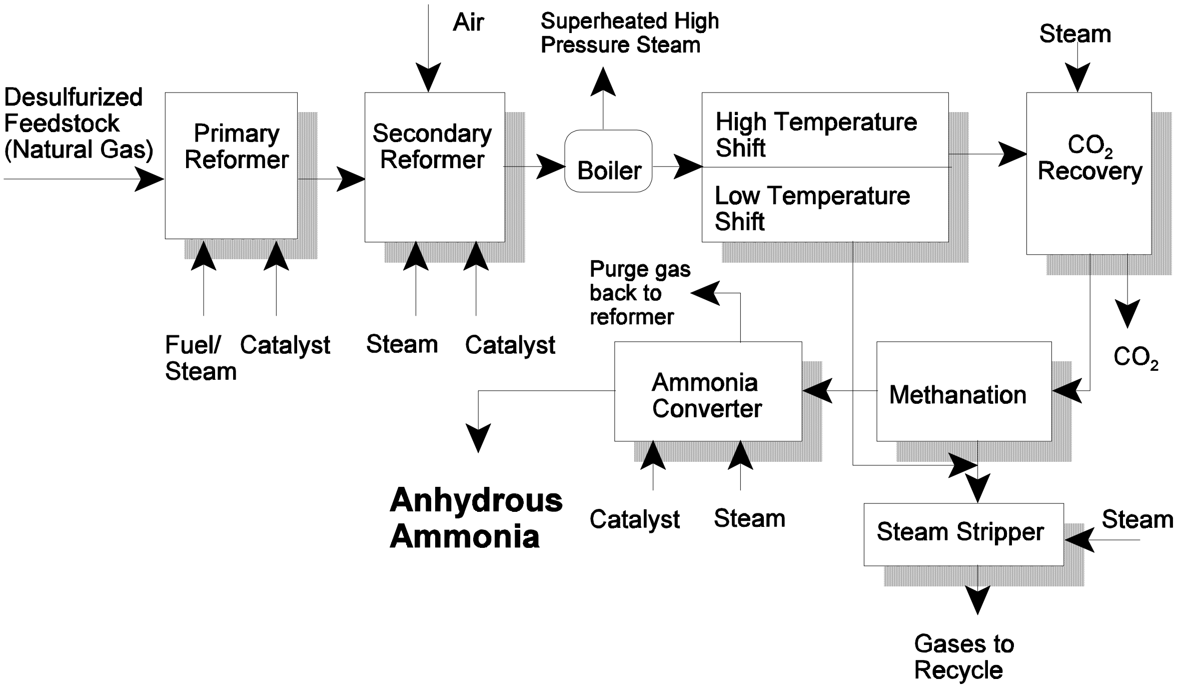

Figure 5-2. Manufacture of Ammonia (EPA 1997a, Orica 1999, HP 1999)

Key Energy and Environmental Facts - Ammonia Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 12,150 Btu/lb (includes fuel and feedstock)*	*Largest source - fugitive emissions of ammonia*	*Largest source - process water*	*Carbon dioxide*

While all plants use a process similar to that described above, configurations will vary with respect to feedstocks (natural gas, hydrocarbon gases, naphtha), operating temperatures, pressures, and other parameters. In most cases, the natural gas feedstock will need to be desulfurized to prevent poisoning of the nickel catalyst used in steam reforming. Most ammonia plants use activated carbon fortified with metallic oxide additives for this purpose.

Carbon dioxide is produced as a byproduct of the ammonia manufacturing process, and is utilized in various ways–as a feedstock for urea production, or liquified and sold to food and beverage markets. Excess carbon dioxide may also be vented to the atmosphere (Process Description: EPA 1997a, Orica 1999, HP 1999).

5.1.2 Urea Manufacture

Urea Is Produced by Solution Synthesis of Ammonia and Carbon Dioxide

About 50 percent of the ammonia manufactured is used to produce **urea** (also known as carbamide or carbonyl diamide) in both solid and liquid forms. Most solids are produced as prills or granules, and are used as fertilizers, protein supplements in animal feed, and in plastics.

A typical flow diagram for production of urea is shown in Figure 5-3. The actual configuration will depend on whether urea is to be produced in solid (crystalline) or liquid form. In the solution synthesis process, ammonia and carbon dioxide are first reacted under high pressure, 140–250 atmospheres, and moderate temperatures, 350ºF–400ºF (175ºC–200ºC). The resulting mixture is about 35 percent urea, 8 percent ammonium carbamate, 10 percent water, and 47 percent ammonia.

The ammonia is distilled, and the solution is dehydrated to form a 70–77 percent aqueous urea solution. The urea solution can be used in this form, or it can be further concentrated using vacuum concentration, crystallization, or atmospheric evaporation.

If a solid product is being manufactured, additives are often used to reduce the caking of solids and formation of urea dust during its storage and handling.

Concentration produces a urea "melt" that can then be used to produce solid urea through prilling or granulation methods. Prilling produces solid particles directly from molten urea; granulation, the process used more frequently, builds solids by creating layers of seed granules that are started by cooling (Process Description: EPA 1993d, Orica 1999, Enviro-Chem 1999c, HP 1999).

5.1.3 Nitric Acid Manufacture

Nitric Acid Is Made by Direct Oxidation of Ammonia

Nitric acid was made years ago by the reaction of sulfuric acid and salt peter (a common name for potassium nitrate or sodium nitrate).

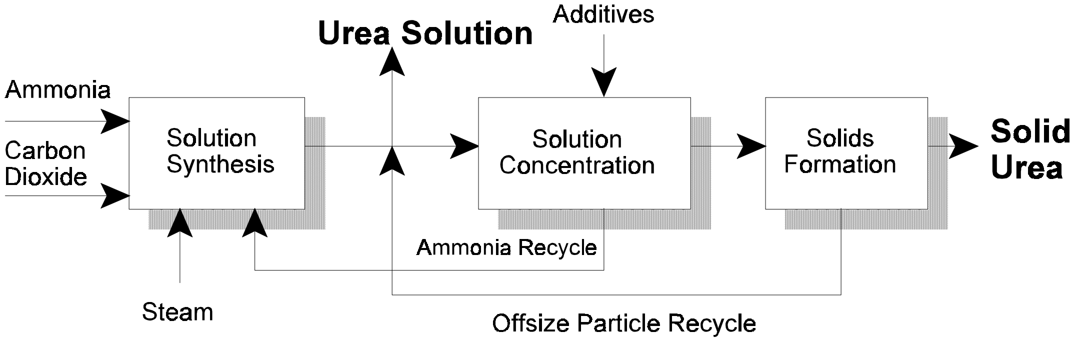

Figure 5-3. Manufacture of Urea
(EPA 1993d, Orica 1999, HP 1999, Enviro-Chem 1999c)

Key Energy and Environmental Facts -Urea Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 732 Btu/lb*	*Largest source - fugitive emissions (ammonia, formaldehyde, methanol) and particulates*	*Largest source - process water*	*Inert gases*

Today, most nitric acid is produced by high-pressure and -temperature catalytic oxidation of ammonia. A typical process flow for nitric acid production is shown in Figure 5-4.

While configurations may differ somewhat between plants, three essential steps are commonly employed. In the first step, ammonia is oxidized to nitric oxide (NO) in a catalytic convertor over a platinum catalyst (90 percent platinum, 10 percent rhodium gauze). The reaction is exothermic (heat-releasing) and produces nitric oxide in yields of 93–98 percent. The reaction proceeds at high temperatures ranging from 1380ºF–1650ºF (750ºC–900ºC).

The resulting mixture from this reaction is then sent to a waste heat boiler where steam is produced. In the second step, nitric oxide is oxidized by passage through a cooler/condenser, where it is cooled to temperatures of 100ºF (38ºC) or less, at pressures of up to 116 psia. During this stage, the nitric oxide reacts with residual oxygen to form nitrogen dioxide and nitrogen tetroxide.

The final step introduces this mixture of nitrogen oxides into an absorption process where the mixture flows countercurrent to deionized water and additional liquid dinitrogen tetroxide. The tower is packed with sieve or bubble cap distillation type trays. Oxidation

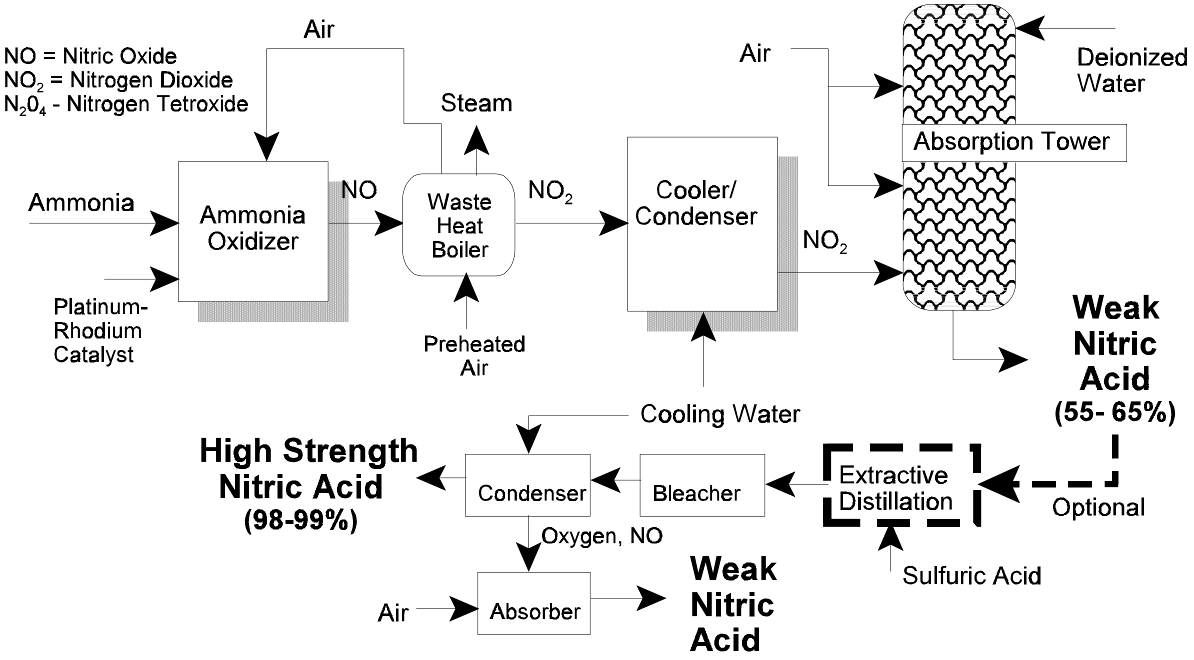

Figure 5-4. Manufacture of Nitric Acid
(EPA 1997b, Orica 1999, EFMA 1999, Enviro-Chem 1999a)

Key Energy and Environmental Facts -Nitric Acid Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy Exporter: *Net Steam: 311 Btu/lb*	*Largest source - fugitive emissions (oxides of nitrogen, nitric acid mist, ammonia)*	*Largest source - process water*	*Nitrogen oxides, spent catalysts, inert gases*

takes places in between the trays in the tower; absorption occurs on the trays. An exothermic reaction between NO_2 and water occurs in the tower to produce nitric acid and NO. Air is introduced into the tower to re-oxidize the NO that is being formed and to remove NO_2 from the nitric acid. A weak acid solution (of 55–65 percent, although this varies) is withdrawn from the bottom of the absorption tower.

To produce high strength nitric acid, the weak nitric acid solution is concentrated using extractive distillation with a dehydrating agent. Concentrated sulfuric acid is often used as the agent. During this process, the sulfuric acid and weak nitric solution are fed to the top of a packed dehydrating column at atmospheric pressure. Concentrated nitric acid leaves the top of the column as 99 percent vapor, with small amounts of NO_2 and oxygen. The concentrated vapor is sent to a bleacher and condenser system to condense the strong acid and separate oxygen and any nitrogen oxide byproducts, which are recycled. Inert gases are vented to the atmosphere (Process Description: EPA 1997b, Orica 1999, EFMA 1999).

5.1.4 Ammonium Nitrate

Neutralizing Nitric Acid with Ammonia Produces Ammonium Nitrate

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. The final product can be liquid, or a solid in the form of prills, grains, granules, or crystals, depending upon whether the end-use is for fertilizers or explosives. High-density solids are generally used as fertilizers, while low-density grains are typically used in explosives manufacturing.

Figure 5-5 illustrates the processing of both liquid and solid ammonia nitrate. Ammonia and nitric acid are first introduced into a stainless steel reactor, where the heat of neutralization boils the mixture and concentrates it to about 85 percent nitrate. If a liquid product is desired, it is drawn off at this time.

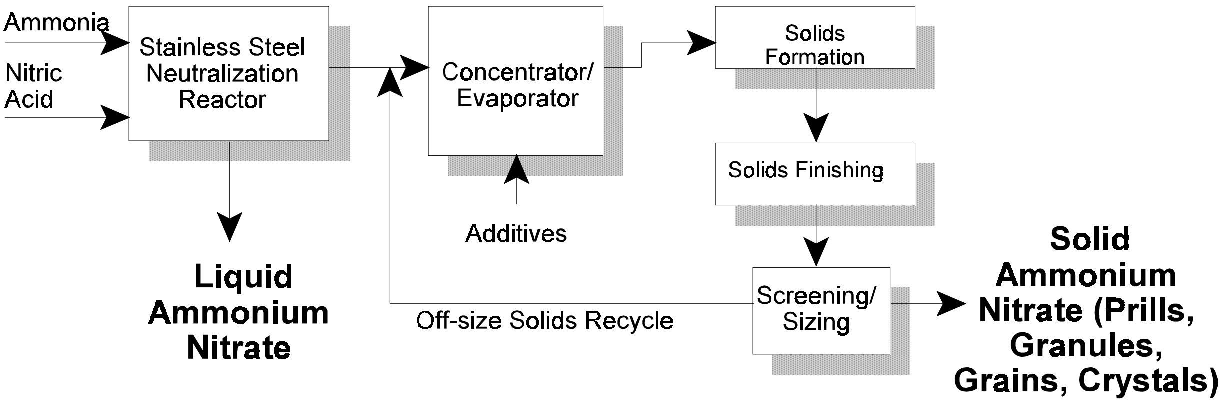

Figure 5-5. Manufacture of Ammonium Nitrate (EPA 1993c, Chenier 1992)

Key Energy and Environmental Facts - Ammonium Nitrate Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 341 Btu/lb*	*Largest source - particulates (ammonium nitrate and coating materials), ammonia and nitric acid*	*Largest source - process water*	*negligible*

About 60 percent of ammonium nitrate is currently produced in solid form. To create the solid, the 85 percent nitrate solution is further concentrated through vacuum evaporation or in a concentrator. The resulting "melt" contains from 95 to 99.8 percent ammonium nitrate. The melt can then be used to produce a solid product in prill towers or rotary drum granulators.

Additives such as magnesium nitrate or magnesium oxide may be introduced into the melt prior to solidification to raise the crystalline transition temperature, act as a desiccant (removing water), or lower the temperature of solidification. Products are sometimes coated with clays or diatomaceous earth to prevent agglomeration during storage and shipment, although additives may eliminate the need for coatings. The final solid products are screened and sized, and off-size particles are dissolved and recycled through the process (Process Description: Chenier 1992, EPA 1993c).

5.1.5 Ammonium Sulfate Production

Ammonium Sulfate Can Be Synthesized Directly or Produced as a Byproduct

Ammonium sulfate was one of the first popular fertilizers, primarily because it was produced as a byproduct of coke ovens as early as 1893. While it is still widely used, it has been supplanted somewhat by urea and other fertilizers that promote green growth in plants. It is still often used as a component in many fertilizer blends.

Ammonium sulfate can be produced as a byproduct of caprolactam (see Section 4, The BTX Chain), as a coke oven byproduct, or by direct synthesis. A typical flow diagram for the synthetic process is shown in Figure 5-6. In this process, anhydrous ammonia and sulfuric acid are combined in a pipe reactor. A highly exothermic reaction occurs, producing ammonium sulfate and a bisulfate solution.

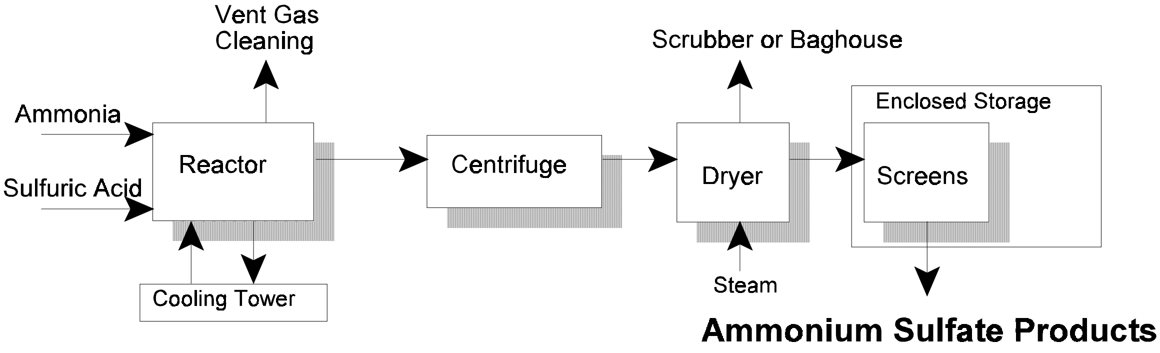

Figure 5-6. Manufacture of Ammonium Sulfate (EPA 1997d, Orica 1999)

Key Energy and Environmental Facts -Ammonium Sulfate Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 4,000 Btu/lb*	*Largest source - particulates (ammonium sulfate)*	*Largest source - process water*	*negligible*

Ammonium sulfate crystals are formed by circulating the solution through an evaporator where it thickens. A centrifuge separates the crystals from the mother liquor. The crystals contain 1 percent to 2.5 percent moisture, and are dried in a fluidized bed or rotary drum dryer. Dryer exhaust gases are sent to a particulate collection system (e.g., wet scrubber) to control emissions and recover residual product. Coarse and fine granules are separated by screening before they are stored or shipped (Process Description: EPA 1997d, Orica 1999).

5.1.6 Sulfuric Acid Manufacture

Most Sulfuric Acid Is Made by Oxidation of Sulfur

Historically, **sulfuric acid**[2] has been an important chemical, at least as far back as the tenth century. Processes for making sulfuric acid were first described in the fifteenth century, when chemists told of burning sulfur with potassium nitrate (sometimes called salt peter). The lead chamber process was introduced in the eighteenth century, which involved the oxidation of sulfur to sulfur dioxide by oxygen, further oxidation to sulfur trioxide with nitrogen oxide, and hydrolysis of sulfur trioxide to achieve the final product. Nineteenth century modifications made the early process economical until the 1940s, when it was displaced by the contact process.

Today, 99 percent of sulfuric acid is made using the contact method, an oxidation process based on the burning of elemental sulfur (brimstone) with dry air (see Figure 5-7) or the roasting of pyrite ore. Sources of elemental sulfur include mining or oxidation of hydrogen sulfide (via the Claus process) from “sour”natural gas wells or petroleum refineries.

The contact process utilizes the techniques of interpass absorption or double absorption. The typical flow diagram for this process is shown in Figure 5-7. Molten sulfur is burned at high temperatures (>1800ºF, or >980ºC) in excess dry air to produce sulfur dioxide. The sulfur dioxide is cooled in a waste heat boiler (that produces high-pressure steam and usually powers a turbine for electricity generation).

After cooling, the sulfur dioxide is sent along with oxygen to a staged converter with a set of chambers containing a vanadium catalyst. After passing through the third chamber, about 95 percent of the sulfur dioxide has been converted to sulfur trioxide. The mixture is then charged to a two-stage absorption process where it combines with water to form sulfuric acid. The exiting sulfuric acid can be passed over the vanadium catalyst again to attain a 99.7 percent conversion if desired. After the second absorption stage, the final concentration of sulfuric acid is 98 percent or greater.

If **oleum** is produced (a mixture of excess sulfur trioxide and sulfuric acid), sulfur trioxide from the converter is passed to an oleum tower that is fed with 98 percent acid from the absorbers. The gases from this tower are then pumped to the absorption column where sulfur trioxide is removed. Various concentrations of oleum can be produced. Common ones include 20 percent oleum (20 percent sulfur trioxide in 80 percent sulfuric acid, with no water), 40 percent oleum, and 60 percent oleum.

The sulfuric acid conversion process is highly exothermic, providing opportunities for energy recovery in many areas (e.g., after the sulfur burner, after the converter pass, and in the absorption towers). Energy recovered is used for process heating and/or electricity generation (Process Description: Chenier 1992, EPA 1992a, Enviro-Chem 1999b, Orica 1999).

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[2] A colorless, odorless, heavy, oily liquid that was once referred to as ”oil of vitriol”

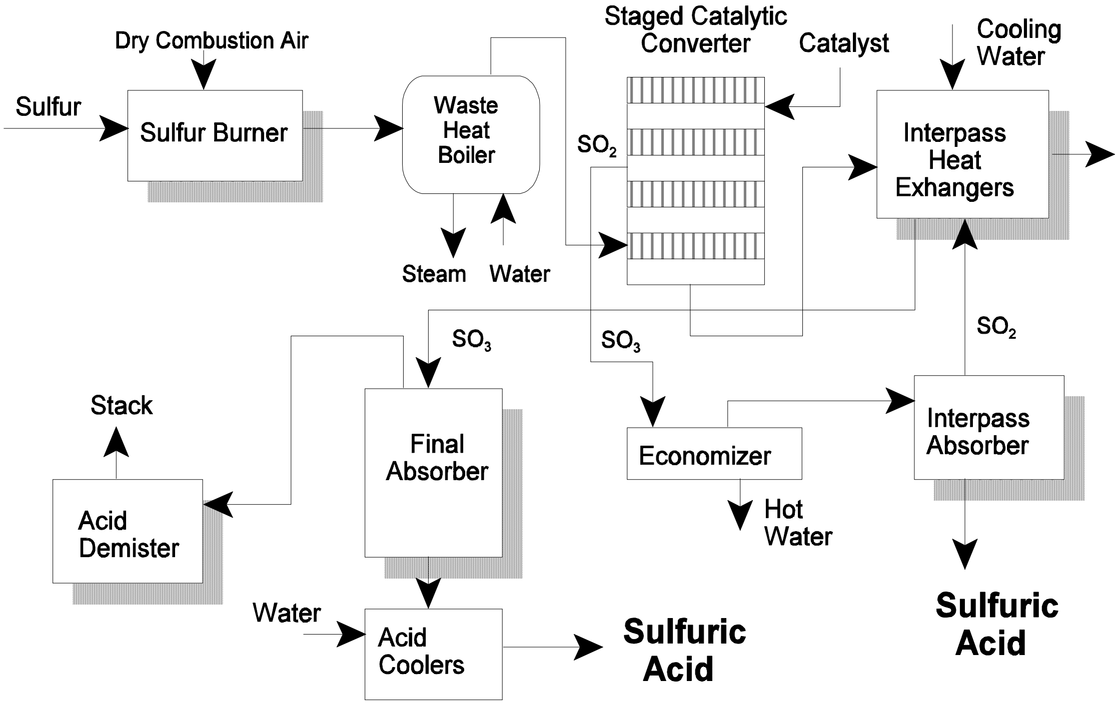

Figure 5-7. Manufacture of Sulfuric Acid
(EPA 1992a, Enviro-Chem 1999b, Orica 1999)

Key Energy and Environmental Facts - Sulfuric Acid Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy Exporter : *(1,047 Btu/lb product)*	*Largest source - sulfur dioxide, acid mist*	*Largest source - process water*	*Spent catalysts*

5.1.7 Phosphoric Acid Manufacture

Wet and Thermal Processing Methods Produce Different Grades of Phosphoric Acid

Phosphoric acid is the most important derivative of sulfuric acid. It has been used as fertilizer for hundreds of years, and is a key ingredient in today's phosphate fertilizers. The **wet process** is used to produce fertilizer-grade phosphoric acid, and accounts for more than 90 percent of phosphoric acid production (in the form of phosphorus pentoxide, or P_2O_5). The **thermal process** (sometimes called the furnace process) accounts for about 10 percent of production, and is used to make high purity phosphoric acid for use in manufacturing specialty chemicals, pharmaceuticals, detergents, food products, and beverages.

In the wet process (see Figure 5-8), sulfuric acid is reacted with naturally occurring phosphate rock. The rock usually contains a high percentage of fluorine, and if this is the case, the mineral is called fluorapetite. It is mined in

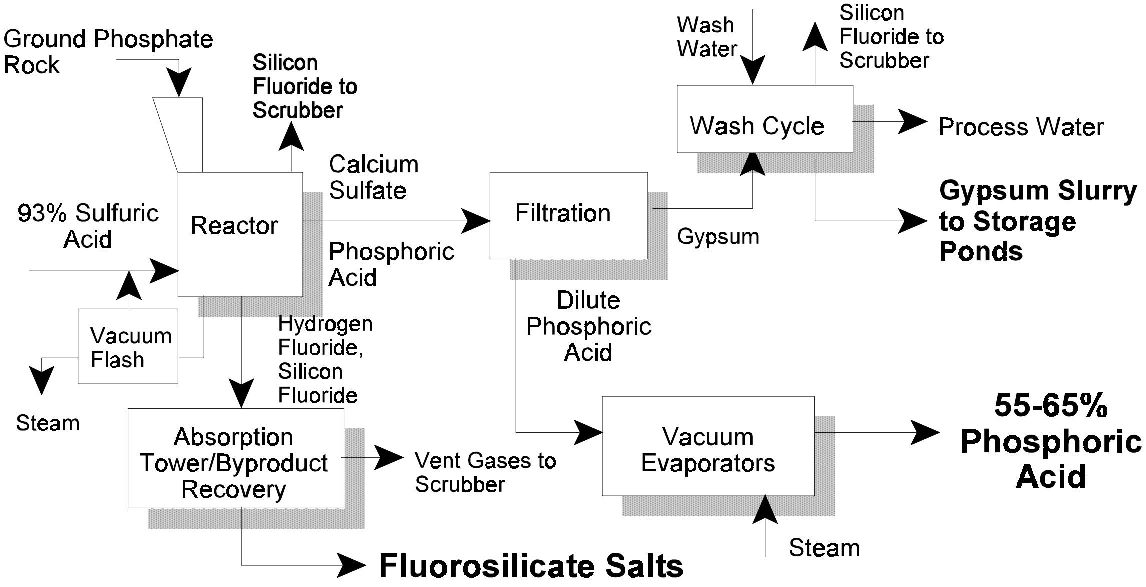

Figure 5-8. Manufacture of Phosphoric Acid - Wet Process (Chenier 1992, EPA 1997e)

Key Energy and Environmental Facts - Phosphoric Acid Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 1,810 Btu/lb*	*Largest source - gaseous fluorides (SiF_4 and HF) and particulates*	*Largest source - acidic cooling water with high concentrations of phosphorus and fluoride*	*Fluorosilicate salts, uranium oxides, gypsum slurry, silicon fluoride*

Florida, Texas, North Carolina, Idaho, and Montana; 30 percent of world reserves are in the United States.

The phosphate rock is dried, crushed, and fed continuously into a reactor along with sulfuric acid. During the reaction, calcium from the phosphate rock is combined with sulfate, forming calcium sulfate (gypsum) and phosphoric acid. Sulfuric acid with a concentration of 93 percent is used to decrease evaporation costs and ensure production of the strongest possible phosphoric acid. The four to eight reactors are heated to about 175°F (80°C) for four to eight hours. Considerable heat is generated in the reactors. A portion of the reactor slurry is cooled by vacuum flashing and subsequently recycled back to the reactor for heat control and recovery.

U.S. plants typically use dihydration to produce gypsum in the form of calcium sulfate with two water molecules attached (calcium sulfate dihydrate). Hemihydration processes are popular in Japan and produce calcium sulfate with a half molecule of water, which yields phosphoric acid with a higher phosphorus pentoxide concentration and fewer impurities. In recent years, some U.S. firms have switched to the hemihydration process.

After the gypsum crystals are formed, filtration is used to separate them from the solution. The separated crystals are washed to yield 99 percent or better recovery of filtered phosphoric acid. The final wet phosphoric acid product contains about 26 to 30 percent P_2O_5, and is further concentrated to 40 to 55 percent by vacuum evaporation to make it suitable for fertilizer production.

After washing, the gypsum slurry is sent to a pond for storage. Water from this pond is recycled back to the phosphoric acid process. Water storage requirements are substantial: approximately 0.7 acres of cooling and settling pond area are required for every ton of P_2O_5 produced per day.

Side products from the reaction include fluorosilicate salt (H_2SiF_6) and uranium oxides (U_3O_8). Both silicon oxide and uranium occur in many phosphate rocks in small percentages. Fluorosilicate salts are used in ceramics, pesticides, wood preservatives, and concrete hardeners. Processes for extraction of uranium are available (MEAB 1999), but it is often not economical to recover the uranium.

During the **thermal process**, liquid elemental phosphorus is burned in ambient air to form P_2O_5. The P_2O_5 is then hydrated to produce strong phosphoric acid. Demisting is used to remove the phosphoric acid mist from the combustion gas stream before it is released to the atmosphere (Process Description: Chenier 1992, EPA 1997e).

High-purity phosphoric acid (in a concentration of up to 50 percent and greater) can also be recovered from the wet process by using selective solvent extraction. A new membrane process was developed recently that does not require the use of solvents (KEMWorks 2000).

5.1.8 Phosphate Fertilizers

Ammonium Phosphate and Superphosphates Are Processed Differently

Ammonium phosphate is the most widely used phosphate fertilizer, and is found in both solid and liquid forms. Granular ammonium phosphate fertilizer is produced by the reaction of phosphoric acid with anhydrous ammonia in ammoniation-granulation plants. In the United States, 95 percent of ammoniation-granulation plants use a slightly inclined open-end rotary drum mixer for this process.[3]

The ammoniation-granulation process is shown in Figure 5-9. Phosphoric acid is first mixed in a surge tank with 93 percent sulfuric acid and recycled acid. The acids are neutralized with liquid or gaseous anhydrous ammonia in an acid reactor with a brick lining. The reactor produces a slurry of about 22 percent ammonium phosphate and water, which is sent through steam-trace lines to the rotary drum ammoniator-granulator.

The reactor slurry is distributed on a bed in the granulator, while the remaining ammonia is sparged underneath. Granulation occurs through agglomeration and by coating particles with slurry. Part of this process occurs in the rotary drum, and is completed in a rotary concurrent dryer.

Ammonia-rich off-gases are produced, and these are passed through a wet scrubbing system before venting to the atmosphere. Cooled granules pass to a screening unit, where oversized and undersized granules are separated out and recycled back to the granulator (Process Description: EPA 1993e, EPA 1997f).

Normal superphosphates are made by reacting ground phosphate rock with a 65 to 75 percent concentration of sulfuric acid. Both virgin and spent (recycled) sulfuric acid from other industrial processes may be used, although spent acid may impart unusual colors, odors, or toxicity to the product. The amount of iron and aluminum present in the rock is also a consideration, as they can impart a condition of extreme stickiness to the superphosphate and make it difficult to handle.

In this process, ground phosphate rock and acid are mixed in a reaction vessel, stored until the

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[3] Developed and patented by the Tennessee Valley Authority (TVA)

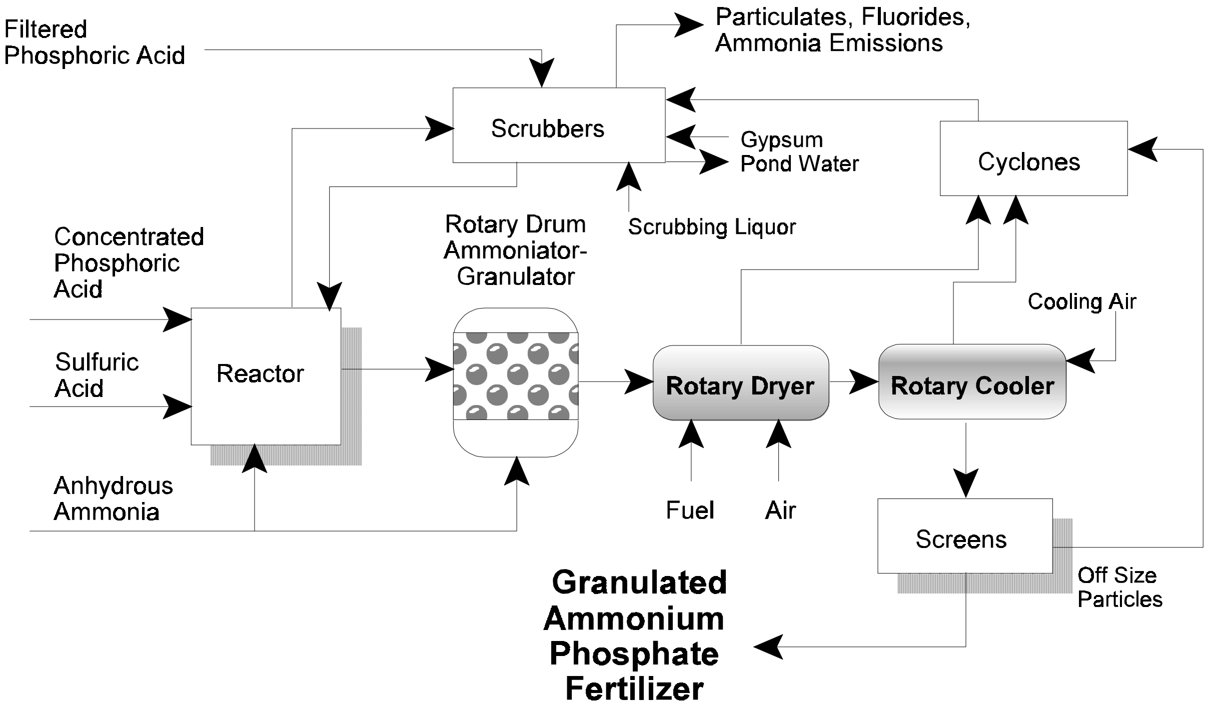


Figure 5-9. Manufacture of Ammonium Phosphate (EPA 1993e, Brown 1996)

Key Energy and Environmental Facts - Ammonium Phosphate Manufacture

Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 206 Btu/lb*	*Largest source - gaseous ammonia, fluorides (SiF_4 and HF) and particulate ammonium phosphate*	*Largest source - acidic wastewater*	*Gypsum slurry, fertilizer dust*

reaction is completed (about 30 minutes), and transferred to a storage pile for curing. These processes are all conducted in enclosed areas to prevent venting of toxic emissions. After curing, the superphosphate is typically used as an additive to granular fertilizers, or it can be granulated in a rotary drum granulator/dryer/ cooing system.

Triple superphosphates are usually produced using the Dorr-Oliver granular process (see Figure 5-10). In this process, ground phosphate rock or limestone is reacted with low-concentration phosphoric acid in a reactor(s). A sidestream of the resulting slurry is continuously removed and distributed onto dried, recycled fines, where the granular surfaces become coated and increase in size.

Rotating drum granulators are often used for granulation. They are open-ended, slightly inclined rotary cylinders with a cutter mounted inside. A bed of dry material is maintained in the unit, while slurry is introduced through pipes under the bed. The granules are wetted by the slurry and discharged to a rotary dryer to evaporate water and accelerate the chemical reaction to completion. Screening is used to remove off-size particles, which are recycled Process Description: Brown 1996, EPA 1997a).

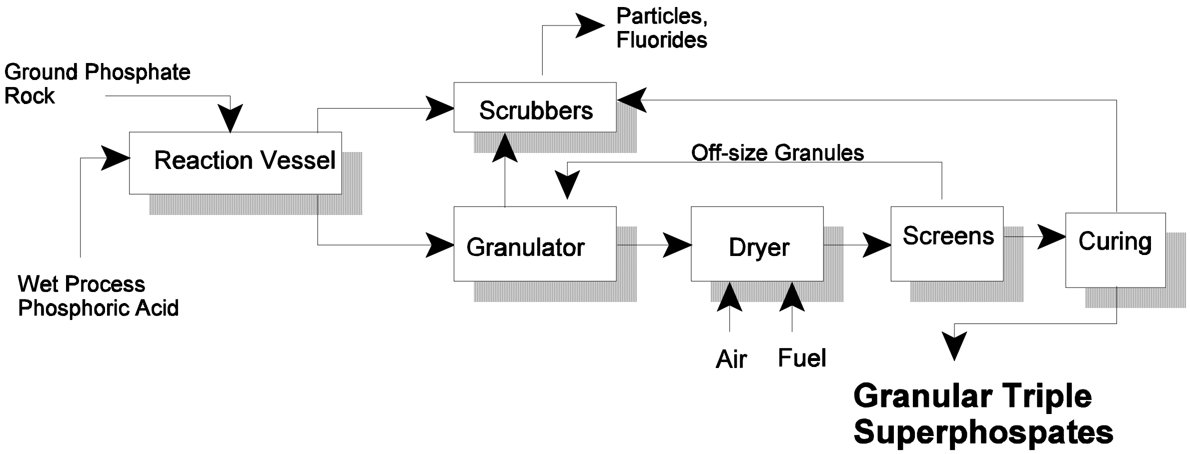


Figure 5-10. Manufacture of Triple Superphosphates
(EPA 1993e, Brown 1996)

Key Energy and Environmental Facts - Triple Superphosphates Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *Process Energy: 690 Btu/lb*	*Largest source - gaseous fluorides (SiF_4 and HF), rock dust, particulates*	*Largest source - acidic wastewater*	*Rock dust, fertilizer dust*

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 Agricultural Chemicals chain.

Ammonia

Inputs:	Outputs:
Natural Gas	Anhydrous Ammonia
Air	Carbon Dioxide
Catalyst	Export Steam
Steam/Fuel	Recycle Gases
Electricity	Process Water

Urea

Inputs:	Outputs:
Ammonia	Solid Urea
Carbon Dioxide	Urea Solution
Additives	Process Water
Process Water	
Steam/Fuel	
Electricity	

Nitric Acid

Inputs:	Outputs:
Ammonia	Weak Nitric Acid
Deionized Water	High Strength Nitric Acid
Sulfuric Acid	Process Water
Catalyst	Steam
Air/Oxygen	Spent Catalyst
Bleaching Agent	Nitrogen Oxides
Process Water	Inert Gases
Steam/Fuel	
Electricity	

Ammonium Nitrate

Inputs:	Outputs:
Ammonia	Solid Ammonium Nitrate
Nitric Acid	
Additives	
Electricity	

Ammonium Sulfate

Inputs:	Outputs:
Ammonia	Ammonium Sulfate
Sulfuric Acid	Scrubber Products
Cooling Water	Vent Gas
Steam/Fuel	Process Water
Electricity	

Sulfuric Acid

Inputs:	Outputs:
Elemental Sulfur	Sulfuric Acid
Dry Combustion Air	Sulfur Dioxide
Catalyst	Process Water
Cooling Water	Export Steam
Steam/Fuel	Export Electricity
Electricity	Spent Catalyst

Phosphoric Acid

Inputs:	Outputs:
Phosphate Rock	Phosphoric Acid
93% Sulfuric Acid	Fluorosilicate Salts
Process Water	Uranium Oxide
Steam/Fuel	Silicon Fluoride
Electricity	Export Steam
	Gypsum Slurry
	Process Water

Ammonium Phosphate

Inputs:	Outputs:
Phosphoric Acid	Ammonium Phosphate Fertilizer
Sulfuric Acid	Process Water
Anhydrous Ammonia	Gypsum Slurry
Air	Gypsum Pond Water
Process Water	
Gypsum Pond Water	
Scrubbing Liquor	
Steam/Fuel	
Electricity	

Normal Superphosphates

Inputs:	Outputs:
Ground Phosphate Rock	N-Superphosphates
Sulfuric Acid	Rock Dust
Air	
Electricity	

Triple Superphosphates

Inputs:	Outputs:
Ground Phosphate Rock	Triple Superphosphates
Air	Process Water
Process Water	Rock/Fertilizer Dust
Steam/Fuel	
Electricity	

5.3 Energy Requirements

Process Energy for Some Agricultural Chemicals Is Relatively High

The **process and feedstock energy** used for the production of agricultural chemicals are shown in Tables 5-3 through 5-12 (PNNL 1994, Brown 1996, HP 1997d, Enviro-Chem 1999a, 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. Each table also shows Total Process Energy, which includes processing energy for the final product, minus any steam or fuel generated by the process, plus electricity losses. Electricity losses are those incurred during the generation and transmission of electricity (regardless of whether it is purchased or produced on-site). Thus, Total Process Energy is the total primary energy consumption associated with production of the individual chemical.

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

Processing energy consumption for heat and power associated with the production of **ammonia** is relatively high, on the order of 12,000 Btu/lb. Most of this energy is in the form of steam used for the reforming of methane, ammonia conversion, and vent gas stripping. The large energy input results primarily from the need for multiple passes over the catalyst to achieve acceptable product yields.

Feedstock energy in the form of natural gas or mixed hydrocarbon gases is required for ammonia production, and is included in the processing energy since it is normally reported this way in

Table 5-3. Estimated Energy Use in Ammonia Manufacture- 1997

Energy	Specific Energy[d] (Btu/lb)	Average Specific Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	885 - 953	919	26.1
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	121 - 130	126	3.6
Natural Gas	9,888 - 10,649	10,269	291.6
Coal and Coke	403 - 434	418	11.9
Other[c]	403 - 434	418	11.9
NET PROCESS ENERGY	**11,700 - 12,600**	**12,150**	345.1
Electricity Losses	1,838 - 1,979	1,908	54.2
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**13,538 - 14,579**	**14,058**	**399.3**

[a] Does not include losses incurred during the generation and transmission of electricity.
[b] 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 (e.g., renewables).
[d] 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 ICI Katalco/Synetix, Linde AG, and Kellogg, Brown & Root, Inc. (EEA 1983, HP 1999, EFMA 1999).
[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values for ammonia (28.4 billion lbs) (CMA 1998).

Table 5-4. Estimated Energy Use in Urea Manufacture- 1997

Energy	**Specific Energy (Btu/lb)**	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	23 - 188	106	1.2
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	19 - 25	22	0.3
Natural Gas	483 - 652	567	6.7
Coal and Coke	63 - 85	74	0.9
Other[c]	63 - 85	74	0.9
NET PROCESS ENERGY	650 - 1,035	843	9.9
Electricity Losses	48 - 390	219	2.6
Energy Export	(94) - (127)	(111)	(1.3)
TOTAL PROCESS ENERGY	**604 - 1,298**	**951**	**11.2**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d 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 CO_2 and NH_3 stripping, isobaric double recycle, and advanced processes (EFMA 1999, HP 1999).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values for urea (11.8 billion lbs) (CMA 1998).

Table 5-5. Estimated Energy Use in Manufacture of Nitric Acid - 1997

Energy	**Specific Energy[d] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	2 - 3	3	0.0
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	7 - 9	8	0.1
Natural Gas	178 - 229	203	2.7
Coal and Coke	23 - 30	26	0.4
Other[c]	23 - 30	26	0.4
NET PROCESS ENERGY	**233 - 300**	**267**	**3.6**
Electricity Losses	4 - 6	5	0.1
Energy Export	(594) - (561)	(578)	(7.8)
TOTAL PROCESS ENERGY	**(255) - (357)**	**(306)**	**(4.1)**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values based on published fuel and electricity requirements for licensed technologies (Enviro-Chem, Inc.,1999a).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (13.5 billion lbs) (CMA 1998).

Table 5-6. Estimated Energy Use in Ammonium Nitrate Manufacture- 1997			
Energy	**Specific Energy (Btu/lb)**	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	55 - 187	121	1.5
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	5 - 8	7	0.1
Natural Gas	127 - 212	169	2.1
Coal and Coke	17 – 28	22	0.3
Other[c]	17 - 28	22	0.3
NET PROCESS ENERGY	**220 - 462**	**341**	**4.2**
Electricity Losses	114 - 388	251	3.1
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**334 - 850**	**592**	**7.3**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d 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 (EFMA 1999).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (12.3 billion lbs) (CMA 1998).

Table 5-7. Estimated Energy Use in Manufacture of Ammonium Sulfate - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	720	3.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	98	0.4
Natural Gas	2,526	10.4
Coal and Coke	328	1.3
Other[c]	328	1.3
NET PROCESS ENERGY	**4,000**	**16.4**
Electricity Losses	1,495	6.1
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**5,495**	**22.5**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d 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 (PNNL 1994).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (4.1 billion lbs) (CMA 1998).

Table 5-8. Estimated Energy Use in Manufacture of Sulfuric Acid - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	28	2.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	1	0.1
Natural Gas	23	1.7
Coal and Coke	3	0.2
Other[c]	3	0.2
NET PROCESS ENERGY	**58**	**4.1**
Electricity Losses	58	4.2
Energy Export	(1,047)	(74.8)
TOTAL PROCESS ENERGY	**(931)**	**(66.5)**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for licensed technologies (Enviro-Chem, Inc.,1999b).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (71.4 billion lbs) (CMA 1998).

Table 5-9. Estimated Energy Use in Manufacture of Phosphoric Acid (Wet Process) - 1997			
Energy	**Specific Energy (Btu/lb)**	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	186 - 464	325	3.1
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	17 - 73	45	0.4
Natural Gas	424 - 1,863	1,143	10.9
Coal and Coke	55 - 242	149	1.4
Other[c]	55 - 242	149	1.4
NET PROCESS ENERGY	**736 - 2,884**	**1,810**	**17.2**
Electricity Losses	386 - 963	675	6.4
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**1,122 - 3,847**	**2,485**	**23.6**

a Does not include losses incurred during the generation and transmission of electricity. Does not include electricity for grinding phosphate rock, which requires about 4,180 Btu/lb (Brown 1996).
b 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 (e.g., renewables).
d Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for wet process technologies (EFMA 1999, Brown 1996).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (9.5 billion lbs) (CMA 1998). The wet process is used for about 96 percent of phosphoric acid manufacture.

Table 5-10. Estimated Energy Use in Manufacture of Phosphoric Acid (Furnace Process) - 1997

Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	14,581	58.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	3	0.0
Natural Gas	82	0.0
Coal and Coke	24,003	9.6
Other[c]	21	0.0
NET PROCESS ENERGY	**38,690**	**15.5**
Electricity Losses	30,277	12.1
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**68,967**	**27.6**

[a] Does not include losses incurred during the generation and transmission of electricity. Includes electricity for grinding phosphate rock..

[b] 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 (e.g., renewables).

[d] Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for furnace process technologies (Source: Brown 1996).

[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values (0.4 billion lbs) (CMA 1998). The furnace process is used for about 4 percent of phosphoric acid manufacture.

the literature (see Table 5-3). Feedstock requirements usually comprise about 50–60 percent of combined processing energy. Despite their origin in hydrocarbon feedstocks, ammonia-derived compounds are generally considered inorganic. Thus, any organic feedstock energy embodied in the ammonia input is not considered in the remainder of the energy tables.

Process energy requirements for manufacture of **urea, ammonium nitrate, and ammonium sulfate** are relatively low. The bulk of energy is in the form of steam used for process heating. Electricity is used mostly for the centrifuging and screening of solid products.

Processes used for manufacturing **nitric acid** are generally net steam exporters, requiring very small amounts of electricity for driving air compressors and pumps. Steam consumption is somewhat higher in plants utilizing dual-pressure (rather than single-pressure) operations.

The **sulfuric acid** plants are large net steam exporters. Large amounts of high-pressure steam are used to power a turbo-alternator for electricity generation. The waste heat boiler used for cooling sulfur dioxide is the largest source of export steam, although energy may be recovered in many places throughout the process. Steam export values range from about 1,000 Btu/lb to over 2,600 Btu/lb of sulfuric acid in well-optimized, state-of-the art plants. Optimizing energy recovery from plants lowers production costs, and improvements are continually being made in this area. With advanced technology, net steam export values can reportedly double in amount (Enviro-Chem 1999d, EFMA 1999).

Table 5-11. Estimated Energy Use in Manufacture of Ammonium Phosphate - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	82	1.6
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	7	0.1
Natural Gas	186	3.5
Coal and Coke	24	0.5
Other[c]	24	0.5
NET PROCESS ENERGY	**323**	**6.1**
Electricity Losses	170	3.2
Energy Export	(117)	(2.2)
TOTAL PROCESS ENERGY	**376**	**7.1**

[a] Does not include losses incurred during the generation and transmission of electricity.
[b] 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 (e.g., renewables).
[d] Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for licensed technologies (Brown 1996).
[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values (18.9 billion lbs) (TFI 1999).

The wet process is used for 96 percent of the **phosphoric acid** manufactured. This process is moderately energy-intensive, requiring about 6,130 Btu/lb. An alternative method, the furnace process, is used for the remaining 4 percent of production and it is highly energy-intensive, consuming nearly 40,000 Btu/lb. This process is used solely for producing high-quality, chemical-grade phosphoric acid, not fertilizer-grade product.

Production of phosphate fertilizers requires very modest energy consumption, primarily in the form of steam used for drying. Ammonium phosphate processes also generate export steam. Electricity is used for granulating, milling, crushing, and screening solid products.

Table 5-12. Estimated Energy Use in Manufacture of Superphosphates - 1997		
Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	340	1.2
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	11	0.1
Natural Gas	270	0.9
Coal and Coke	35	0.1
Other[c]	35	0.1
NET PROCESS ENERGY	**690**	**2.4**
Electricity Losses	706	2.4
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**1,396**	**4.8**

a Does not include losses incurred during the generation and transmission of electricity.
b 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 (e.g., renewables).
d Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for granulated triple superphosphate processes (Brown 1996).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values for normal and triple superphosphates (3.4 billion lbs) (TFI 1999).

5.4 Air Emissions

Ammonia and Sulfur Compounds Are the Primary Source of Air Contaminants from Production of Agricultural Chemicals

The primary sources of emissions in the agricultural chemicals chain are fugitive and point air source emissions of particulates and volatile compounds emitted from equipment and process operations. Fugitive emissions of volatile compounds arise from leaks in valves, pumps, tanks, flanges, and other similar sources. Particulates arise from granulation processes used for production of solid fertilizers, and from rock dust during ore processing.

Ammonia is one of the top five toxic chemicals released every year, primarily from point air and fugitive emissions sources. Ammonia is released during its manufacture as well as during its use in other chemical processes. Releases of ammonia are reported annually in the Toxic Release Inventory (TRI). In 1996, nearly 110 million pounds of ammonia were released by the chemical industry to the air, land, and water. Over 10 million pounds were also released from petroleum refineries (EPA 1998, EPA 1997c).

Pollutants from **ammonia manufacture** are emitted from regeneration of the desulfurization bed, heating of the catalytic steam, regeneration of carbon dioxide scrubbing solution, and steam stripping of the process condensate. Emission factors for each of these emission points are given in Table 5-13. Nearly all U.S. ammonia plants use activated carbon fortified with metallic oxide additives to desulfurize feedstocks. These beds are regenerated about once a month. The vented regeneration steam contains sulfur oxides and hydrogen sulfide, some hydrocarbons, and carbon monoxide.

Carbon dioxide is a byproduct of the reaction and is removed from the synthesis gas by scrubbing with hot potassium carbonate or similar compounds. Regeneration of this scrubbing solution liberates water, ammonia, carbon monoxide, and volatile scrubbing solution compounds. Stripping of process condensate yields steam, which is vented to the atmosphere and contains ammonia, carbon dioxide, and methanol.

The primary emissions from **urea manufacture** are ammonia and particulates. Small amounts of volatile additive components (e.g., methanol, formaldehyde) may also be emitted. Additives like Formalin^{TM}, for example, may contain up to 15 percent methanol. Ammonia may be emitted during solution synthesis and production of solid products. Particulates are emitted throughout the process. Table 5-14 provides emission factors for urea production.

The recycling of carbamate gases or liquids allows some emission control. Emissions from the synthesis process are usually combined with those from concentrating the solution and vented through stacks. Particulate control is usually only carried out in the solids-producing areas; other emissions of particulates are small by comparison. In the solids-screening process, dust is generated as urea particles collide and the screen vibrates. In urea manufacture, almost all the screening operations are enclosed or covered to reduce emissions. Coating of the product may emit entrained clay dust during loading and product transfer, but no emission factors are available to quantify this source (EPA 1993d).

Emissions from the **manufacture of nitric acid** include mostly nitrogen oxides (NO and NO_2), and trace amounts of ammonia and nitric acid mist. The tail gas from the acid absorption tower is the largest source of nitrogen oxide emissions. These emissions can increase when insufficient air is supplied to the oxidizer and absorber, under low absorber pressure conditions, and during high temperature conditions in the cooler/condenser and absorber. Other factors may contribute, such as high throughputs, very high-strength products, or faulty compressors or pumps. Emission factors for nitric acid plants are shown in Table 5-15.

Table 5-13. Air Emissions from Ammonia Manufacture

Emission Point	CO (lb/ton)	SO_2 (lb/ton)	TOC[a] (lb/ton)	NH_3 (lb/ton)	CO_2 (lb/ton)
Desulfurization unit regeneration[b]	13.8	0.0576	7.2		ND
Carbon dioxide regenerator	2.0		1.04[c]	2.0	2440
Condensate steam stripper			1.2[d]	2.2	6.8 (±60%)

a Total organic compounds.
b Intermittent source; regeneration is done every 30 days. SO_2 is a worst case factor (all sulfur entering tank is emitted).
c 0.1 lb/ton is monoethanolamine.
d Primarily methanol.

Source: EPA 1997a.

Control of emissions from nitric acid plants is usually accomplished through either extended absorption or catalytic reduction. Extended absorption works by increasing the efficiency of the absorption process. Catalytic reduction oxidizes nitrogen oxides in the tail gas and reduces them to nitrogen. While catalytic reduction is more energy-intensive, it achieves greater emission reductions than the extended absorption method. Less-used control options include wet scrubbers or molecular sieves, both of which have higher capital and operating costs than the other options (EPA 1997b).

The **manufacture of ammonium nitrate** produces particulate matter, ammonia, and nitric acid emissions. Emission factors are shown in Table 5-16. Emissions from ammonia and nitric acid occur primarily when they form solutions (neutralizers and concentrators), and when they are used in granulators.

Particulate matter is the largest source and is emitted throughout the process during the formation of solids. Prill towers and granulators are the largest sources of particulates. Microprills can form and clog orifices, increasing fine dust loading and emissions.

Emissions occur from screening operations by the banging of ammonium nitrate solids against each other and the screens. Most of these screening operations are enclosed or have partial covers to reduce emissions. The coating of products may also create some particulate emissions during mixing in the rotary drums. This dust is usually captured and recycled to coating storage. Another source of dust is bagging and bulk loading, mostly during final filling when dust-laden air is displaced from bags (EPA 1993c).

Table 5-14. Air Emissions from Urea Manufacture

Type of Operation	Particulates (lb/ton)		Ammonia (lb/ton)	
	Uncontrolled	Controlled	Uncontrolled	Controlled
Solution formation and concentration[a]	0.021		18.46	
Nonfluidized bed prilling[b]	3.7	0.063	0.87	
Fluidized bed prilling[c]	4.9	0.63	3.53	2.08
Drum Granulation[c]	241	0.234	2.15	
Rotary Drum Cooler	7.78	0.20	0.051	
Bagging	0.19			

a Emissions from synthesis are usually combined with those from solution concentration and vented through a common stack. In synthesis, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled.

b Controlled factors are based on ducting exhaust through a downcomer, then a wetted fiber filter scrubber (98.3% efficient), a higher degree of control than is typical in the industry.

c Controlled factors are based on use of an entrainment scrubber.

Source: EPA 1993d.

Table 5-15. Air Emissions from Nitric Acid Plants		
Source	**Control Efficiency %**	**Nitrogen Oxides (lbs/ton[a])**
Weak Acid Plant Tail Gas		
Uncontrolled[b]	0	57
Catalytic Reduction		
Natural Gas	99.1	0.4
Hydrogen	97-98.5	0.8
Natural Gas/Hydrogen	98-98.5	0.9
Extended Absorption		
Single-Stage	95.8	1.9
Dual-Stage		2.1
Chilled Absorption & Caustic Scrubber	n/a	2.2
High Strength Acid Plant	n/a	10

a Based on 100% nitric acid.
b Single-stage pressure process.

Source: EPA 1993b.

Table 5-16. Air Emissions from Ammonium Nitrate Manufacture				
Process	**Particulate Matter (lb/ton)**		**Ammonia (uncontrolled) lb/ton**	**Nitric Acid lb/ton**
	Uncontrolled	**Controlled[a]**		
Neutralizer	0.090-8.6	0.004-0.44	0.86-36.0	0.084-2.0
Evaporation/concentration operations	0.52		0.54-33.4	
Solids Formation operations	298.8	2.2	58.5	
Coolers and Dryers[b]	220.4	2.2	1.93	
Coating Operations	<4.0	<0.04		

a Based on the following efficiencies for wet scrubbers: neutralizer, 95%; high density prill towers, 62%; low density prill towers, 43%; rotary drum granulators,99.9%; pan granulators,98.5%; coolers, dryers, and coaters,99%.
b Combined cooler and precooler emissions, and combined dryer and predryer emissions.

Source: EPA 1993c.

Table 5-17. Air Emissions from Ammonium Sulfate Manufacture

Dryer Type	Particulate (lb/ton)	VOC[a] (lb/ton)
Rotary Dryers		
(Uncontrolled)	46	1.48
(Wet Scrubber)	0.04	0.22
Fluidized-bed Dryers		
(Uncontrolled)	218	1.48
(Wet Scrubber)	0.28	0.22

a VOC emissions occur only at caprolactam plants where ammonium sulfate is produced as a byproduct. The emissions are caprolactam vapor.

Source: EPA 1997d.

Particulate ammonium sulfate is the air emission occurring in the largest amount from manufacture of this fertilizer. Dryer exhaust is the primary source of the particulates, and emission rates are dependent on gas velocity and particle size distribution. Particulate rates are higher for fluidized bed dryers than for the rotary drum type of dryer. Most plants use baghouses to control particulates of ammonium sulfate, although venturi and centrifugal wet scrubbers are better suited for this purpose.

Some volatile carbon emissions may be present in caprolactam plants where ammonium sulfate is produced as a byproduct. Emission factors for controlled and uncontrolled emissions of ammonium sulfate are shown in Table 5-17 (EPA 1997d).

Sulfur dioxide is the primary emission from **sulfuric acid manufacture**, and is found primarily in the exit stack gases. Conversion of sulfur dioxide to sulfur trioxide is also incomplete during the process, which gives rise to emissions. Dual absorption is considered the Best Available Control Technology (BACT) for meeting new source performance standards (NSPS) for sulfur dioxide. In addition to stack gases, small amounts of sulfur dioxide are emitted from storage and tank-truck vents during loading, from sulfuric acid concentrators, and from leaking process equipment. Emission factors for sulfur dioxide from sulfuric acid plants are shown in Table 5-18.

Acid mists may also be emitted from absorber stack gases during sulfuric acid manufacture. The very stable acid mist is formed when sulfur trioxide reacts with water vapor below the dew point of sulfur trioxide. Acid mist emission factors for controlled and uncontrolled plants are shown in Table 5-19 and Table 5-20. Typical control devices include vertical tube, vertical panel, and horizontal dual pad mist eliminators (EPA 1992a).

Major emissions from **wet process phosphoric acid manufacture** are comprised of gaseous fluorides in the form of silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). The source of fluorides is phosphate rock, which contains from 3.5 to 4.0 percent fluorine. The fluorine is generally precipitated out with gypsum, leached out with phosphoric acid product, or vaporized in the reactor or evaporator.

The reactor where phosphate rock is contacted with sulfuric acid is the primary source of emissions. Vacuum flash cooling of the reactor slurry will minimize these emissions as the system is closed. During acid concentration, 20 to 40 percent of the fluorine in the rock may vaporize. Emission factors for fluorides from wet processing are shown in Table 5-21.

Table 5-18. Air Emissions from Sulfuric Acid Manufacture

SO_2 to SO_3 Conversion Efficiency	SO_2 Emissions (lb/ton of product)
93	96
94	82
95	70
96	55
97	40
98	26
99	14
99.5	7
99.7	4
100	0.0

Source: EPA 1992a.

Table 5-19. Acid Mist Emissions from Uncontrolled Sulfuric Acid Plants

Raw Material	Oleum Produced (% total output)	Uncontrolled (lb/ton)
Recovered Sulfur	0-43	0.348-0.8
Bright Virgin Sulfur	0	1.7
Dark Virgin Sulfur	0-100	0.32-6.28
Spent Acid	0-77	2.2-2.4

Source: EPA 1992a.

Table 5-20. Acid Mist Emissions from Controlled Sulfuric Acid Plants

Raw Material	Oleum Produced (% total output)	Controlled (lb/ton)
Elemental Sulfur	-	0.64
Dark Virgin Sulfur	0-13	0.26-1.8
Spent Acid	0-56	0.014-0.20

Source: EPA 1992a.

Table 5-21. Air Emissions from Wet Process Phosphoric Acid Manufacture

Source	Controlled Fluorine (lb/ton P_2O_5 produced)	Controlled Fluorine (lb/ton P_2O_5 produced)
Reactor	3.8×10^{-3}	0.38
Evaporator	0.044×10^{-3}	0.0044
Belt filter	0.64×10^{-3}	0.064
Belt filter vacuum pump	0.15×10^{-3}	0.015
Gypsum settling and cooling ponds[a]	Site-specific	Site-specific

[a] Acres of cooling pond required range from 0.1 acre per daily ton phosphoric acid produced in the summer in the southeast U.S., to 0 (zero) in colder locations in winter months when cooling ponds are frozen. There are still considerable uncertainties in measurement of fluoride from gypsum ponds.

Source: EPA 1997e.

Table 5-22. Emission Factors for Thermal Process Phosphoric Acid Manufacture

Source	Particulate Acid Mist (lb/ton P_2O_5 produced)
Packed Tower	2.14
Venturi Scrubber	2.53
Glass fiber mist eliminator	0.69
Wire mesh mist eliminator	5.46
High pressure drop mist	0.11
Electrostatic Precipitator	1.66

Source: EPA 1997e.

Scrubbers (venturi, wet cyclonic, and semi-cross flow) are used to control emissions of fluorine. Leachate fluorine may settle in settling ponds, and if the water becomes saturated, it will be emitted to the air as fluorine gas.

Thermal or furnace processing of phosphoric acid results in phosphoric acid mist, which is contained in the gas stream exiting the hydrator. A large amount of phosphorus pentoxide product may be present as liquid phosphoric acid particles suspended in the gas stream, so most plants attempt to control this loss. Control equipment includes venturi scrubbers, cyclonic separators with wire mesh mist eliminators, fiber mist eliminators, high energy wire mesh contactors, and electrostatic precipitators. Emission factors for thermal processing are given in Table 5-22.

Normal superphosphate manufacture produces emissions of gaseous fluorides in the form of silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). Particulates composed of fluoride and phosphate material are also emitted. Sources include rock unloading and feeding, mixing operations, storage, and fertilizer handling (see Table 5-23 for emission factors).

Sources of emissions for **triple superphosphates manufacture** include the reactor, granulator, dryer, screens, cooler, mills, and transfer conveyors (see Table 5-24). Particulates may be emitted during unloading, grinding, storage, and transfer of ground phosphate rock. Baghouses, scrubbers, or cyclonic separators are used to control emissions.

Emissions from **production of ammonium phosphate fertilizers** come from the reactor, the ammoniator-granulator, dryers, coolers, product sizing, material transfer, and the gypsum pond (see Table 5-25). Silicon tetrafluoride (SiF_4), hydrogen fluoride (HF), gaseous ammonia, and ammonium phosphate particulates are produced by the reactor and ammoniator-granulator. These emissions are controlled by primary and secondary scrubbers. Exhaust gases from the dryer and cooler contain similar emissions and are passed through cyclones and scrubbers, as are emissions from product sizing and material transfer (EPA 1997f).

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. Current emission factors for process heaters and boilers are discussed in Section 7, Supporting Processes.

Table 5-23. Air Emissions from Normal Superphosphate Manufacture

Emission Point	Particulates (lb/ton)	PM 10[c] (lb/ton)	Fluoride (lb/ton)
Rock unloading[a]	0.56	0.29	-
Rock feeding[a]	0.11	0.06	-
Mixer and den[b]	0.52	0.44	0.20
Curing building	7.2	6.1	3.80

a Factors are for baghouses with estimated collection efficiency of 99 percent.
b Factors are for wet scrubbers with an estimated 97 percent control efficiency.
c Particulate matter 10 microns and above. Based on AIRS listing for criteria air pollutants.

Source: EPA 1997f.

Table 5-24. Air Emissions from Triple Superphosphate Manufacture

Emission Point	Particulates (lb/ton)	PM 10[c] (lb/ton)	Fluoride (lb/ton)
Rock unloading[a]	0.18	0.08	-
Rock feeding[a]	0.04	0.02	-
Reactor, granulator, dryer, cooler, and screens[b]	0.1	0.08	0.24
Curing building	0.20	0.17	0.04

a Factors are for baghouses with estimated collection efficiency of 99 percent.
b Factors are for wet scrubbers with an estimated 97 percent control efficiency.
c Particulate matter of 10 microns and larger. Based on AIRS listing for criteria air pollutants.

Source: EPA 1997f.

Table 5-25. Air Emissions from Ammonium Phosphate Manufacture

Emission Point	Fluoride as F (lb/ton)	Particulate (lb/ton)	Ammonia (lb/ton)	SO_2 (lb/ton)
Reactor / ammoniator-granulator	0.05	1.52	ND	
Dryer/Cooler	0.04	1.50		
Product sizing and material transfer	0.002	0.06		
Total Plant Emissions	0.04	0.68	0.14	0.08

Source: EPA 1997f.

5.5 Effluents

Wastewaters May Contain Phosphorus, Fluorides, Nitrogen Compounds, Carbon Dioxide, or Acids

Wastewaters from manufacture of agricultural chemicals consist mostly of wash water, scrubber water, boiler and vaporizer blow down, or stripper water. These may contain phosphorus, fluorides, ammonia, carbon dioxide, or weak acids. Many of these waters are treated and recycled to the process. Valuable components (e.g., ammonia) may also be recovered. Water scrubbing of the purge gases in **ammonia** production, for example, creates an ammonia water solution that can be used in another process (e.g., urea production). In **urea** production, ammonia, carbon dioxide, and urea are removed from process waters by water treatment, and the gases are recycled to the synthesis process (EFMA 1999).

Plants producing **nitric acid and ammonium nitrate** produce waste waters containing these compounds as well as ammonia. Wastewater containing ammonia and nitric acid must be neutralized to produce ammonium nitrate.

In **phosphoric acid** production, the fluorine released from reactors and evaporators is usually recovered as a by-product that can be sold. The remainder is passed to the condenser that produces a liquid effluent with mostly fluoride and small amounts of phosphoric acid. Closed systems recycle this effluent; in other cases, it is discharged to open waters (EFMA 1999).

Limitations for toxic or hazardous compounds contained in these wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, Part 418, which was originally promulgated in 1974 and has undergone several revisions. The chemicals in the agriculturalchain are covered under Subparts A-G.

Specific limitations for restricted compounds and total suspended solids (TSS) are shown in Tables 5-26 through 5-30. BPT indicates the use of best practicable control technology currently available; BAT refers to the best available technology economically achievable.

Table 5-26. Effluent Pretreatment Standards: Phosphate Fertilizers		
Effluent	**Maximum for any 1 day (micrograms/liter)**	**Maximum for Monthly Average (micrograms/liter)**
Total Phosphorus (as P)	105	35
Fluoride	75	35
Total Suspended Solids	150	50

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart A.

Table 5-27. Effluent Pretreatment Standards: Ammonia		
Effluent	**BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)**	**BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)**
Ammonia (as N)	0.0625	0.025
pH	6.0-9.0	-

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart B.

Table 5-28. Effluent Pretreatment Standards: Urea				
Effluent	**BPT Standards: Average Daily Value for 30 Consecutive Days (Micrograms/liter)**		**BAT Standards: Average Daily Value for 30 Consecutive Days (micrograms/liter)**	
	Solution Urea	**Prills or Granules**	**Solution Urea**	**Prills or Granules**
Ammonia (as N)	0.48	0.59	0.27	0.27
Organic Nitrogen	0.33	0.8	0.24	0.46

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart C.

Table 5-29. Effluent Pretreatment Standards: Ammonium Nitrate		
Effluent	**BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb/product)**	**BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)**
Ammonia (as N)	0.39	0.04
Nitrate (as N)	0.37	0.07

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart D.

Table 5-30. Effluent Pretreatment Standards: Nitric Acid

Effluent	BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lbs product)		BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lbs product)	
	Gaseous Form	Liquid Form	Gaseous Form	Liquid Form
Ammonia (as N)	0.0007	0.008	0.00045	0.008
Nitrate as N	0.044	0.044	0.023	0.023

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart E.

5.6 Wastes, Residuals, and Byproducts

Spent Catalysts, Sludges, and Baghouse Dust Are Residuals of Agricultural Chemical Manufacture

The manufacture of agricultural chemicals produces some solid wastes and byproducts, the majority from spent catalysts and particulates that have been trapped in various capture systems. Solid wastes from **ammonia production**, for example, include spent catalysts and molecular sieves that are removed and sent off-site for removal of valuable precious metals. Sulfur may be recovered in plants that use partial oxidation (EFMA 1999).

Solid wastes from **nitric acid** manufacture include spent catalysts that are either returned to the manufacturer or disposed of. Dust from the catalyst may settle out in the equipment, but if it contains precious metals, it is recovered and sent for reprocessing to an outside vendor. Precious metals (e.g., platinum) lost from the ammonia oxidation catalyst are captured by a recovery gauze (getter), which must be replaced periodically and is reprocessed by a gauze manufacturer. Filters used for ammonia/air filtration must also be replaced. They are often disposed of, but can be recycled (EFMA 1999).

During the production of **sulfuric acid,** a sludge is produced in the carbon dioxide removal unit used to absorb solvent gas. A hydrocarbon solvent is used in the unit, which breaks down into a hydrocarbon sludge during the process. This sludge is usually combusted in another part of the process. Sulfuric acid manufacture also produces a solid waste containing the heavy metal vanadium, when the convertor catalyst is regenerated or screened. This waste is sent to an off-site vendor for reprocessing. Additional solid wastes from sulfuric acid production may contain both vanadium and arsenic, depending on the raw materials used, and care must be taken to dispose of them properly in landfills (EFMA 1999).

The production of **solid fertilizers** produces dust, some of which is collected in baghouses. It must be disposed of or is recycled to the process when possible. Some processes (e.g., thermal processing of phosphoric acid) produce an acid mist consisting of entrained acid particles in gas. This particulate acid is usually controlled and recovered as a valuable product.

The manufacture of **phosphoric acid** produces a gypsum slurry that is sent to settling ponds to allow the solids to settle out. About 5 pounds of phosphogypsum are generated per pound of phosphoric acid. This phosphogypsum contains trace elements from phosphate rock, such as cadmium and uranium. Pond systems are usually fitted with lining systems and collection ditches to maintain control of trace elements and avoid contamination of ground water (EFMA 1999).

6

The Chlor-Alkali Industry

6.1 Overview of the Chlor-Alkali Industry

Chlorine, Sodium Hydroxide, and Sodium Carbonate Are Primary Products of the Chlor-Alkali Industry

The caustics chain begins with sodium chloride (NaCl) and forms the basis for what is often referred to as the **chlor-alkali** industry. Major products of the chlor-alkali industry include **chlorine**, **sodium hydroxide (caustic soda)**, **soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate**. Of these products, chlorine, sodium hydroxide, and soda ash account for the largest share of shipments from the chlor-alkali industry. These products are also very important economically, being the chemicals produced in the eighth, ninth, and tenth largest amounts in the United States (in 1997, their combined production was over 72 billion pounds) (CMA 1998).

U.S. Production of Major Products in the Caustics Chain (1997)

Chlorine (26.0 billion lbs)
Sodium Carbonate (23.7 billion lbs)
Sodium Hydroxide (22.7 billion lbs)

Source: CMA 1998.

Most of the **chlorine** produced in the United States (about 70 percent) is used to manufacture organic chemicals (e.g., vinyl chloride monomer, ethylene dichloride, glycerine, chlorinated solvents, glycols). Nearly 40 percent is used for the production of vinyl chloride, an important building block for poly vinyl chloride (PVC) and a number of petrochemicals (see Figure 6-1). Chlorine is also important to the pulp and paper industry, which consumes about 15 percent of the chlorine produced annually. Other major uses for chlorine include the manufacture of inorganic chemicals, disinfection of water, and production of hypochlorite (CMA 1998, Orica 1999).

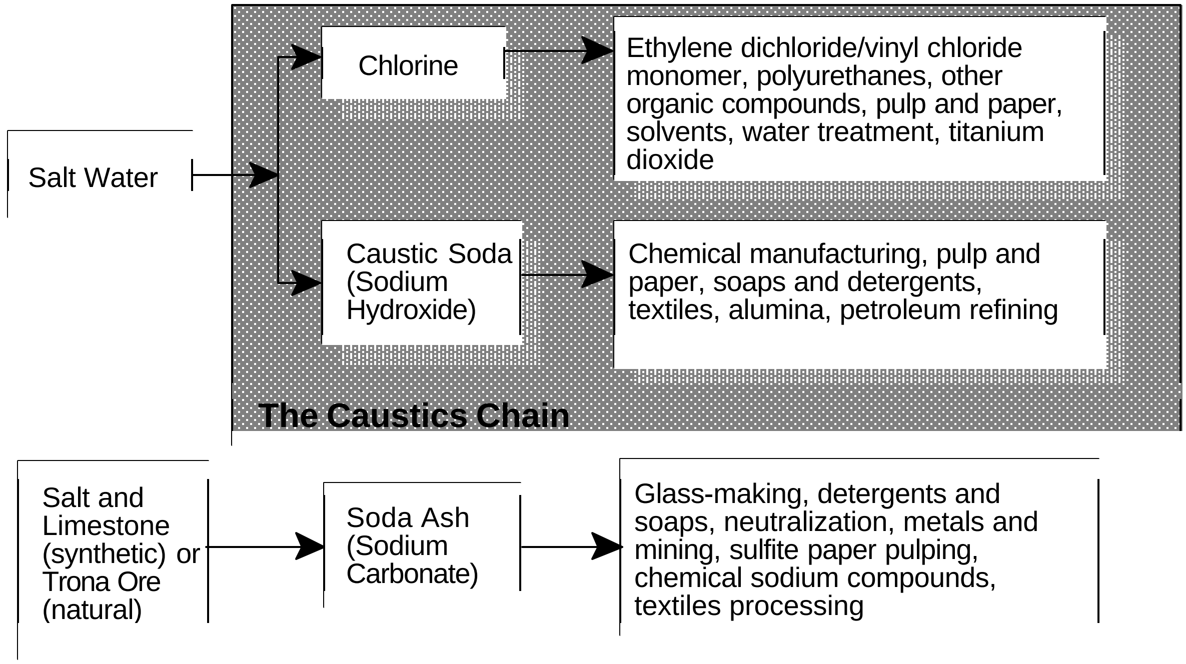


Figure 6-1. Chlor-Alkali Products Chain (CMA 1998)

About 30 percent of the **sodium hydroxide** produced is used by the organic chemical industry and about 20 percent is consumed by the inorganic chemical industry for neutralization and off-gas scrubbing, and as an input into the production of various chemical products (e.g., alumina, propylene oxide, polycarbonate resin, expoxies, synthetic fibers, soaps, detergents, rayon, cellophane). Another 20 percent of sodium hydroxide production is used by the pulp and paper industry for pulping wood chips and for other processes. Sodium hydroxide is also used to manufacture soap and cleaning products, and as drilling fluid for oil and gas extraction (CHEMX 1999, Orica 1999).

Soda ash is used primarily by the glass industry as a flux to reduce the melting point of sand. It is also a raw material in the manufacture of sodium phosphates and sodium silicates, important components of domestic and industrial cleaners. Other uses are in the production of metals in both the refining and smelting stages, in sulfite paper pulping processes, and in textiles processing. Soda ash is also an intermediate in the production of sodium compounds, including phosphates, silicates, and sulfites.

Demand for Sodium Hydroxide and Chlorine Is Impacted by Global Economies

The chlor-alkali industry has been growing at a slow pace over the last 10 years and this rate is expected to continue in the early years of the new century. Chlorine and sodium hydroxide are co-products, and the demand for one will highly influence the demand for the other. Over the last several decades, market forces have switched between chlorine and sodium hydroxide a number of times. Chlorine demand drives the chlor-alkali industry, but the demand is cyclical, with chlorine and caustic soda out of phase in the marketplace. When caustic soda reaches a high level of demand, the direction of product flow is dependent upon Asian and European economies and the foreign exchange rate. Foreign producers may often export caustic soda to the

United States to keep chlorine production high, which impacts both markets and production in this country (DOW 1999).

Prices for both chlorine and caustic soda are impacted by changes in vinyl exports to Asia and weakness in the pulp and paper industry. Important Asian economies (e.g., Japan) will continue to drive demand for both these products and set the pace of new production facilities in the United States. The fact that the United States remains competitive in the chlorine-caustic-vinyl cycle can be attributed to three factors: our large supplies of energy and raw materials (salt and ethylene), and our large-scale economy. With the exception of Taiwan, world scale vinyl plants are not being built in Asia (DOW 1999).

Other forces affecting the market for chlor-alkalis include environmental regulations aimed at curtailing chlorine use. For example, restrictions on the production or disposal of products that require large amounts of chlorine (e.g., PVC, chlorinated solvents) have had a negative impact on the chlorine market. Several environmental groups and initiatives (e.g., International Joint Commission of Great Lakes Water Quality) are calling for a gradual phaseout or immediate ban on chlorine and chlorinated compounds as industrial feedstocks, which is also impacting commercial use of chlorine (CCC 1995, EPA 1995a, CCC 1996, Ayres 1997).

However, demand for PVC has been a significant driver in the growth of chlorine use both in the United States and globally. The industrialization of Asia is expected to drive PVC demand and chlorine growth well into the next century. Until a non-chlorine replacement for PVC is developed, demand will remain strong (DOW 1999).

Demand for sodium hydroxide may also be impacted by users switching to soda ash to avoid shortages of sodium hydroxide (like the worldwide shortage that occurred in the late 1980s). Soda ash is very plentiful in the United States and is obtained almost entirely from natural sources of trona ore . However, it is more expensive to mine soda ash than to produce 50 percent caustic, so increased use of soda ash is not likely to occur unless the price of caustic is relatively high (Chenier 1992, DOW 1999). Demand for sodium hydroxide may also be impacted as pulp and paper mills increasingly look for cost-effective ways to recycle sodium hydroxide from spent pulping liquor. Currently, however, most of these alternatives cannot compete on a capital and cost basis with caustic soda production, and will only impact demand when they become economically viable (EPA 1995a, CHEMWK 1999).

Chlorine is difficult to store and transport economically. As a result, chlorine and caustic soda are usually produced in close proximity to end-users (primarily chemical manufacturers and pulp and paper mills). Geographically, about 72 percent of chlorine production takes place in chlor-alkali facilities located along the Gulf Coast; other production occurs in the vicinity of pulp mills of the Southeast and Northwest.

6.1.1 Manufacture of Chlorine and Sodium Hydroxide

Chlorine and Sodium Hydroxide Are Co-Products of Brine Electrolysis

Chlorine was first discovered in 1774 by the German chemist Scheele, and was identified as an element in 1810 by an English scientist named Davy. Caustic soda, or sodium hydroxide, has been an important industrial chemical since1853. Until 1892 sodium hydroxide was produced by the reaction of slaked lime and soda ash. That year, the electrolysis of brine was discovered as a method of making both sodium hydroxide and chlorine. Since the 1960s electrolysis has been the predominant technique employed to manufacture these two important chemicals (Chenier 1992, Orica 1999).

Although electrolysis of brine is the primary production method, technologies for converting aqueous hydrochloric acid to chlorine are also used in the United States and Europe. A process to convert anhydrous hydrochloric acid to chlorine, developed jointly by Dupont and Kvarner Chemetics, was also recently unveiled. Similar technology is also being marketed in Europe by DeNora, an Italian firm.

Chlorine and sodium hydroxide are co-products that are produced in roughly equivalent amounts through electrolysis of common salt in a brine solution (about 1.1 tons of sodium hydroxide for every ton of chlorine produced). Hydrogen is also produced in equal molar amounts with chlorine and caustic. Chemical demand for hydrogen on the Gulf Coast is significant, and it is often transported by pipeline long distances to meet the needs of oil refineries. There is also an opportunity to use fuel cell technology to closely couple the hydrogen produced with electrical power units that can feed DC power to chlorine cells. Some demonstration units using this technology are in operation outside the United States (DOW 1999).

During electrolysis, two electrodes are immersed in a brine solution. When a source of direct current is attached to the electrodes, sodium ions begin to move toward the negative electrode (cathode) and chlorine ions toward the positive electrode (anode) (Sittig 1977, IND CHEM 1990, EPA 1995a, Orica 1999).

If the primary products from salt electrolysis remain in contact after formation, they can react with each other to form oxygenated compounds of chlorine. Three electrolytic processes are available and use different methods to keep the chlorine produced at the anode separated from the caustic soda and hydrogen produced at the cathode. In historical order, these cells include diaphragm cells, mercury cathode or "amalgam" cells, and membrane cells. Table 6-1 provides a comparison of the various aspects of the three electrolysis cells, including electrical energy consumption.

Diaphragm cells use a simple and economical brine system and require less electrical energy than mercury cells. A primary disadvantage of the diaphragm cell is the low concentration of the caustic soda solution, which requires several concentrative operations to achieve the purity needed for industrial use. The caustic contains 2 to 3 percent NaCl, requiring further purification for some industrial uses. The diaphragm cell is also known to be a source of pollution from asbestos fibers, the primary material of the diaphragm.

Because of these disadvantages, mercury cathode cells began to compete with diaphragm cells early in the twentieth century. Mercury cells produce a much purer and extremely concentrated caustic product that can be used without further treatment in most cases. However, mercury has extremely serious ecological impacts and when dispersed from chemical process effluents, can enter the food chain and lead to mercury poisoning in humans.

Membrane cells are the most environmentally benign of all the cell technologies, and have electricity requirements similar to those of diaphragm cells. The caustic solution produced is also essentially salt-free and more concentrated than that produced from diaphragm cells. Chemical companies have been slow to adopt membrane technology because of operational problems encountered in early installations, and because existing facilities are fully depreciated but still functional (IND CHEM 1990, Ayres 1997).

Diaphragm and mercury cells include an anode and cathode in contact with a brine solution. The membrane cell cathode is only in contact with 20 to 32 percent NaOH, with very low chloride content. Features that distinguish the cells from each other include the method used to keep the three major products separated and unable to mix (chlorine gas, sodium hydroxide, and hydrogen), and the resulting product concentration (see Figure 6-2). Hydrogen *must* be separated from the chlorine gas as mixtures of these two gases can be explosive.

Diaphragm cells account for 71 percent of domestic production, mercury cells for 12 percent, and membrane cells for 16 percent, with other methods producing about 1 percent (CI 1999). Total production costs for using cells are a function of raw materials, energy, operating costs, and capital depreciation. Today, membrane cell technology is only a small factor in new capacity. Membrane cell technology requires a secondary brine treatment, disposal or recycling of spent anolyte, and has relatively high capital costs. Most diaphragm cell producers continue to rebuild their existing diaphragm cells, rather than convert to membranes.

Chemical Reaction in Salt Electrolysis

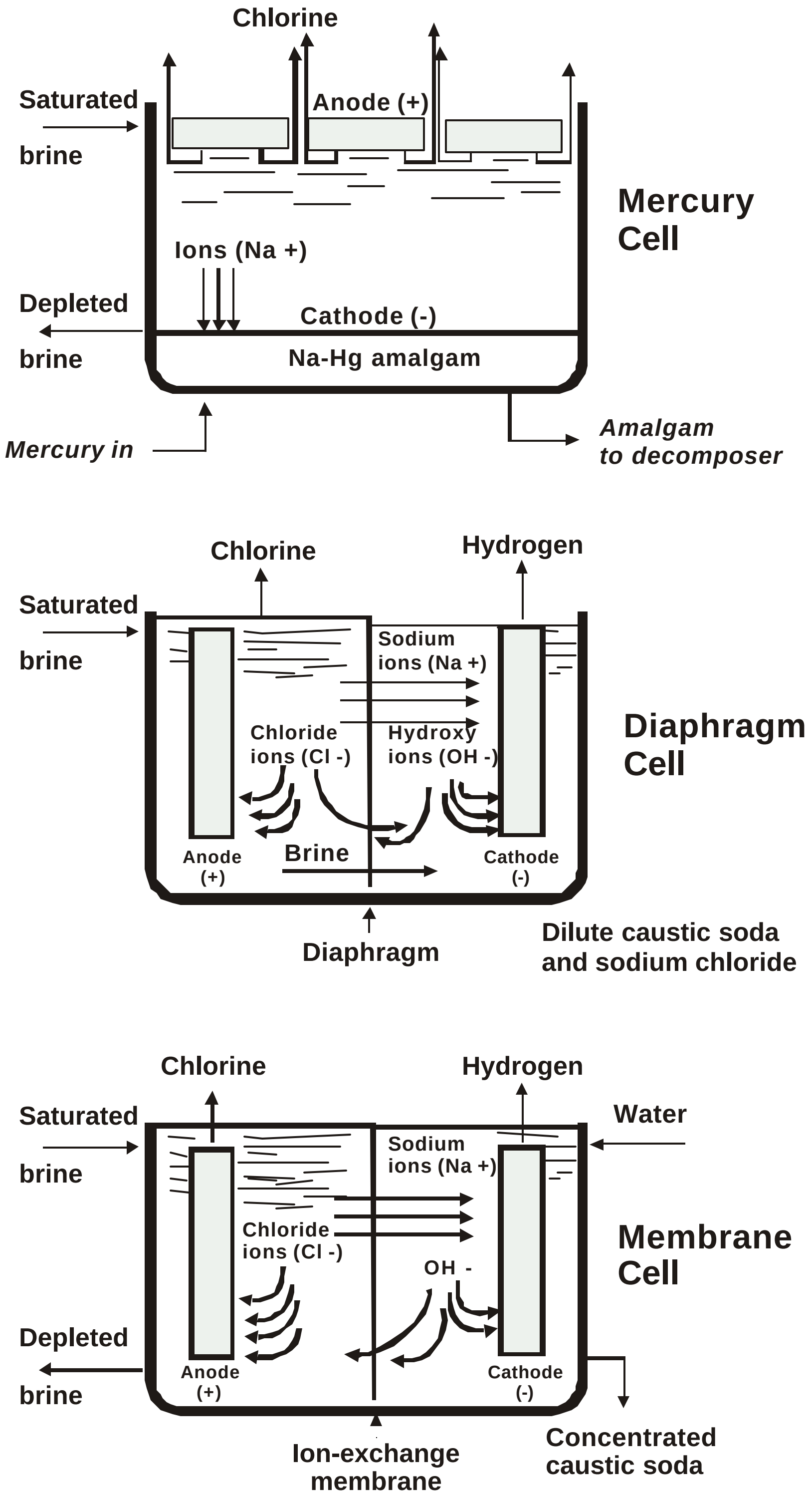
$2NaCl$ +	$2\,H_2O$ →	$2NaOH$ +	Cl_2 +	H_2
Salt	Water	Sodium Hydroxide	Chlorine	Hydrogen

Table 6-1. Characteristics of Various Chlorine/Sodium Hydroxide Electrolysis Cells

Component	Diaphragm Cell	Mercury Cell	Membrane Cell
Cathode	Steel/steel coating with nickel	Mercury flowing over steel	Steel or nickel with a nickel-based coating
Anode	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life
Diaphragm/ Membrane Material	Asbestos and fibrous polytetrafluoroethylene	None	Ion-exchange membrane (fluorinated polymers)
Cathode Product	10 to15% sodium hydroxide solution, containing 15 to17% salt (NaCl) (sent to evaporator for further processing); hydrogen gas	Sodium amalgam (sent for further processing through a decomposer cell)	30-33% sodium hydroxide solution (sent to evaporator for further processing); hydrogen gas
Anode Product	Chlorine gas containing some oxygen, salt, water vapor, and sodium hydroxide	Chlorine gas containing some oxygen, salt, and water vapor	Chlorine gas containing some oxygen, salt, and water vapor
Evaporator/Decomposition Product	50% sodium hydroxide solution containing 1% salt; solid salt from evaporator	50% sodium hydroxide solution; hydrogen gas	50% sodium hydroxide solution with very little salt
Electricity Consumption	2,550 to 2,900 kWh/ton chlorine gas	3,250 to 3,450 kWh/ton chlorine gas	2,530 to 2,600 kWh/ton chlorine gas

Sources: Sittig 1977, EPA 1990, EPA 1992b, EPA 1995b, DOW 1999.

Figure 6-2. Comparison of Chlorine/Sodium Hydroxide Electrolysis Cells (IND CHEM 1990, EPA 1995a)



In a **diaphragm cell**, multiple cells containing an anode and cathode pair are mounted vertically and parallel to each other (see Figure 6-3). Cathodes are usually a flat hollow steel mesh or perforated steel sheet covered with asbestos fibers and fibrous polytetrafluoro-ethylene (PFTE), and function as the diaphragm. The mix of fibers is typically about 75 percent asbestos and 25 percent PFTE. The anode is usually constructed of titanium plates covered with layers of Group VIII oxides with metal conductivity (ruthenium oxide, titanium oxide).

The overall process flow is shown in Figure 6-4. Brine flows continuously into the anode chamber and then through the diaphragm to the cathode. Chlorine gas is formed at the anodes, and sodium hydroxide solution and hydrogen gas are formed directly at the cathode. By allowing liquid to pass through to the cathode, but not the fine chlorine gas bubbles, the diaphragm prevents the mixing of hydrogen and chlorine. The diaphragm also limits the back-diffusion of hydroxide ions formed at the cathode. The back-migration of hydrogen

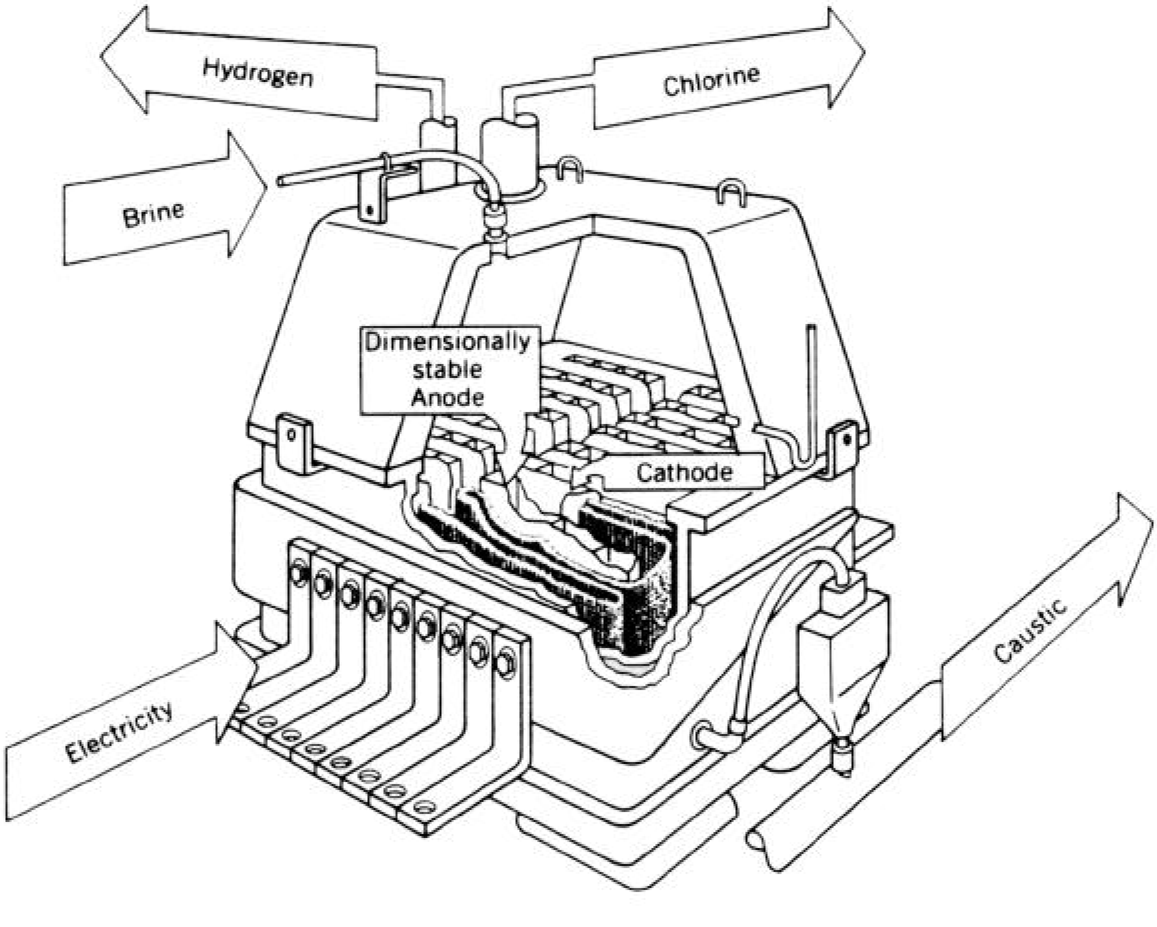


Figure 6-3. Typical Diaphragm Cell (Chenier 1992)

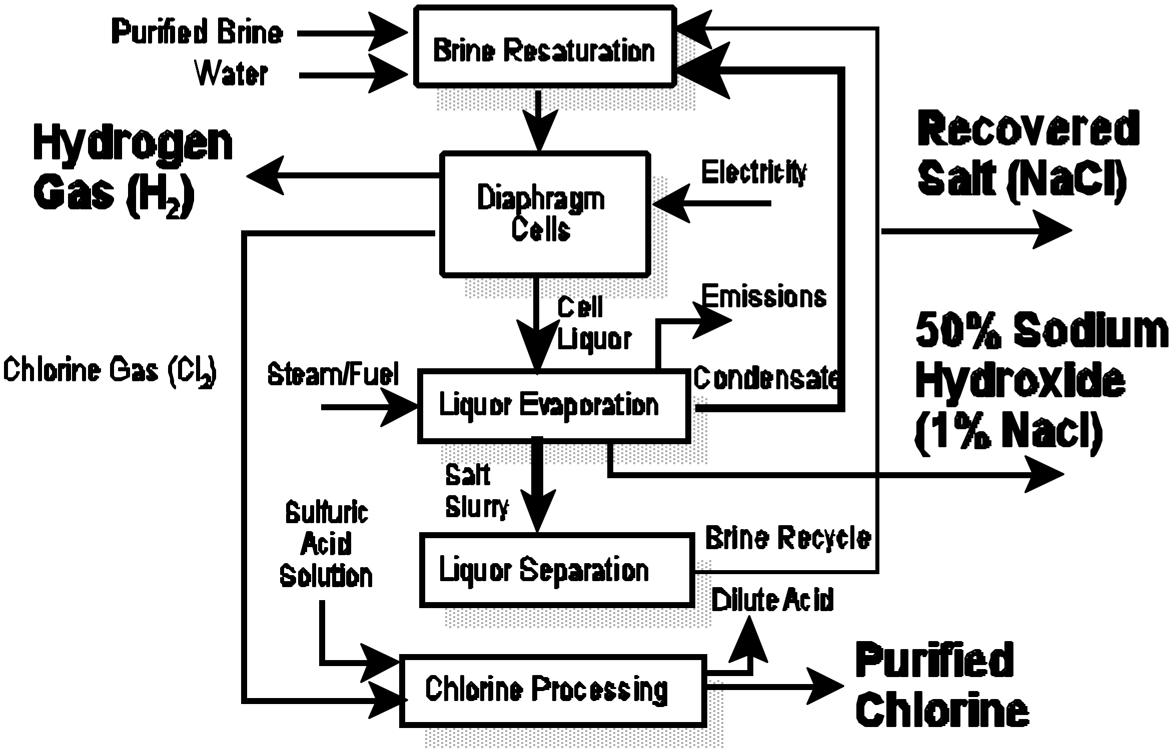


Figure 6-4. Diaphragm Cell Process (IND CHEM 1990, EPA 1992b, EPA 1995a)

Key Energy and Environmental Facts - Diaphragm Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *4,649 Btu/lb chlorine* *2,725 kWhr/ton chlorine*	*Largest source - fugitive and point source emissions (chlorine gas, carbon dioxide, carbon monoxide, hydrogen, and Freon)*	*Largest source - wash water from chlorine processing (spent sulfuric acid, which is reclaimed and reused)*	*Scrapped diaphragms (lead, asbestos) and cell parts*

ions across the diaphragm represents the most inefficient aspect of the cell. The hydrogen gas and chlorine gas are drawn off separately from the top of the cell, and the residual brine containing 10 to 15 percent sodium hydroxide is taken from the bottom of the cell. After being de-humidified and cooled, the hydrogen is sent to storage. For a less pure product, the chlorine is first cooled (using a Freon or similar refrigerant), then washed with sulfuric acid in a packed column to dry it. The spent sulfuric acid is recovered and reused. Diaphragm cells will have dissolved air and carbon dioxide that enter with the brine, and leave the process via chlorine purification.

Demand for purified chlorine is high, and represents the largest share of chlorine produced. Purified chlorine is produced by compressing and cooling the gas to a liquid state. The liquid chlorine is fractionally distilled to remove chlorinated tars called “taffy” in the heavy fraction. The light fraction contains inerts such as air, carbon dioxide, and impurities such as bromine and iodine. Gaseous chlorine is transferred for use by pipeline or liquid chlorine is transported by rail car to offsite customers (DOW 1999). Rail cars and barges are generally purged with nitrogen to remove the chlorine and the chlorine is scrubbed in a tower with caustic. The resulting hypochlorite is treated with bisulfite and the effluent is treated for disposal.

The dilute sodium hydroxide solution contains residual salt and must undergo an evaporative process to produce a product at a usable concentration. The greatest disadvantage to diaphragm cells is the large amount of salt that must be removed at this stage. The need for salt columns, centrifuges, cyclones, clarifiers, and filters increases the complexity, capital cost, and energy use in a diaphragm-based caustic plant (DOW 1999).

Figure 6-5 shows the general arrangement for the concentration and production of the final sodium hydroxide product. This process concentrates the cell liquor from the diaphragm cell by evaporating water from the dilute caustic and separating the residual salt. The end result is a 50 percent sodium hydroxide solution with 1 percent residual sodium chloride.

The advantage of diaphragm cells is that they operate at a lower voltage than mercury cells and use less electricity. The brine feedstock can also be less pure than that required by mercury or membrane cells.

The **mercury cell** process (see Figure 6-6) uses two cells: an electrolyzer cell and a decomposer cell. The electrolyzer is essentially an electrolysis cell consisting of a large steel container shaped like a rectangular parallelogram with lined walls under a covering of flexible and anti-explosive rubber. A thin layer of mercury of about 3 millimeters in depth flows over the bottom of the steel container, serving as the cathode for the process. A saturated brine solution of about 25 percent NaCl by weight flows through the container above the mercury.

The anode, consisting of titanium sheet coated with ruthenium oxide and titanium oxide, is incorporated into the cell cover and suspended horizontally in the brine solutions. The height of the anodes in the brine is adjusted to obtain an optimum distance from the mercury cathode.

In the electrolyzer, chlorine evolves from the electrolytic decomposition of NaCl and moves upward through gas extraction slits in the cell cover. The chlorine gas is removed, purified, and sent to storage. Sodium ions are absorbed in the mercury layer, and the resulting sodium and mercury mixture (amalgam) is sent on to the decomposer cell.

The decomposer is essentially a short-circuited galvanic cell and consists of a small cylindrical steel tower divided into two parts. The amalgam is semi-decomposed in the upper section, and the decomposition is then completed in the lower part. Graphite serves as the anode and amalgam serves as the cathode. The amalgam and water flowing through the cell come into direct contact with the graphite. In both parts of the tower the amalgam is decomposed by water with the formation of sodium hydroxide, the reformation of mercury, and the production of hydrogen gas.

The mercury generated can be reused in the primary electrolytic cell. A relatively highly concentrated (50 percent) solution of sodium hydroxide is formed and can be used as it is or after it is further concentrated. The hydrogen gas is purified and used elsewhere in the plant.

The depleted brine leaving the cell contains a high concentration of NaCl (21 to 22 percent by weight). Dissolved chlorine is removed from this solution, and it is resaturated with NaCl and purified for re-use. The high concentration of sodium hydroxide solution produced and the absence of residual salt are the major advantages of the mercury cell. No further evaporation or salt separation is needed to produce the finished product. However, mercury cells require higher voltage than both diaphragm and membrane

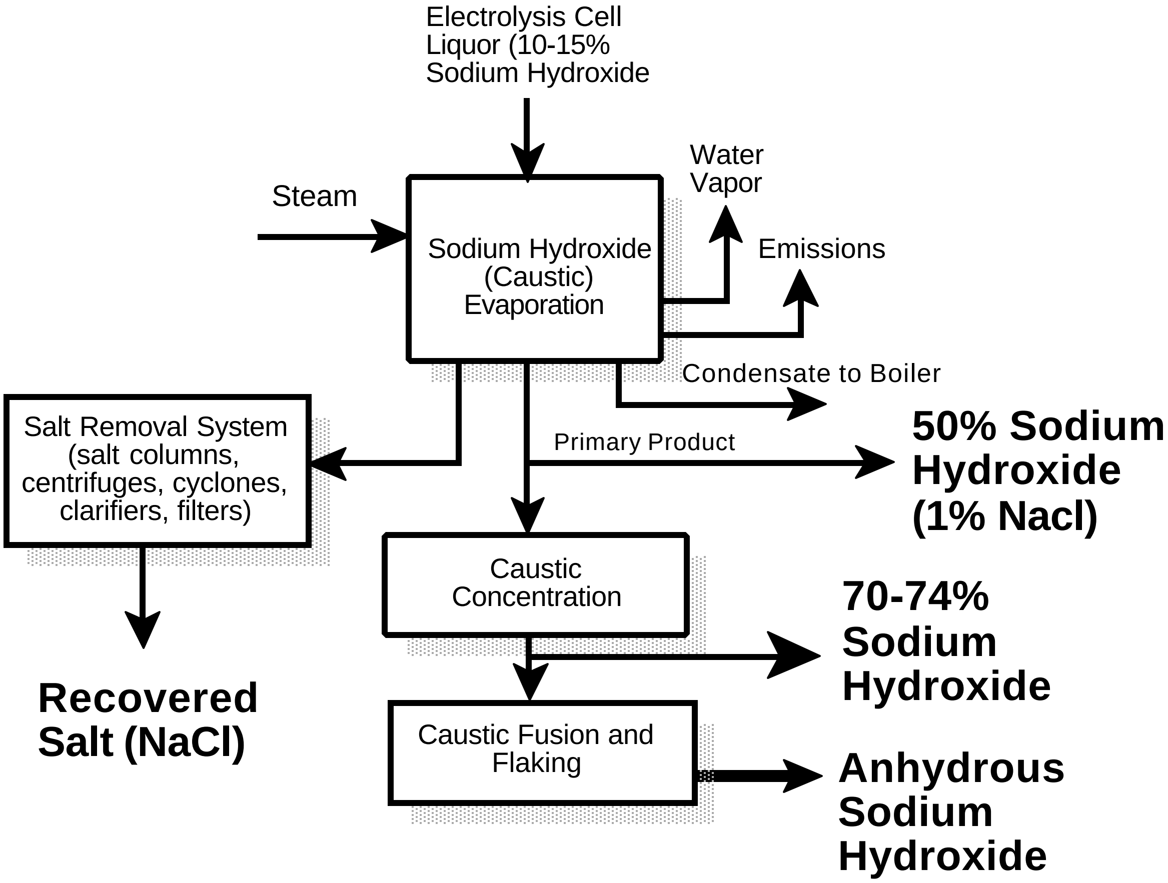


Figure 6-5. Sodium Hydroxide (Caustic) Evaporation Process
(Sittig 1977, IND CHEM 1990, Chenier 1992, EPA 1992b, Orica 1999)

cells, and use more energy. The process also requires as input a very pure brine solution without metal contaminants.

There are also environmental consequences to the use of mercury. Through contaminated effluents it can enter the food chain via plankton and accumulate in the adipose tissue of fish. Fish products can then act as a vehicle in conveying mercury compounds with neurotoxic properties (e.g., mercury poisoning). Tremendous improvements in the cell technology have significantly reduced emissions from these plants. However, precautions are taken to prevent releases of mercury to the environment. Liquid effluents from the mercury process are treated with sodium sulfide to remove mercury before any discharge. The mercury compounds are combined with brine treatment sludges for further treatment and disposal. Traces of mercury occur in caustic soda and hydrogen generated from the mercury cell process. These are removed from caustic soda by filtration. With hydrogen, they are removed by cooling followed by absorption with activated carbon (Orica 1999, DOW 1999).

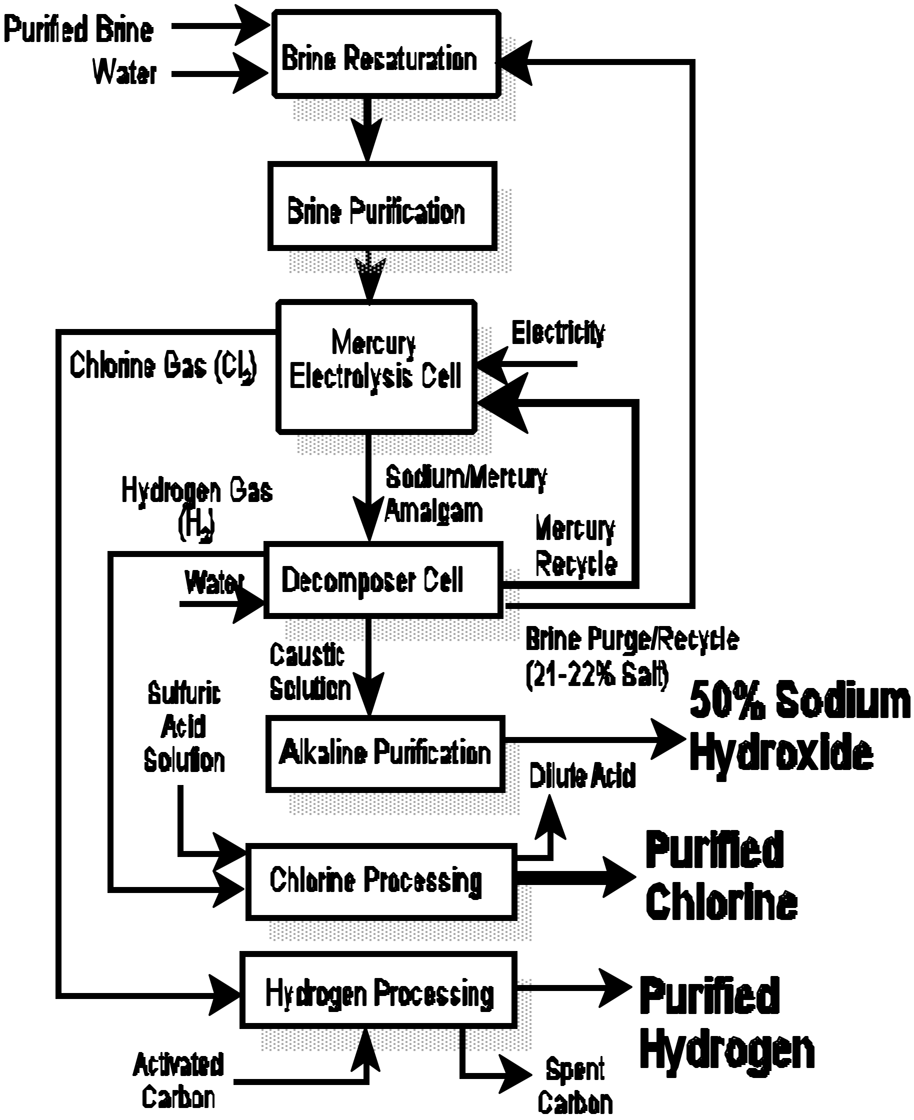


Figure 6-6. Mercury Cell Process
(IND CHEM 1990, EPA 1992b, EPA 1995a, Orica 1999)

Key Energy and Environmental Facts - Mercury Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *Gross: 5,715 Btu/lb chlorine* *3,350 kWhr/ton chlorine*	*Largest source - fugitive and point source emissions (chlorine, Freon, and mercury)*	*Largest source - wastewater from brine pumps, cell wash water, sumps (small amounts of mercury); chlorine processing wastewater (sulfuric acid)*	*Spent graphite from decomposer cells, spent caustic filtration cartridges from the filtration of caustic soda solution, spilled mercury from sumps, and mercury cell "butters"*

In a **membrane cell** the anode and cathode are separated by a water-impermeable, ion-conducting membrane (see Figure 6-7). In this process the brine solution flows through the anode compartment and chlorine gas is generated at the anode. Sodium ions migrate through the membrane to the cathode compartment, where sodium hydroxide solution is flowing. Water hydrolizes at the cathode and releases hydrogen gas and hydroxide ions.

The combination of sodium and hydroxide ions produces sodium hydroxide which reaches a concentration of about 30 to33 percent before leaving the cell. The membrane preferentially passes positive sodium ions from the anode chamber to the cathode chamber. Negatively charged chloride and hydroxide ions are primarily rejected by the membrane. As a result, the sodium hydroxide solution typically contains less than 100 ppm NaCl. The depleted brine leaves the anode compartment and is resaturated with salt for reuse in the membrane cell.

Stainless steel or nickel is typically used as a cathode in the membrane cell. The cathodes are also often coated with a catalyst (nickel-sulfur, nickel-aluminum, nickel-nickel oxide, platinum group metals) to increase surface area and reduce the hydrogen evolution potential. Anodes are similar to those used in both diaphragm and mercury cells (ruthenium and titanium oxide on titanium).

The membrane’s material and design are critical to cell operation. Membranes must maintain stability after exposure to both chlorine and strong caustic solution. They require low electrical resistance and must allow the transport of sodium ions but not chloride ions. Membrane materials currently in use are fluorinated polymers with pendant functional groups that make them ion-selective.

The advantage of membrane cells is the relatively pure sodium hydroxide solution produced and the lower electricity requirements than either diaphragm or mercury cells. In addition, membrane cells do not require the use of toxic materials (e.g., asbestos, mercury).

Disadvantages of the membrane cell include the need for processing of the chlorine gas to remove oxygen and water vapor, and for moderate evaporation to increase the concentration of the caustic solution. Another disadvantage is that the brine entering a membrane cell must be of very high purity to prevent contamination of the membrane, which requires costly purification of the brine prior to electrolysis. The membrane separator in these cells is expensive and easily damaged, and has a shorter lifetime than diaphragm and mercury separators.

6.1.2 Brine Production

Brine Production and Purification Are Required for All Cells

Regardless of the type of cell employed, a suitable brine must be prepared prior to entering the cell. Different levels of purification are required for the various cells, and some require removal of metals or other impurities.

Salt is obtained from the mining of natural deposits or from seawater (via solar evaporation), and contains impurities that must be removed before it can be used in the electrolytic cell. Impurities include primarily calcium, magnesium, barium, iron, aluminum, sulfates, and trace metals. Impurities can negatively affect the electrolytic cell by precipitating out and blocking or damaging membrane or diaphragm materials. Impurities can also poison the catalytic coating on the anode and cathode. In the case of the mercury cell, some trace metals (e.g., vanadium) can reduce efficiency and cause the production of potentially dangerous amounts of hydrogen gas. Impurities can also lead to the production of chlorinated compounds, a situation that can negatively impact cell performance (EPA 1995a).

The first phase of brine preparation includes the dissolution of sea salt and rock salt in a water and dilute brine mix (see Figure 6-8). The amount of material dissolved is a function of brine concentration, residence time, and temperature. In all cases the brine-solid salt mixture is allowed to reach equilibrium so that a saturated solution of approximately 25 weight percent is produced. Purification is accomplished through two steps:

- The addition of Na_2CO_3 (soda ash) and NaOH (caustic soda) to precipitate Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+} ions
- The addition of NaOCl if there is any ammonia present, and $CaCl_2$ to eliminate $(SO^{2-})_4$ ions

Sulfate levels in the brine can be controlled by adding calcium chloride to a side stream to precipitate the sulfate as calcium sulfate. The sludge containing this compound can then be removed and disposed of in a landfill. In some cases the brine is evaporated to a solid salt to remove sulfates (DOW 1999, Orica 1999).

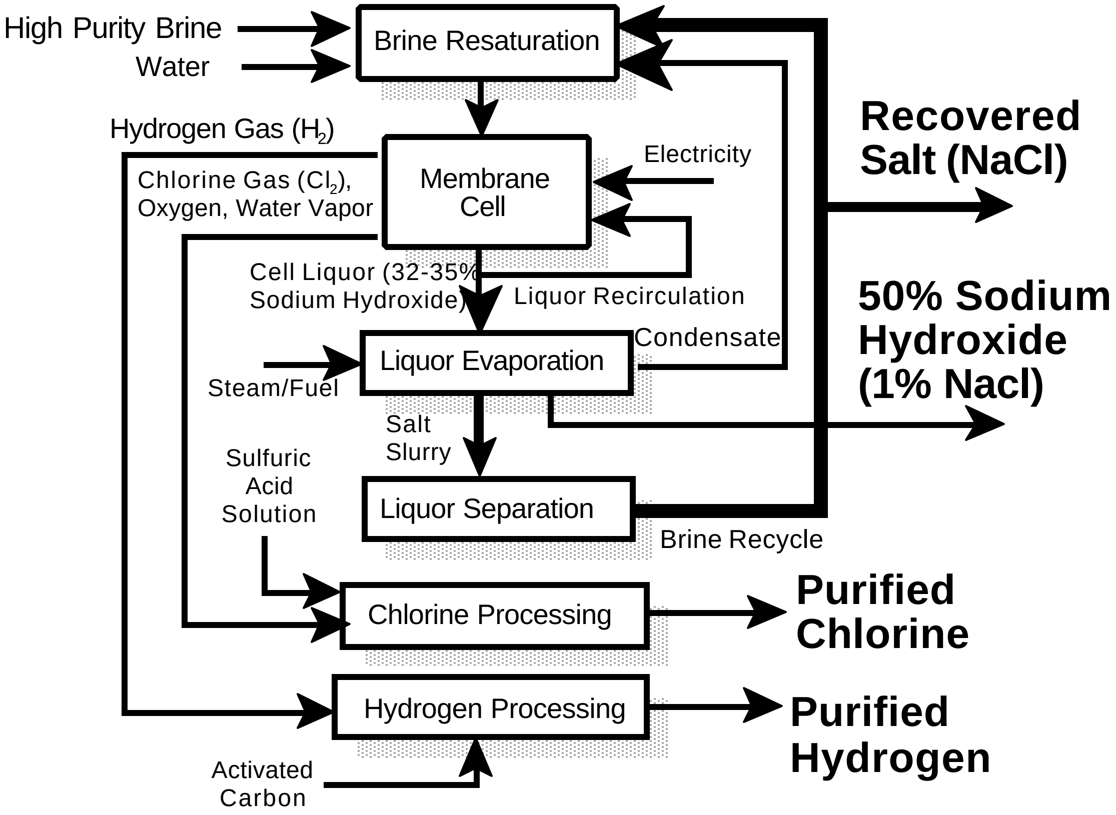


Figure 6-7. Membrane Cell Process
(IND CHEM 1990, EPA 1992b, EPA 1995a, Orica 1999)

Key Energy and Environmental Facts - Membrane Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *4,375 Btu/lb chlorine* *2,565 kWhr/ton chlorine*	*Largest sources - fugitive and point source emissions (chlorine and Freon)*	*Largest source - chlorine processing wastewater (sulfuric acid); ion-exchange wash water.*	*Scrapped cell parts (used membranes, anodes, cathodes)*

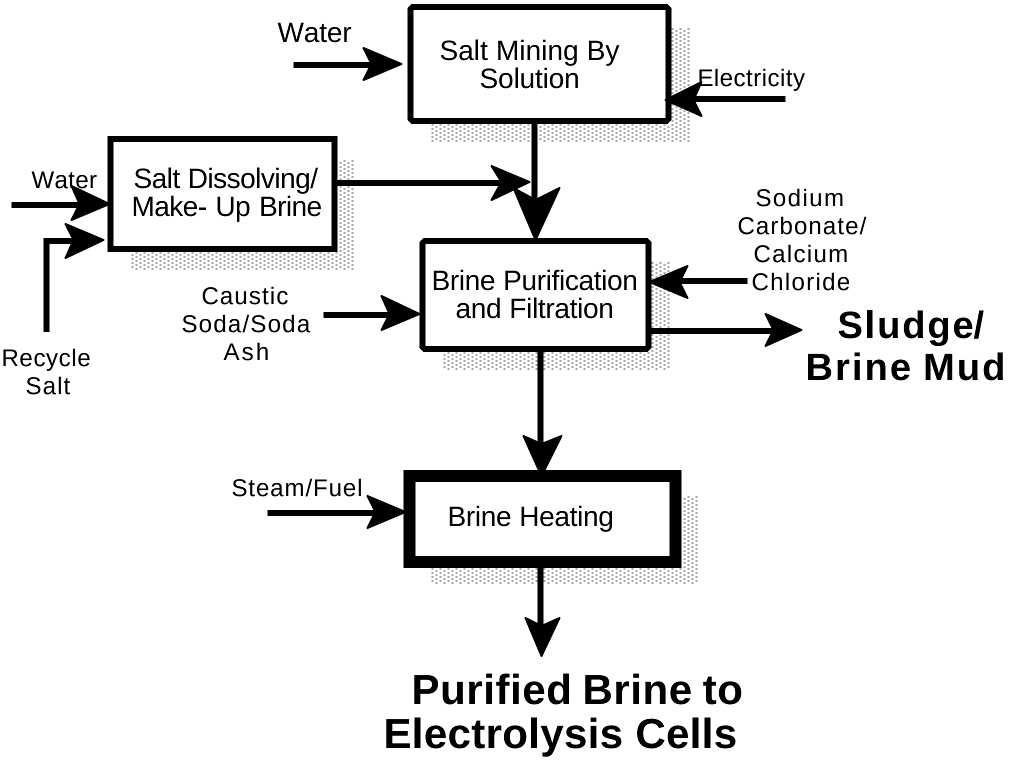


Figure 6-8. Brine Purification (Sittig 1977, EPA 1995a)

Key Energy and Environmental Facts - Brine Purification			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *1,424 Btu/lb chlorine*	*Largest sources - heater stack gas (CO, SOx, NOx, hydrocarbons, and particulates)*	*Recycle brine/brine purge*	*Brine mud (magnesium hydroxide, calcium carbonate, and barium sulfate; mercury in elemental form or as mercuric chloride; calcium sulfate; mercury sulfide)*

Purification creates a precipitation sludge (brine mud) that is washed to recover entrained sodium chloride and then disposed of in a landfill. If the mercury process is used, brine purification sludges will contain trace levels of mercury. In this case the sludge is treated with sodium sulfide to bind the mercury as mercury sulfide (an insoluble compound) and the sludge may be further bound by casting the sludge into concrete blocks. These blocks are tested for leachability and then disposed of into a controlled landfill.

The second step in brine preparation includes clarification, filtration, the addition of recycled brine, adjustment of pH value, and collection into tanks to feed the cells. Sand filters are commonly used for clarification and filtration.

Brine for mercury and diaphragm processes contains less than 4 parts per million (ppm)of calcium and 0.5 ppm of magnesium. Membrane cell processes require a more purified brine (less than 20 parts per billion of magnesium and calcium combined), which is usually passed through ion exchange columns to remove impurities to the needed level.

After purification the purified brine is heated to bring it up to the correct process temperature for each cell (Sittig 1977, EPA 1995a).

Table 6.2 Average Operating Conditions for Cells

Cell Type	Brine Concentration (g//l)	Limits on Impurities			Temperature °F	pH
		CaO	MgO	SO_2		
Diaphragm	315-330	5 ppm	0.8 ppm	0-0.3 g/l	194-221	10.5 - 11
Mercury	300-320	< 5 ppm	< 3 ppm	< 2g/l	165 -185	3-5
Membrane	~ 445	nil[a]	nil[a]	nil	165 - 195	7

[a] less than 20 parts per billion of calcium and magnesium combined.

Sources: IND CHEM 1990, Ayres 1997.

6.1.3 Manufacture of Soda Ash

Trona Ore Is the Feedstock for U.S. Soda Ash Production

In 1864, a Belgium chemist named Ernest Solvay invented the ammonia-soda or Solvay process for manufacture of **sodium carbonate (soda ash)**. While this process is still popular world-wide, in the United States all soda ash is produced from natural trona ore. In the 1940s, large deposits of this ore were found in Wyoming, which ultimately led to the closing of the last Solvay process plant in 1986. Conversion from the synthetic Solvay process to natural soda ash has been touted as one of the most successful transformations of the chemical industry during the 1970s and 1980s (Chenier 1992).

Trona ore, also called sesquicarbonate, is a complex of sodium, carbon, hydrogen, and oxygen ($2NA_2CO_3 \bullet NAHCO_3 \bullet 2H_20$). Upon heating it produces soda ash and carbon dioxide (see Figure 6-8). Approximately 1.8 tons of trona ore are required to produce one ton of soda ash.

There are four methods currently used to mine Wyoming trona ore: 1) solution mining, 2) room-and-pillar, 3) longwall, and 4) shortwall. In solution mining, dilute sodium hydroxide is injected into the trona ore to dissolve it. The solution is then treated with carbon dioxide to precipitate out sodium carbonate. The crystals are then dissolved again in water, precipitated with carbon dioxide, and filtered. Calcining is then employed to produce a dense soda ash.

All other methods of trona ore mining require blasting. A combination of prilled ammonium nitrate and fuel oil is the most commonly used blasting agent. In this process the trona ore is crushed, dissolved in water, filtered to remove insoluble impurities, subjected to vacuum crystallization to precipitate sesquicarbonate, then calcined to produce sodium carbonate.

Alternatively, a monohydrate process is employed. In this process crushed trona ore is calcined in a rotary kiln, yielding dense soda ash and carbon dioxide as byproducts. The calcined material is combined withwater to settle out impurities, and is then concentrated using triple effect evaporators or mechanical vapor recompression. For every pound of soda ash created in this process, 0.42 pounds of carbon dioxide are also produced and vented to the atmosphere (Brown 1996, EPA 1997g, EIA 1998).

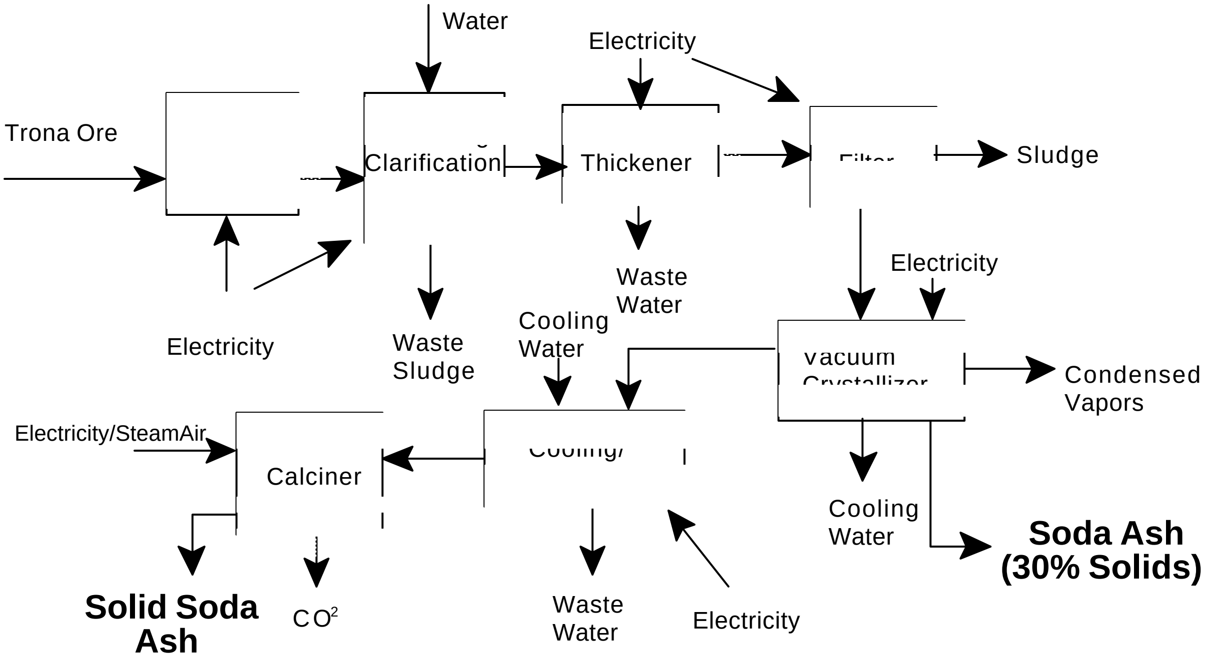


Figure 6-8. Manufacture of Soda Ash (Brown 1996)

Key Energy and Environmental Facts - Soda Ash Manufacture

Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *3,393 Btu/lb*	*Largest sources - carbon dioxide, boiler emissions, particulates (soda ash)*	*Waste water*	*Clarification sludge, condensed vapors*

6.2 Summary of Inputs and Outputs

The following is a summary of inputs and outputs for important chemicals of the chlor-alkali industry.

Chlorine/Sodium Hydroxide

Inputs:	Outputs:
Purified Brine	Chlorine
Sulfuric Acid	Sodium Hydroxide
Hydrochloric Acid	Hydrogen
Water	Recycle Brine
Electricity	Water Vapor
Steam	Sludge
Cooling Water	Process Water
Anode/Cathode Materials	Salt

Soda Ash

Inputs:	Outputs:
Trona Ore	Soda Ash
Cooling Water	Carbon Dioxide
Steam/Fuel	Condensed Vapors
Electricity	Waste Sludge
Air	Waste Water

Brine Purification

Inputs:	Outputs:
Salt	Purified Brine
Water	Brine Mud/Sludge
Make-up Brine	
Sodium Carbonate	
Caustic Soda/ Soda Ash	
Steam/Fuel	
Electricity	

6.3 Energy Requirements

Electricity Is the Largest Energy Source Used for Production of Chlorine and Sodium Hydroxide

Data on the process energy used for the co-production of **chlorine and sodium hydroxide** is shown in Table 6-3. Electricity fuels the electrolysis process and represents the primary energy source. The amount of electricity required depends on the design of the cell, the design operating current, concentration of electrolytes, temperature, and pressure. The values shown in Table 6-3 represent an average of energy consumption for the various cell types. Energy in the form of fuels or steam is used primarily for evaporation of the sodium hydroxide solution to a useable state. Some fuels are also consumed in the production and purification of brine feedstock before it is sent to the electrolysis cell.

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

Among the three types of chlorine cells, the mercury cell is the **most energy-intensive**, with electricity requirements of nearly 3600 kWhr per metric ton of chlorine. The membrane cell is the least energy-intensive in terms of both steam and electricity requirements. Steam requirements are less than half those of the diaphragm or mercury cell. Electricity requirements for the membrane cell are in the range of 2800 kWhr per metric ton of chlorine. The diaphragm cell is intermediate between these energy consumption ranges.

Overall, the **electrical energy requirements** for chlorine electrolysis cells are high, accounting for nearly 130 trillion Btu annually. When losses due to transmission and generation of electricity are considered, they reach nearly 400 trillion Btu annually. Thus, efficient operation of the cell is critical to optimized energy use and cost-effective production. Sources of energy losses in chlorine cells include anode or cathode overvoltage, too large a drop across the diaphragm, oxygen evolution on the anode, and failure to recover heat and energy from hydrogen, chlorine, and cell liquor streams.

A key consideration in membrane processes is the purity of the brine. Using very pure brine at an optimum flow rate minimizes blockage through the membrane and allows sodium to penetrate freely. Brine purity is also important in mercury cells. Impurities tend to increase hydrogen by-product and reduce the current efficiency.

Another issue is brine flowrate. Flowrates that are too high increase cell temperature and electrical conductivity of the medium. Brine rates that are too low create temperatures and high cell voltages that are higher than the most efficient voltage (3.1 to 3.7 volts) (Sittig 1977, Orica 1999).

Table 6-3. Estimated Energy Use in Manufacture of Chlorine/Sodium Hydroxide (Caustic Soda) Co-Products - 1997

Energy	Specific Energy[d] (Btu/lb of Cl_2)	Average Specific[d] Energy (Btu/lb of Cl_2)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	4,353 - 5,561	4,957	128.8
Fuel Oil and LPG[b]	62 - 112	87	2.3
Natural Gas	1,601 - 2,880	2,240	58.3
Coal and Coke	208 - 374	291	7.6
Other[c]	208 - 374	291	7.6
NET PROCESS ENERGY	6,432 - 9,301	7,867	204.5
Electricity Losses	9,039 - 11,547	10,293	267.6
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**15,471 - 20,848**	**18,160**	**472.2**

[a] Does not Include losses incurred during the generation and transmission of electricity. Conversion factor: 3412 Btu/kWh. Based on range of cell currents for diaphragm, mercury, and membrane cells. Includes electricity for brine purification.

[b] 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 (e.g., renewables).

[d] 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 diaphragm, mercury, and membrane cell technologies . Includes steam for brine purification and caustic evaporation (Sources: IND CHEM 1990, Brown 1996, Orica 1999, Ayres 1999).

[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values for chlorine (26 billion lbs) (CMA 1998). Note that 1.12 to1.43 lbs of sodium hydroxide are produced for every lb of chlorine.

At present, U.S. chlorine production is dominated by the diaphragm cell, and the use of the more energy-intensive mercury cell continues to decline. In Europe, however, production is still dominated by use of the mercury cell, although European manufacturers have committed to build no new mercury cells in the future (Ayres 1997).

Energy requirements for the manufacture of **sodium carbonate from trona ore** are shown in Table 6-4. A large share of the energy consumed is in the form of steam used for vacuum crystallization of the trona solution to produce an initial 30 percent solids solution of sodium carbonate, and for calcining. Electricity is used for dissolution, clarifying, thickening, precipitation, dewatering, and calcining. Overall electricity use for this process is very low, about 127 Btu per pound of solid product. Annual energy use for producing sodium carbonate, however, is considerable–over 80 trillion Btus–due to the large production value of nearly 24 billion pounds annually.

Table 6-4. Estimated Energy Use in Manufacture of Sodium Carbonate (Soda Ash) From Trona Ore - 1997

Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	127	3.0
Fuel Oil and LPG[b]	98	2.3
Natural Gas	2,515	59.6
Coal and Coke	327	7.7
Other[c]	327	7.7
NET PROCESS ENERGY	**3,393**	**80.4**
Electricity Losses	264	6.3
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**3,657**	**86.7**

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

[b] 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 (e.g., renewables).

[d] 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 process based on trona ore (Brown 1996).

[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values for sodium carbonate (23.7 billion lbs) (CMA 1998).

6.4 Air Emissions

Chlorine Gas and Freon Are Primary Air Emissions from Brine Electrolysis

Air emissions from brine electrolysis include chlorine gas and freon emissions (both fugitive and point source) and other vapors. Fugitive emissions arise from cells, scrubbers, and vents throughout the system. While individual leaks may be minor, the combination of fugitive emissions from various sources can be substantial. In 1995, nearly 3 million pounds of chlorine fugitive and point source emissions were reportedly released by the inorganic chemical industry (EPA 1997c). These emissions are controlled through leak-resistant equipment modifications, source reduction, and programs to monitor such leaks. Table 6-5 lists emission factors for mercury emissions from chlor-alkali production (EPA 1992b).

Diaphragm cells and **membrane cells** release chlorine as fugitive emissions from the cell itself and in process tail gases, which are wet-scrubbed with soda ash or caustic soda to remove chlorine. The spent caustic solution from this wash is neutralized and then discharged to water treatment facilities (EPA 1992b, EPA 1995a).

Mercury cells release small amounts of mercury vapor and chlorine gas from the cell itself. Process tail gases from chlorine processing, caustic soda processing, and hydrogen processing also release small amounts. Mercury is removed from the hydrogen gas stream by cooling followed by absorption with activated carbon. (EPA 1992b, Orica 1999).

Before the hazards of mercury emissions were fully recognized, actual emissions from mercury cells were as high as 3 kg per metric ton. Mercury emissions from chlorine production have dramatically declined in response to tighter regulations, better housekeeping, and technology improvements. However, there are considerable variations in the estimated mercury emissions from chlorine manufacture (Ayres 1997).

Varying Estimates of Mercury Emissions per Ton of Chlorine Manufactured

0.6 gram/metric ton (EPA 1992b)
0.47 gram/metric ton (Habersatter 1991)
2.47 gram/metric ton (Manzone 1993)
2.50 gram/metric ton (Euro Chlor 1995)
3.00 gram/metric ton (SRI 1989)

Brine preparation and caustic evaporation processes release emissions through the combustion of fuels in process heaters and in boilers that produce process steam. When operating in an optimum condition and burning cleaner fuels (e.g., natural gas, refinery gas), these heating units create relatively low emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbon emissions. A table of emission factors for combustion of fossil fuels in fired heaters and boilers is provided in Chapter 7, Supporting Processes.

During the production of **sodium carbonate**, particulate emissions are created from ore calciners, soda ash coolers and dryers, ore crushing, screening and transporting, and product handling and shipping. Combustion products (SO_x, NO_x, CO, particulates, and volatile hydrocarbons) are also emitted from direct-fired process heating units (ore calcining kilns, soda ash dryers). Little data is available on combustion products from these units, although emissions from similar equipment are categorized by the U.S. Environmental Protection Agency for the mineral industries, in *AP 42 Chapter 11, Mineral Products Industry*.

Production of sodium carbonate from trona ore also creates emissions of carbon dioxide, a suspected greenhouse gas. Emission factors for carbon dioxide emitted from this process are given in Table 6-6. Additional carbon dioxide may be emitted as sodium carbonate is processed in other manufacturing processes (glass-making, water treatment, flue gas desulfurization, soap and detergent production, pulp and paper making). Data is listed on releases of carbon dioxide from these processes.

According to a recent study (EIA 1998), approximately 113 metric tons of carbon are released for every 1000 metric tons of soda ash consumed in glass manufacturing or flue gas desulfurization. The same source indicates about 97 million metric tons of carbon released for every 1000 tons of trona ore produced annually for sodium carbonate production.

In 1997, reported annual emissions of carbon dioxide from manufacture of sodium carbonate were 1.08 million metric tons; emissions from use of sodium carbonate were 0.86 million metric tons (EIA 1998). More than 88 percent of emissions from the use of sodium carbonate were associated with flue gas desulfurization.

Controlled and uncontrolled emissions of filterable and total particulate matter from sodium carbonate production processes are shown in Table 6-7. Emissions of particulates from calciners and dryers are most often controlled by venturi scrubbers, electrostatic precipitators, or cyclones. The high moisture content of exiting gases makes it difficult to use baghouse-type filters. Control of particulates from ore and product handling systems, however, is often accomplished by baghouse filters or venturi scrubbers. These are essential to the cost-effectiveness of the process as they permit capture and recovery of valuable product.

Table 6-5 Mercury Emissions from Chlorine/Caustic Soda Manufacture		
Source	**Mercury Gas (lb/ton of chlorine produced)**	**Mercury Gas (grams/metric ton of chlorine produced)**
Uncontrolled Hydrogen vent	0.0033	0.17
Controlled Hydrogen vents	0.0012	0.6
End Box	0.010	5.0

Source : EPA 1992b.

Table 6-6. Uncontrolled Emission Factors for Carbon Dioxide from Sodium Carbonate Production	
Process	**lb CO_2/ton of sodium carbonate**
Trona ore process: rotary ore calciner	310
Trona ore process: fluid bed calciner	180
Rotary soda ash dryers	130

Source: EPA 1997g.

Table 6-7 Particulate Emission Factors for Sodium Carbonate Manufacture			
Source	**Controlled Emissions (lb/ton of sodium carbonate)**		**Uncontrolled Emissions (lb/ton of sodium carbonate)**
	Filterable	**Total**	
Ore mining	0.0033	no data	3.3
Ore crushing and screening	0.0021	0.0035	3.5
Ore transfer	0.0002	0.0002	0.2
Trona ore process: rotary calciner	0.72	0.73	72
Trona ore process: fluid bed calciner	0.043	no data	4.3
Rotary soda ash dryers	0.50	0.52	50
Fluid bed soda ash dryers/coolers	0.030	0.39	3.0
Soda ash screening	0.019	0.026	19
Soda ash storage/loading/unloading	0.0041	0.0051	5.2

Source: EPA 1997g.

6.5 Effluents

Wastewater Is Treated To Remove Chlorine and Acids Prior to Discharge

Wastewater from **diaphragm and membrane cells** originates from caustic evaporation, chlorine drying, washing of the ion-exchange resin, and from purification of salt recovered from evaporators.

Caustic evaporation, where the sodium hydroxide solution is concentrated to a 50 or 70 percent solution, evaporates about 5 tons of water per ton of 50 percent caustic soda produced. The water vapor from the evaporators is condensed, and in the case of the diaphragm process, will contain about 15 percent caustic soda solution and a relatively high salt content of 15 to 17 percent. If sodium sulfate is not removed during the brine purification process, salt recovered from evaporators may be recrystallized to avoid buildup of sulfate in the brine. If the salt is recrystallized, the wastewater may contain sodium sulfates.

Wastewater from membrane processes contains caustic soda solution, but is virtually free of salt or sodium sulfates. Wastewater from caustic soda processing is usually neutralized with hydrochloric acid, then lagooned and discharged to and or to receiving ponds.

During **chlorine gas processing**, water vapor is removed by scrubbing with concentrated sulfuric acid. Between 6 kilograms and 35 kilograms of 79 percent sulfuric acid wastewater is generated per 1000 kilograms of chlorine produced (EPA 1995a). Most of this wastewater is shipped off-site for processing into concentrated sulfuric acid or for use in other processes. The remainder is used for pH control or discharged to water treatment facilities for disposal (EPA 1995a).

Ion-exchange wash water from **membrane cell** processes usually contains dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminum chloride. This wastewater is usually treated along with other acidic wastewaters by neutralization.

Wastewater streams are generated from mercury cells during the chlorine drying process, brine purge, and from other sources. Mercury is present in the brine purge and other sources (floor sumps, cell wash water) in small amounts. This mercury is generally present in concentrations ranging from 0 to 20 parts per million, and is precipitated out using sodium hydrosulfide to form mercuric sulfide. The mercuric sulfide is removed through filtration before the water is discharged (EPA 1995a, Orica 1999).

Sodium carbonate manufacture creates significant volumes of wastewater that must be treated prior to discharge or recycling to the process. These may contain both mineral (e.g., shale) and salt impurities (EPA 1997g). Limitations for toxic or hazardous compounds contained in these wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, Part 415, which was originally promulgated in 1974 and has been revised several times since then. The chemicals in the chlor-alkali industry and sodium carbonate are covered under Subparts F and O. Specific limitations for restricted compounds and total suspended solids (TSS) are shown in Tables 6-8 through 6-10. “BPT Standards” refers to the use of the best practicable control technology currently available. “BAT” refers to the best available technology economically achievable. “NSPS” refers to new source performance standards that apply to new process water impoundment or treatment facilities.

Table 6-10 provides BPT limitations only for the production of **sodium chloride** (the primary input to chlor-alkali manufacture) by solution brine-mining. In this process water is pumped into a salt deposit and a saturated salt solution is removed that is about one-third salt. Provisions are that no process wastewater pollutant may be returned to navigable waters. The exception is unused bitterns (saturated brine solution remaining after precipitation of sodium chloride), which may be returned to the body of water from which the process brine solution was originally withdrawn.

Table 6-8. Effluent Pretreatment Standards: Mercury Cells			
Effluent	**BPT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**NSPS Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.32	--	0.32
Mercury	0.00014	0.00010	0.00010
Total Residual Chlorine	--	0.0019	0.0019
pH	6-9	6-9	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart F.

Table 6-9. Effluent Pretreatment Standards: Diaphragm Cells			
Effluent	**BPT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**NSPS Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.51	--	0.51
Copper	0.0070	0.0049	0.0019
Lead	0.010	0.0024	0.0019
Nickel	0.0056	0.0037	--
Total Residual Chlorine	--	0.0079	0.0079
pH	6-9	6-9	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart F.

Table 6-10. Effluent Pretreatment Standards: Production of Sodium Chloride by Solution Brine-Mining	
Effluent	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.17
pH	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart P.

6.6 Hazardous Wastes and Byproducts

Brine Mud Constitutes the Largest Solid Waste Stream from Chlor-Alkali Production

Brine purification results in brine mud, one of the largest waste streams from the chlor-alkali industry. About 30 kilograms of brine mud are generated for every 1000 kilograms of chlorine produced, but this varies with the purity of the salt used to produce the brine. Pre-purified salts, for example, will generate only about 0.7 to 6.0 kilograms per 1000 kilograms of chlorine produced. The brine mud contains a variety of compounds, typically magnesium hydroxide and calcium carbonate formed during the addition of compounds to purify the brine. The sludge or brine mud containing these impurities must be disposed of in a landfill (EPA 1995a, Orica 1999). If a mercury process is being used, the brine mud may contain trace levels of mercury. In this case, the sludge is treated with sodium sulfide to create mercury sulfide, an insoluble compound. The sludge is further treated by casting it into concrete blocks, which are treated for leachability and sent to a controlled landfill.

Both **diaphragm and membrane cell** processes generate solid wastes from scrapping of cell parts (cell covers, piping, used diaphragms, used membranes, cathodes, and anodes). Discarded cell parts are landfilled on-site or shipped off-site for disposal. Used cathodes and anodes are shipped off-site to a third party recovery facility. Depending on the cell technology, the cathodes may be refurbished and reused, particularly those made of nickel. The anodes for diaphragm cells are refurbished and rec-coated with RuO_2/TiO_2 and returned to service.

Solid wastes from **mercury cells** include spent graphite from decomposer cells, spent caustic filtration cartridges from the filtration of caustic soda solution, spilled mercury from sumps, and mercury cell "butters." (The latter are semi-solid amalgams of mercury with barium or iron, formed when an excess of barium is used during purification). Mercury is recovered from these wastes where possible, and the remainder is disposed of in secure landfills to prevent migration of mercury, which can cause significant damage to the environment.

Mercury cell brine muds may also contain mercury in elemental form or as mercuric chloride. These muds are considered hazardous and must be disposed of in a RCRA Subtitle C landfill after treatment with sodium sulfide, which creates an insoluble sulfide compound (EPA 1995a). Other brine muds are segregated and stored in lagoons, which are periodically dredged or drained and covered over. The dredgings are usually landfilled off-site.

The **processing of hydrogen gas** from mercury cells also creates hazardous waste. In this process, small amounts of mercury present in the hydrogen gas are extracted by cooling the gas. A large part of the condensed mercury is removed in this fashion and returned to the electrolytic cell. Some facilities use activated carbon treatment to further purify the hydrogen of mercury, and the spent carbon is shipped off-site for disposal as a hazardous waste.

The effluents and solid wastes and hazardous wastes from chlor-alkali production are summarized in Table 6-11. Specific wastes from chlor-alkali manufacture that are listed by the EPA as **hazardous** as shown in Table 6-12. Most of the hazardous wastes are generated from the mercury cell process.

The dissolving and clarification steps in **sodium carbonate production** create a waste sludge containing non-hazardous impurities, such as salts and minerals. This sludge is disposed of in landfills.

Table 6-11. Summary of Effluents and Solid and Hazardous Waste Streams from Chlorine/Sodium Hydroxide Production

Source	Diaphragm/ Membrane Cells	Mercury Cells	Caustic Evaporation	Chlorine/ Hydrogen Processing	Brine Purification
Wastewater	Ion-exchange wash water, cell wash water, brine purge	Brine pumps, cell wash water, sumps (small amounts of mercury)	5 tons water/ton 50% caustic soda solution	79% sulfuric acid solution (6 to 35 kg/1000 kg chlorine)	
Solid Wastes	Scrapped cell parts (cell covers, piping, used diaphragms, used membranes, cathodes, and anodes)	Spent caustic filtration cartridges from the filtration of caustic soda solution, spent graphite from decomposer cells			Brine mud (0.7 to 30 kg/1000 kg chlorine)
Hazardous Wastes	Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process (K073)	Spilled mercury from sumps, and mercury cell "butters"; wastewater treatment sludge (K106)		Spent activated carbon	Brine mud containing mercury (K071)

Source: EPA 1995a.

Table 6-12. Hazardous Wastes from Chlor-Alkali Manufacture

Waste Classification	Description	Hazardous Constituents
K071	Brine purification muds from the mercury cell process in chlorine production, where separately pre-purified brine is not used	Mercury
K073	Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process	Chloroform, carbon tetrachloride, hexachloroethane, trichloroethane, tetrachloroethylene, dichloroethylene, 1,1,2,2-tetrachloroethane
K106	Wastewater treatment sludge from the mercury cell process in chlorine production	Mercury

Source: BNA 1995.

7

Supporting Processes: Effluent Treatment and Process Heaters

7.1 Effluents

Pretreatment Standards Apply to Effluents from Chemicals Manufacture

Effluents emitted during the production of chemicals consist primarily of waste waters from washing, crystallization, distillation towers, and cooling water. Much of this process water is recycled for reuse wherever possible. 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 toxic or hazardous compounds contained in wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, which was originally promulgated in 1974 and has been revised several times since. These limitations apply to all facilities that manufacture organic chemicals, plastics, and synthetic fibers. Tables 7-1 and 7-2 provide the standards for effluents generated from the manufacture of commodity organic chemicals.

Table 7-1 Effluent Pretreatment Standards Organic Chemicals (micrograms/liter)

Effluent Characteristics	Maximum for One Day	Maximum Month Average
Benzene	134	57
Carbon Tetrachloride	380	142
Chlorobenzene	380	142
1,2,4-Trichlorobenzene	794	196
Hexachlorobenzene	794	196
1,2-Dichloroethane	574	180
1,1,1-Trichloroethane	59	22
Hexachloroethane	794	196
1,1-Dichloroethane	59	22
1,1,2-Trichloroethane	127	32
Chloroethane	295	110
Chloroform	325	111
1,2-Dichlorobenzene	794	196
1,3 Dichlorobenzene	380	142
1,4-Dichlorobenzene	380	142
1,1-Dichloroethylene	60	22
1,2-trans-Dichloroethylene	66	25

Source: CFR 40 Chapter 1, Part 414.

Table 7-2 Effluent Pretreatment Standards/Organic Chemicals (micrograms/liter)		
Effluent Characteristics	Maximum for One Day	Maximum Monthly Average
1,2-Dichloropropane	794	196
1,3-Dichloropropylene	794	196
Ethylene Benzene	380	142
Methylene Chloride	170	36
Methyl Chloride	295	110
Hexachlorobutadiene	380	142
Nitrobenzene	6402	2237
2-Nitrophenol	231	65
4-Nitrophenol	576	162
4,6-Dinitro-o-cresol	277	78
Tetrachloroethylene	164	52
Toluene	74	28
Trichloroethylene	69	26
Vinyl Chloride	172	97
Total Cyanide	1200	420
Total Lead	690	320
Total Zinc	2610	1050

Source: CFR 40 Chapter 1, Part 414.

A Diversity of Water Pretreatment Processes Are Available

Many chemical industry wastewaters must be pretreated prior to discharge to publicly owned treatment works (POTWs). The characteristics of these wastewaters vary considerably, depending on the chemical manufacturing process they came from. The water stream that exits from each process is likely to have unique pollutants, as well as temperatures, pressures, flow rates, and pH that are different from those of other process streams. The design and successful operation of wastewater treatment facilities on-site at the chemical plant requires continuous sampling and monitoring of these parameters. Some wastewaters will also go through several treatment stages before discharge to POTWs. Common treatment options are shown in Table 7-3.

There are a number of objectives in pretreating wastewater, including the following:

- Attaining a suitable pH for discharge
- Removing oil and grease
- Removing suspended solids
- Reducing/eliminating toxics and VOCs
- Removing heavy metals
- Equalizing wastewater flow

Achieving a **proper pH** is essential for meeting EPA’a effluent pretreatment standards and preventing problems in downstream treatment operations (e.g., biological treatment). Neutralization is required to attain a suitable pH. Acidic wastewaters are neutralized with lime, limestone, or caustic solutions. Alkaline (basic) wastewaters are neutralized with either sulfuric or hydrochloric acids, or carbon dioxide gas.

Oil and grease are generally easy to remove using mechanical separation or dissolved-air flotation, unless they are emulsified in the wastewater. In such cases coagulants are added to the water to coalescence the contaminants into large agglomerates that can be removed.

Suspended solids are present in wastewater in many forms and sizes, and the removal technique will depend on their classification (see Table 7-3). Large solids of 25 mm diameter or larger may interfere with downstream processes if they are not removed using screens. Grit such as sand and gravel are removed by sedimentation. Small particles of between 0.001 and 1 micrometer in diameter are referred to as colloids, and are removed by dissolved-air flotation or chemical coagulation.

Removal of metals is most commonly achieved by precipitating the metal out as an hydroxide using lime or caustic. Once metal hydroxides are precipitated, they must be coagulated or flocculated into larger, heavier particles that will settle out in a sedimentation pond, plate settler, or solids-contact clarifier. After separation, the remaining sludge is dewatered and landfilled (if not hazardous).

Volatile organic compounds (VOCs) are usually stripped by air or steam in packed towers. In thesetowers the air or steam flows countercurrently to the wastewater to remove the contaminant. Activated carbon columns may also be used to remove VOCs by absorption.

Table 7-3. Wastewater Treatment Options

Waste Classification	Option
Acidic (low pH)	Neutralization with lime, limestone, or caustic solutions
Alkaline (high pH)	Neutralization with sulfuric or hydrochloric acids, or carbon dioxide gas
Oil and Grease	Mechanical skimming, dissolved -air flotation, chemical coagulants, carbon filters (soluble oils)
Suspended Solids (<1%)	Screening (bar or fine screens), gravity separation (sedimentation, chemical coagulation followed by sedimentation, dissolved-air flotation), granular media filtration, membrane filtration (microfiltration, ultrafiltration)
Suspended Solids (>1%)	Thickening (gravity thickening, dissolved-air floatation, centrifuging), dewatering (pressure, belt or vacuum filtration, centrifuging, sand-bed drying)
Heavy Metals	Hydroxide precipitation and dewatering, sedimentation, chemical oxidants (chlorine, ozone, hydrogen peroxide, potassium permanganate or chlorine dioxide), greensand filtration (iron, manganese)
Volatile Organic Compounds (VOCs)	Air or steam stripping, activated carbon absorption, incineration, biological treatment, ultrafiltration membranes, nanofiltration membranes, reverse osmosis
Non-Volatile Organic Compounds	Biological treatment (aerobic or anaerobic), ultrafiltration membranes, nanofiltration membranes, chemical oxidants with UV, reverse osmosis
Dissolved or Divalent Salts	Nanofiltration membranes, reverse osmosis
Inorganic Ions/Chlorine	Nanofiltration membranes, activated carbon filtration
Odors	Chemical oxidants
Bacterial/Viral Growth	Chemical oxidants, ultrafiltration membranes, nanofiltration membranes, reverse osmosis
COD	Chemical oxidants

Sources: CE 1991, CE 1992 BIO 1993, WWS 1999, Culligan 1999.

Biological treatments may be employed to destroy both volatile and non-volatile organic contaminants. In these systems the contaminants are consumed by microorganisms, which convert them to new cell matter, gases, or other inert products. These processes may take place with or without oxygen, although aerobic (with oxygen) processes are more common. If enough land is available, outdoor lagoons are often used for carrying out biological aerobic treatment of wastewaters.

The use of biological treatments has accelerated rapidly over the last decade, and is now applied to a much wider variety of organic contaminants. Biological waste-destruction systems are attractive to the chemical industry because of their low cost compared to conventional treatment alternatives. For example, DuPont conducted a study that indicated that controlling VOCs using biofiltration is at least 90 percent less expensive than using activated carbon or incineration processes, and costs 67 percent less than stripping processes (BIO 1993).

Chemical oxidants (e.g., chlorine, ozone, hydrogen peroxide, potassium permanganate, chlorine dioxide) may be used to destroy odors, control bacterial growth, reduce chemical oxygen demand (COD), and remove residual heavy metals from wastewater. Chemical oxidants are also sometimes combined with ultraviolet (UV) radiation for very thorough destruction of some organic contaminants. (Pretreatment descriptions: CE 1991, CE 1992, BIO 1993, WWS 1999, and Culligan 1999).

7.2 Process Heaters

Process Heaters Are Integrated into Every Chemical Process

Process heat from **direct-fired heaters** and **boiler steam** is necessary for nearly every process in the chemical plant. Steam, for example, is used for distillation, chemical reactions, heating, and drying. Most of the energy consumed in chemicals manufacture is used in heaters and boilers. Boilers and process heaters exist in a wide variety of designs, and a discussion of the large number of possible configurations is outside the scope of this report. However, typical combustion emission factors for these units are provided in Table 7-4.

In direct contact operations, the steam is used as a stripping medium or process fluid. In some applications steam may be used in vacuum ejectors to produce a vacuum. Steam is also used for drying, evaporation, and other processes where indirect heating is required.

Process heaters are used extensively to supply heat to raise the temperature of feed streams to a level necessary for chemical reaction or distillation. Maximum fluid temperatures reached by process heaters are about 950ºF (510ºC). Air preheaters are heat exchangers that recover heat in the flue gas by heating up combustion air. They are usually applied on large heaters in areas where NOx emissions are not a severe problem. Heaters with air preheaters produce much more NOx than do heaters that use air at ambient temperatures. A steam convection section can sometimes be used to duplicate the high efficiency obtained from a heater with an air preheater.

Furnaces are used in some cases for the incineration of effluent streams containing air pollutants, toxic chemicals, or hazardous wastes. In these specialized waste-destruction furnaces, temperatures can be much higher than in typical boilers. Excess heat from these systems may be recovered by heat exchange.

Waste heat recovery is an important component of many chemical processes. Reactions that are highly exothermic (e.g., heat-releasing) produce considerable amounts of heat that can be recovered as steam for export throughout the chemical plant. The production of sulfuric acid, for example, generates nearly 2000 Btu/lb of product in high pressure steam for export.

In many cases, however, the available waste heat is not recovered or is incompletely recovered, resulting in the loss of valuable heat energy. These heat losses throughout the chemical industry are estimated to be more than two quads annually, which is significant. Table 7-5 illustrates the potential energy content of waste heat streams in various chemical processes (PNNL 1984).

Table 7-4. Boiler Combustion Emission Factors By Fuel Type (lbs/million Btu)

Fuel Type	SO_x	NO_x	CO_2	Particulates	VOCs[a]
Distillate Fuel	0.160	0.140	0.0361	0.010	0.002
Residual Fuel	1.700	0.370	0.0334	0.080	0.009
Other Oils	1.700	0.370	0.0334	0.080	0.009
Natural Gas	0.000	0.140	0.0351	0.003	0.006
LPG	0.000	0.208	0.0351	0.007	0.006
Propane	0.000	0.208	0.0351	0.003	0.006
Steam Coal	2.500	0.950	0.3044	0.720	0.005
Coke	2.500	0.950	0.3044	0.720	0.005
Electricity	1.450	0.550	0.1760[b]	0.400	0.004

[a] volatile organic compounds

[b] Electricity emissions of carbon dioxide are based on energy consumption for the national grid

Sources: **Particulates, SOx, NOx, VOCs** - U.S. Environmental Protection Agency, 1986, Compilation of Air Pollution Emission Factors, Vol 1, *Stationary Point and Area Sources, Supplement A*; *Supplement B* (September 1988); and 1995 updates.
CO_2 - U.S. Department of Energy. *Emissions of Greenhouse Gases in the United States, 1987-1992; Emissions of Greenhouse Gases in the United States, 1995.*

Table 7-5. Characteristics of Waste Heat Streams in Selected Chemical Sectors

Chemical Process	Million Btu/Ton of Product (Temperature in °F)		
	Flue Gases	Cooling Water	Other
Caustic Soda (Sodium Hydroxide)	4.5 (120)	0.4 (180)	0.1
Chlorine	--	0.24 (190)	2.2
Soda Ash (Sodium Carbonate)	1.22 (400 to 500)	0.16	0.3
Styrene	0.6-0.7 (400 to 500)	29 (100 to120)	--
Ethylene	1.9 (400)	--	--
Ammonia	2.4 (400)	0.5 (100 to120)	0.43

Source: PNNL 1984.

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Appendix A

Standard International Trade Classifications

SITC 51 Organic Chemicals includes hydrocarbons and their derivatives, alcohols, phenols, and other organic compounds.

SITC 52 Inorganic Chemicals includes chlorine and other inorganic elements, acids, metallic salts, and other inorganic compounds.

SITC 53 Dyeing, Tanning, and Coloring includes dyes, color lakes, tanning extracts, paints, pigments, varnishes, inks, and related preparations.

SITC 54 Medicinal and Pharmaceutical Products includes vitamins, antibiotics, hormones, veterinary and other medicaments, and related preparations.

SITC 55 Essential Oils and Perfume Materials includes essential oils, perfume materials, perfumes, cosmetics, toilet preparations, polishes, soaps, and related cleansing preparations.

SITC 56 Fertilizers includes nitrogenous, phosphatic, and other chemical and mineral fertilizers.

SITC 57 Plastics in Non-Primary Form includes polyethylene, PVC, polystyrene, and other plastic resins.

SITC 58 Plastics in Non-Primary Form includes tubes, pipes, hoses, plates, sheets, film, foil, strips, and other shades of plastic.

SITC 59 Chemical Material and Products, not elsewhere classified, includes pesticides, starches, glues, explosives and pyrotechnic products, fuel additives, plasticizers, textile specialties, and other miscellaneous chemical products and preparations.

325 Chemical Manufacturing

The Chemical Manufacturing subsector is based on the transformation of organic and inorganic raw materials by a chemical process and the formulation of products.

3251 Basic Chemical Manufacturing

This industry group comprises establishments primarily engaged in manufacturing chemicals using basic processes, such as thermal cracking and distillation. Chemicals manufactured in this industry group are usually separate chemical elements or separate chemically defined compounds.

32511 Petrochemical Manufacturing

This industry comprises establishments primarily engaged in (1) manufacturing acyclic (i.e., aliphatic) hydrocarbons such as ethylene, propylene, and butylene made from refined petroleum or liquid hydrocarbon and/or (2) manufacturing cyclic aromatic hydrocarbons such as benzene, toluene, styrene, xylene, ethyl benzene, and cumene made from refined petroleum or liquid hydrocarbons.

32512 Industrial Gas Manufacturing

This industry comprises establishments primarily engaged in manufacturing industrial organic and inorganic gases in compressed, liquid, and solid forms.

32513 Synthetic Dye and Pigment Manufacturing

This industry comprises establishments primarily engaged in manufacturing synthetic organic and inorganic dyes and pigments, such as lakes and toners (except electrostatic and photographic).

325131 Inorganic Dye and Pigment Manufacturing^{US}

325132 Synthetic Organic Dye and Pigment Manufacturing^{US}

32518 Other Basic Inorganic Chemical Manufacturing

This industry comprises establishments primarily engaged in manufacturing basic inorganic chemicals (except industrial gases and synthetic dyes and pigments).

325181 Alkalies and Chlorine Manufacturing^{CAN}

This U.S. industry comprises establishments primarily engaged in manufacturing chlorine, sodium hydroxide (i.e., caustic soda), and other alkalies often using an electrolysis process.

US = U.S. industry only; CAN = U.S. and Canadian industries are comparable. (When no superscript appears, U.S., Canadian, and Mexican industries are comparable.)

325182 Carbon Black Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in manufacturing carbon black, bone black, and lamp black.

325188 All Other Basic Inorganic Chemical Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in manufacturing basic inorganic chemicals (except industrial gases, inorganic dyes and pigments, alkalies and chlorine, and carbon black).

32519 Other Basic Organic Chemical Manufacturing

This industry comprises establishments primarily engaged in manufacturing basic organic chemicals (except petrochemicals, industrial gases, and synthetic dyes and pigments).

325191 Gum and Wood Chemical Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in (1) distilling wood or gum into products, such as tall oil and wood distillates, and (2) manufacturing wood or gum chemicals, such as naval stores, natural tanning materials, charcoal briquettes, and charcoal (except activated).

325192 Cyclic Crude and Intermediate Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in (1) distilling coal tars and/or (2) manufacturing cyclic crudes or, cyclic intermediates (i.e., hydrocarbons, except aromatic petrochemicals) from refined petroleum or natural gas.

325193 Ethyl Alcohol Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in manufacturing nonpotable ethyl alcohol.

325199 All Other Basic Organic Chemical Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in manufacturing basic organic chemical products (except aromatic petrochemicals, industrial gases, synthetic organic dyes and pigments, gum and wood chemicals, cyclic crudes and intermediates, and ethyl alcohol).

3252 Resin, Synthetic Rubber, and Artificial Synthetic Fibers and Filaments Manufacturing

32321 Resin and Synthetic Rubber Manufacturing

This industry comprises establishments primarily engaged in one or more of the following: (1) manufacturing synthetic resins, plastics materials, and nonvulcanizable elastomers, and mixing and blending resins on a custom basis; (2) manufacturing noncustomized synthetic resins; and (3) manufacturing synthetic rubber.

325211 Plastics Material and Resin Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in (1) manufacturing resins, plastics materials, and nonvulcanizable thermoplastic elastomers, and mixing and blending resins on a custom basis and/or (2) manufacturing noncustomized synthetic resins.

325212 Synthetic Rubber Manufacturing^{US}

This U.S. industry consists of establishments primarily engaged in manufacturing synthetic rubber.

32522 Artificial and Synthetic Fibers and Filaments Manufacturing^{US}

This industry comprises establishments primarily engaged in (1) manufacturing cellulosic (i.e., rayon and acetate) and noncellulosic (i.e., nylon, polyolefin, and polyester) fibers and filaments in the form of monofilament, filament yarn, staple, or tow or (2) manufacturing and texturing cellulosic and noncellulosic fibers and filaments.

325221 Cellulosic Organic Fiber Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in (1) manufacturing cellulosic (i.e., rayon and acetate) fibers and filaments in the form of monofilament, filament yarn, staple, or tow or (2) manufacturing and texturizing cellulosic fibers and filaments.

325222 Noncellulosic Organic Fiber Manufacturing^{US}

This U.S. industry consists of establishments primarily engaged in (1) manufacturing noncellulosic (i.e., nylon, polyolefin, and polyester) fibers and filaments in the form of monofilament, filament yarn, staple, or tow or (2) manufacturing and texturizing noncellulosic fibers and filaments.

3253 Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing

32531 Fertilizer Manufacturing

This industry comprises establishments primarily engaged in one or more of the following: (1) manufacturing nitrogenous or phosphatic fertilizer materials; (2) manufacturing fertilizers from sewage or animal waste; (3) manufacturing nitrogenous or phosphatic materials, and mixing with other ingredients into fertilizers; and (4) mixing ingredients made elsewhere into fertilizers.

325311 Nitrogenous Fertilizer Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in one or more of the following: (1) manufacturing nitrogenous fertilizer materials and mixing ingredients into fertilizers; (2) manufacturing fertilizers from sewage or animal waste; and (3) manufacturing nitrogenous materials and mixing them into fertilizers.

325312 Phosphatic Fertilizer Manufacturing^{US}

This U.S. industry comprises establishments primarily engaged in (1) manufacturing phosphatic fertilizer materials or (2) manufacturing phosphatic materials and mixing them into fertilizers.

3254 Pharmaceutical and Medicine Manufacturing

3255 Paint, Coating, and Adhesive Manufacturing

32552 Adhesive Manufacturing

3256 Soap, Cleaning Compound, and Toilet Preparation Manufacturing

3259 Other Chemical Product and Preparation Manufacturing

32591 Printing Ink Manufacturing

32592 Explosives Manufacturing

32599 All Other Chemical Product and Preparation Manufacturing