

# 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.

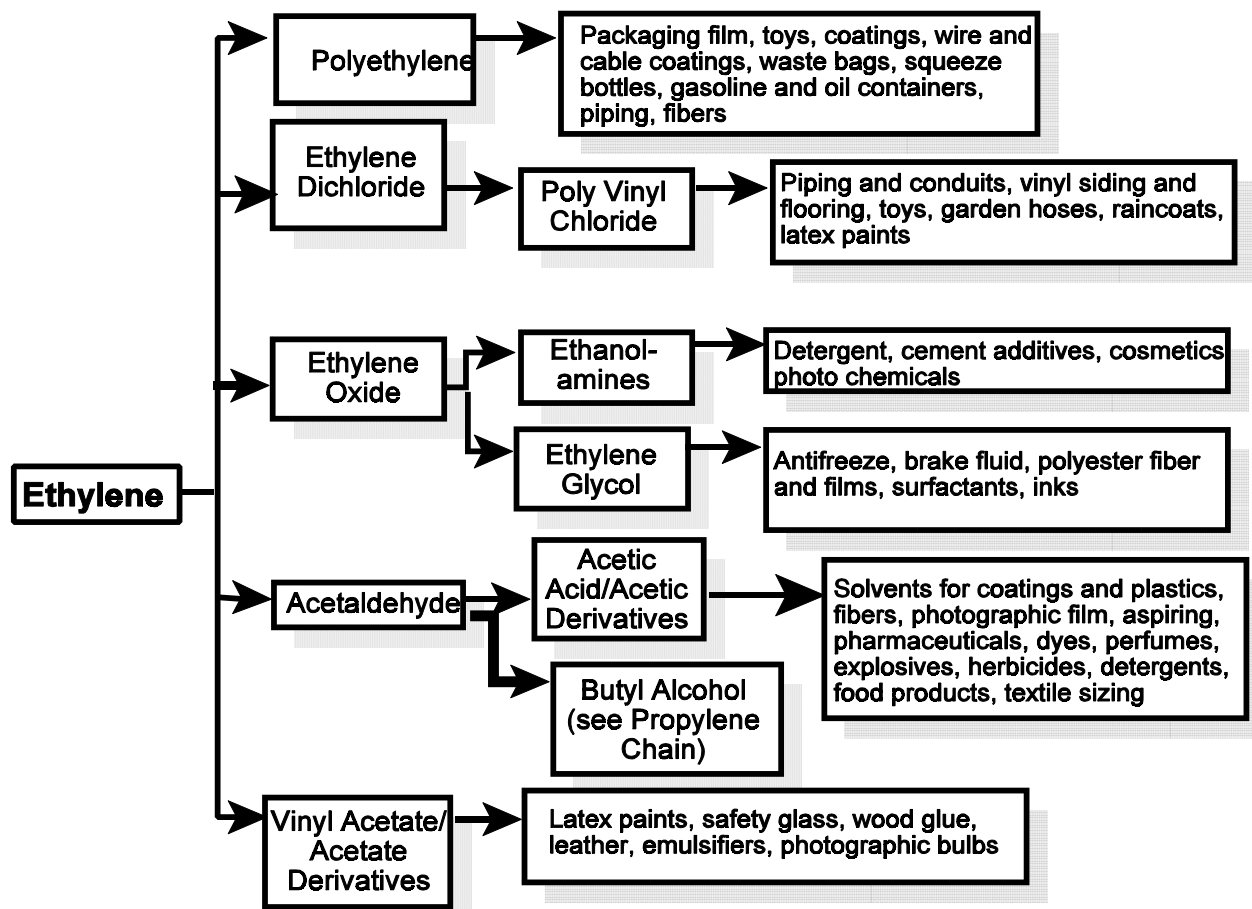


Figure 2-1. The Ethylene Products Chain (CMA 1998)

**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).

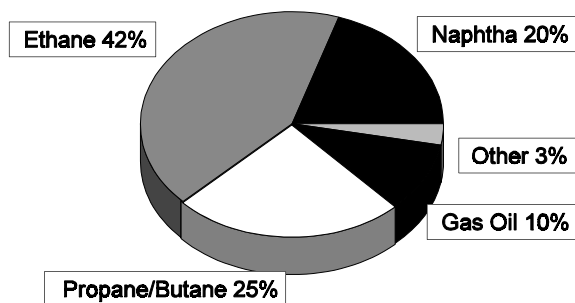
Demand for ethylene is directly related to the demand for its major derivatives, especially PE and PVC. Worldwide the polyethylene industry is a 100 billion pound market with over 150 producers. **Demand for polyethylene** has nearly doubled over the last decade, with the strongest growth markets in 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



**Figure 2-2. Ethylene Feedstocks**

fraction) and 10 percent from gas oil from refinery processing units (see Figure 2-2). In Western Europe, as well as in some Asian countries (South Korea, Taiwan, Japan), naphtha 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

% 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

requirements will differ depending on both the feedstock and the desired product slate.

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

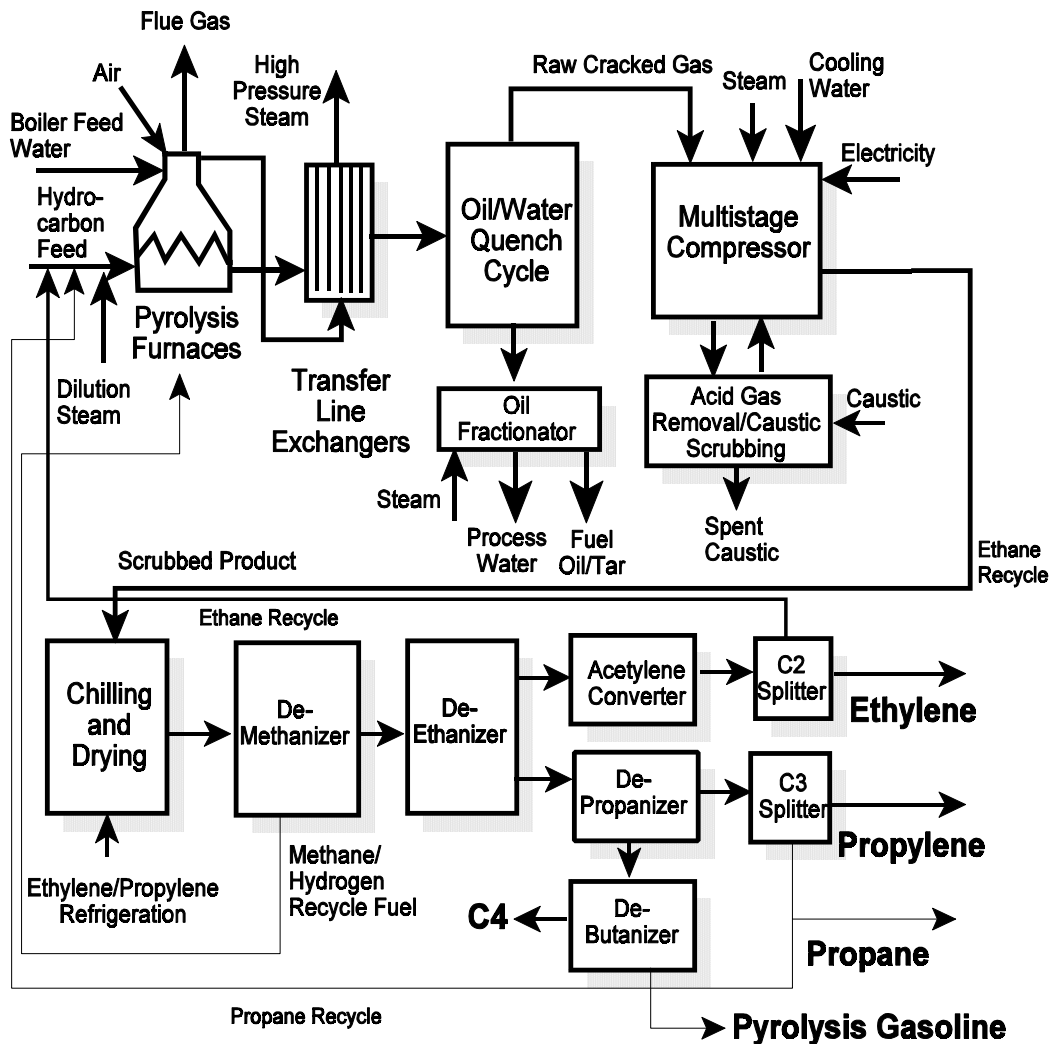
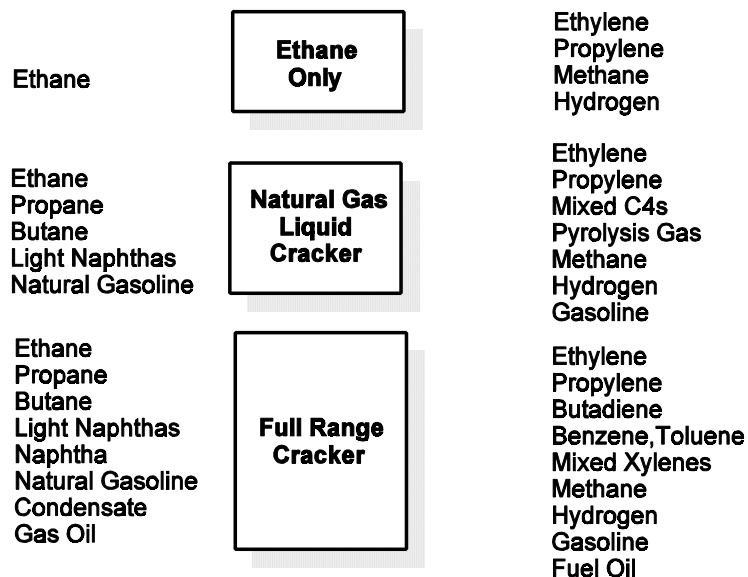


Figure 2-3. Ethylene Manufacture (Orica 1999, HP 1999)

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



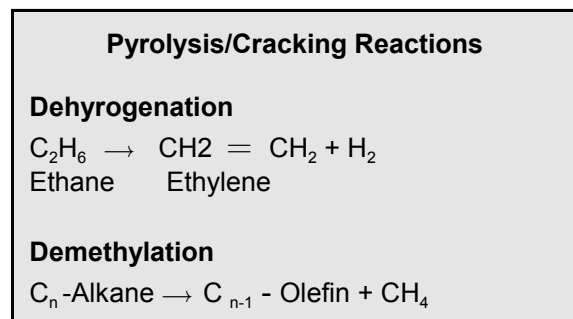
**Figure 2-4. Feedstocks and Associated Products from Pyrolysis**

of about 1400°F- 1600°F (760°C-870°C). 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.

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 desiccant (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.

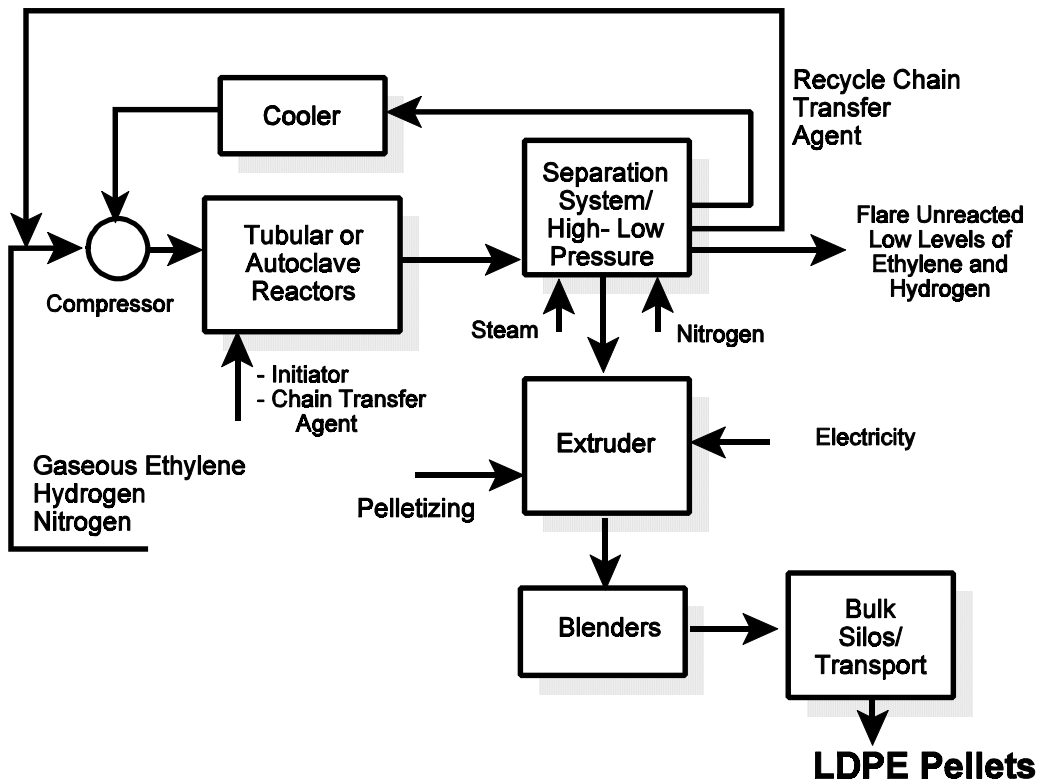


Figure 2-5. High Pressure Manufacture of LDPE (Orica 1999, HP 1999, HP 1997d)

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

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<sup>1</sup> distribution and content, and tacticity (structural organization). With these controlled structures, extremely uniform homo- or copolymers 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.

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<sup>1</sup> 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.

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°C 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.

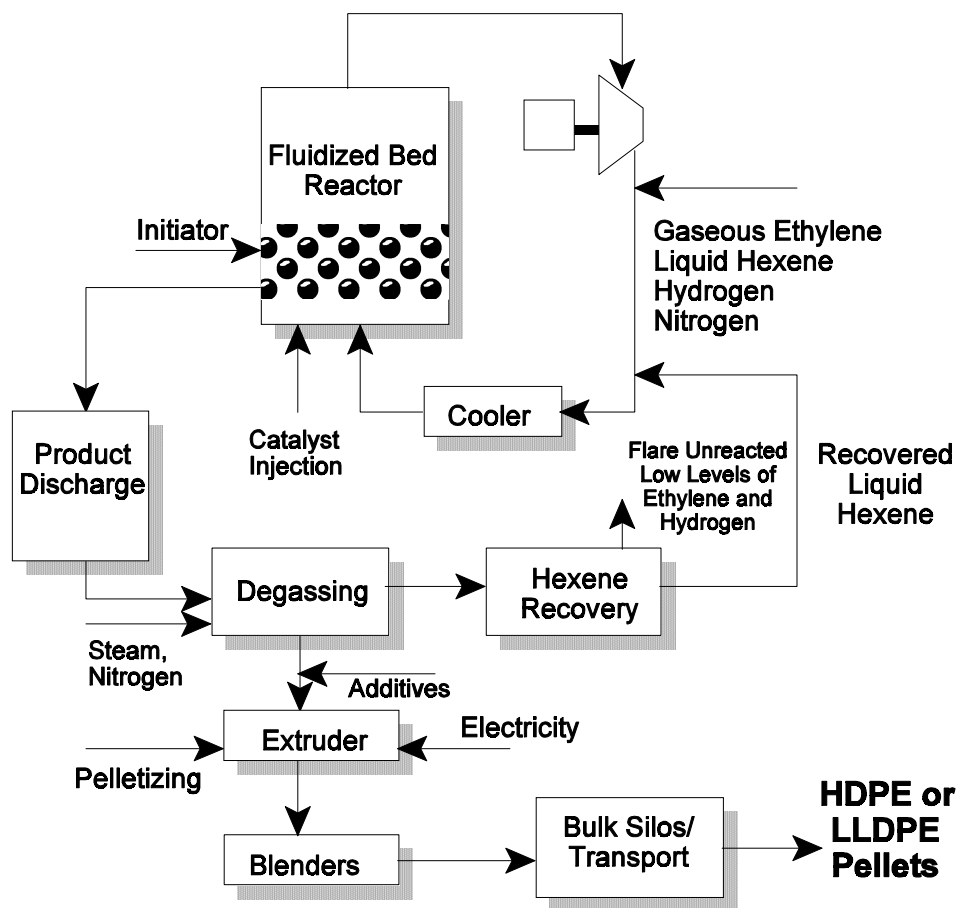
Large stirred autoclave reactors have much larger internal diameters (up to 2 feet), with the outer diameter three times that size. Residence time can range from 30 seconds to 2 minutes, and reactions may be carried out in a zoned vessel to modify the molecular structure.

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**:

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



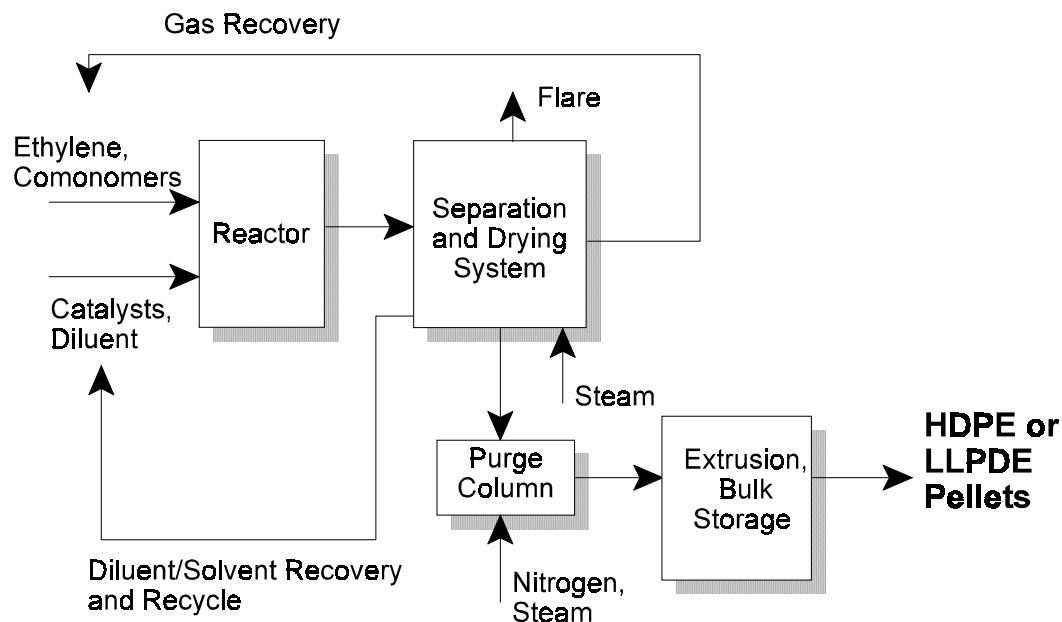


**Figure 2-6. Low Pressure Manufacture of HDPE or LLDPE:  
Gas Phase Fluidized Bed Polymerization (HP 1999, HP 1997d, Orica 1999)**

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

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 212°F (100°C). 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 stabilization 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

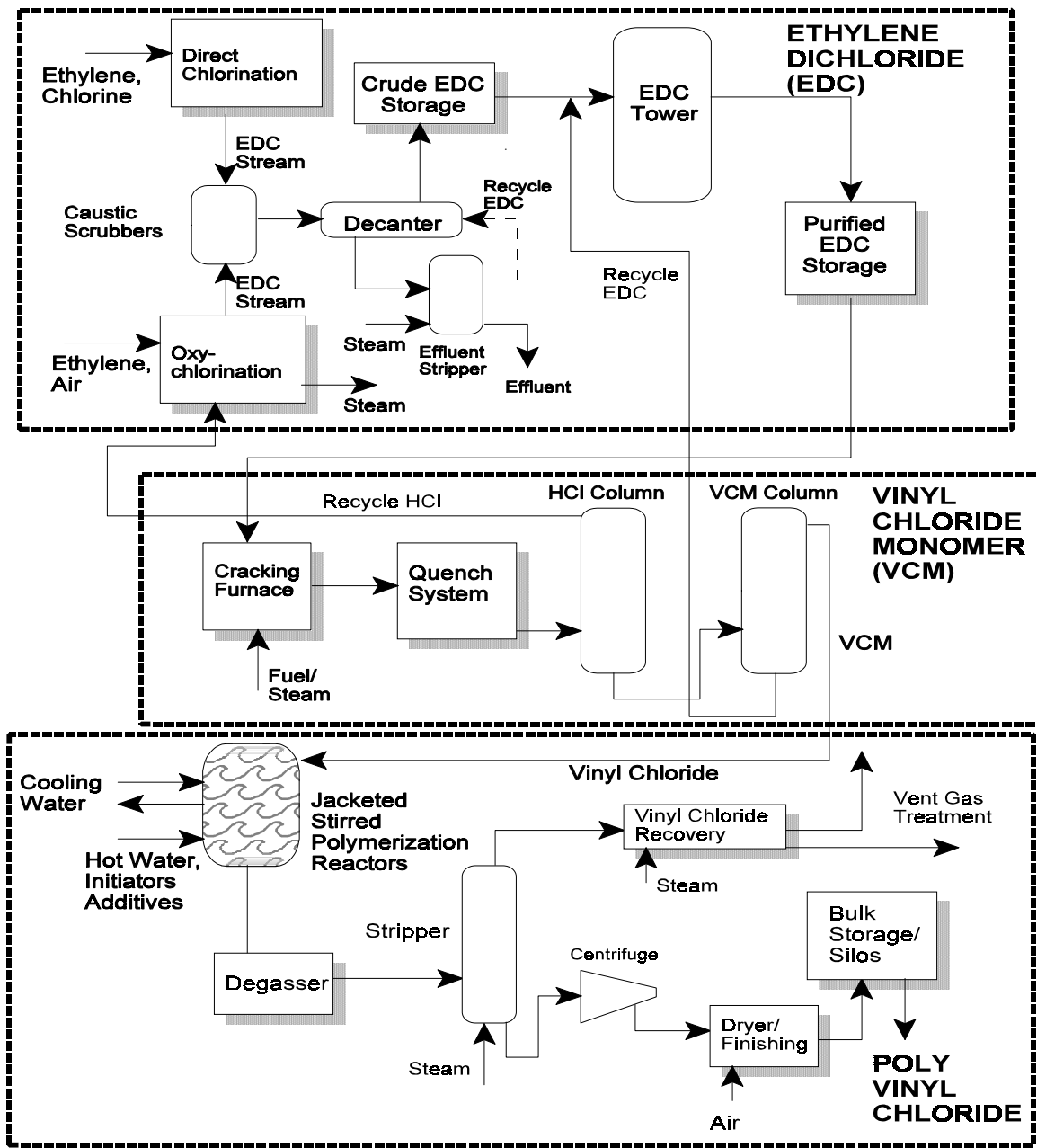


Figure 2-8. Ethylene Dichloride and Poly Vinyl Chloride Manufacture  
(ANL 1980, EPA 1991, Orica 1999, HP 1999)

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 $\Delta H_c$ : 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 160°F (70°C) 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<sup>2</sup> 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 alkalis 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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<sup>2</sup> The epoxy group contains -C-C- triangulated with oxygen (O).

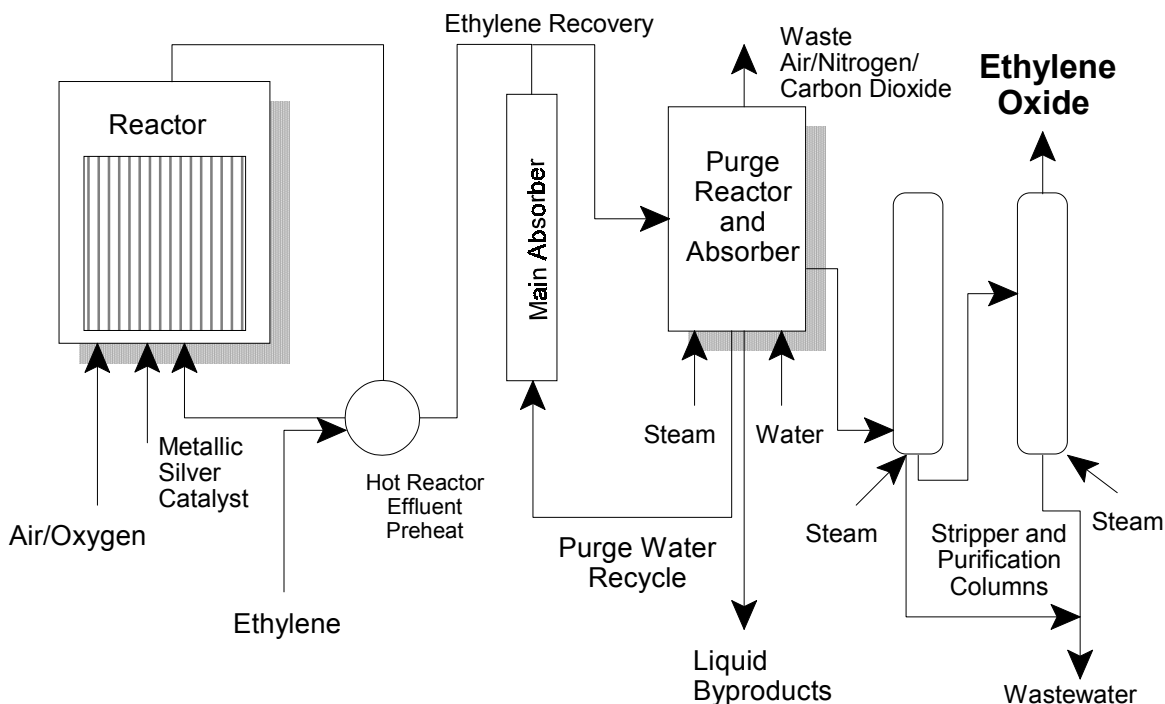


Figure 2-9. Ethylene Oxide Manufacture (ANL 1980, Chenier 1992, HP 1999)

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

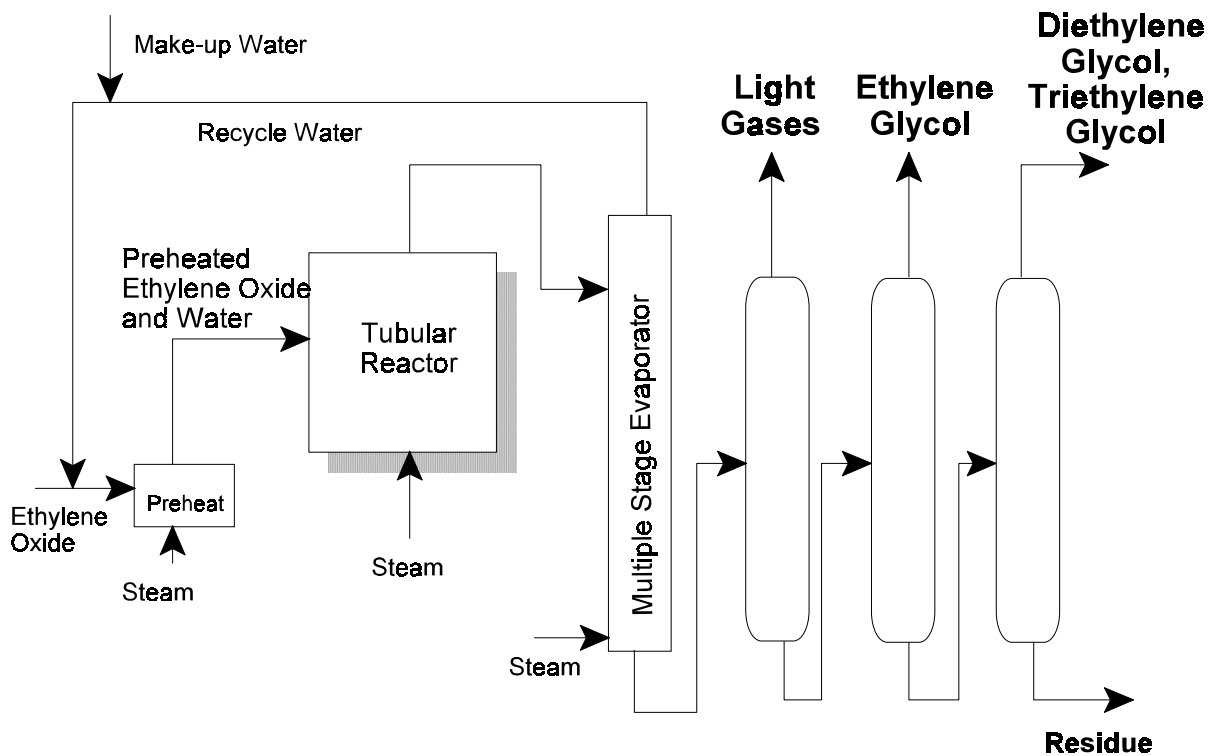
### All Ethylene Oxide Is Made by Direct Oxidation

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 500-550°F (260°C-288°C) 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)

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

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 120°F-210°F (49°C-99°C). The non-catalytic process requires higher pressures (over 190 psi) and temperatures of 300-390°F (149°C-199°C). 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***

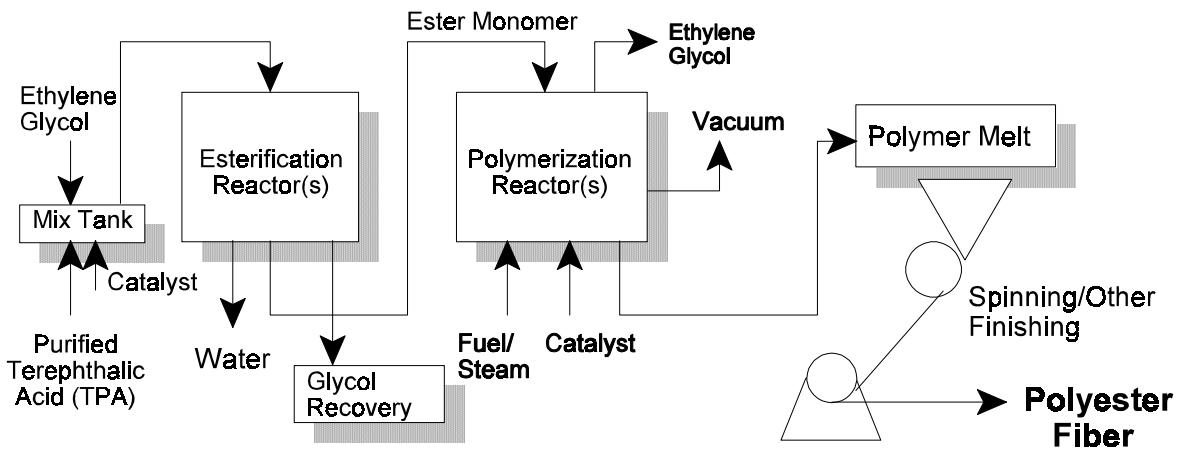
The term polyester is used to describe any polymer with an ester group present in the chain. The most commercially important polyester is polyethylene terephthalate (PET), and is commonly known by trademarked products such as Dacron®, Terelene®, Fortrel® fibers and Mylar® film. Polyester is a thermoplastic (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 bis-hydroxyethyl 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: 390°F-400°F (199°C to 204°C) and 30-150 psi. The liquid product, termed prepolymer, is purified by filtration before entering the polymerizer.





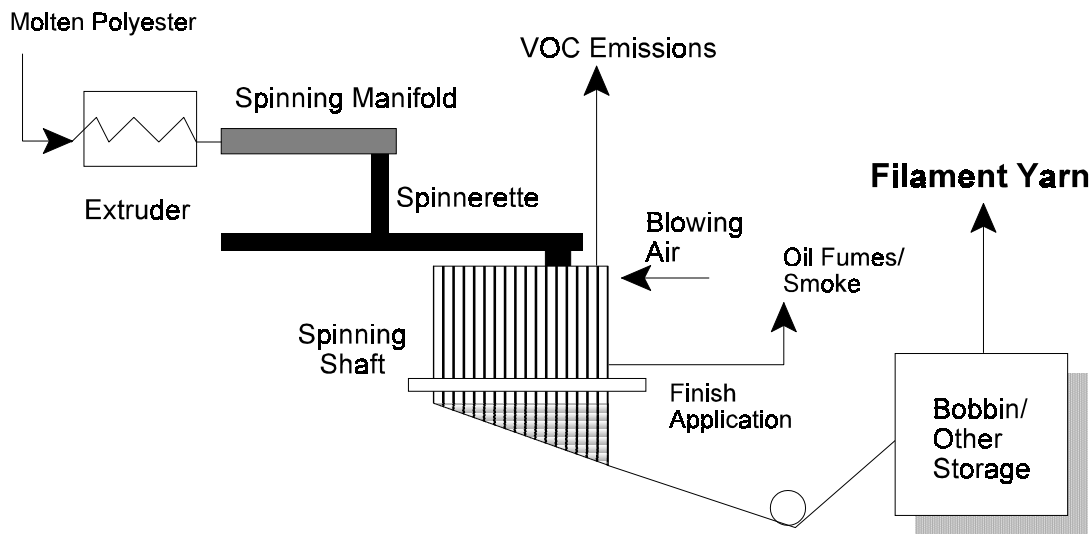
**Figure 2-11. Polyester Manufacture Using TPA (ANL 1980, Chenier 1992)**

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

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 (500°F-570°F), (260°C-299°C) 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 520°F (270°C).



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

<b>Key Energy and Environmental Facts - Polyester Melt Spinning</b>			
<b>Energy</b>	<b>Emissions</b>	<b>Effluents</b>	<b>Wastes or Byproducts</b>
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 spinnerette, 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

<u>Inputs:</u>	<u>Outputs:</u>
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

<u>Inputs:</u>	<u>Outputs:</u>
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

<u>Inputs:</u>	<u>Outputs:</u>
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

<u>Inputs:</u>	<u>Output:</u>
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

<u>Inputs:</u>	<u>Outputs:</u>
Ethylene	Ethylene Oxide
Air/Oxygen	Liquid Byproducts
Metallic Silver Catalyst	Waste Air/Nitrogen
Cooling Water	Waste CO <sub>2</sub>
Fuel/Steam	Wastewater
Electricity	

### Ethylene Glycol

<u>Inputs:</u>	<u>Outputs:</u>
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

<u>Inputs:</u>	<u>Outputs:</u>
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 ( $\Delta H_c$ ). 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

<b>Table 2-1. Estimated Energy Use in Ethylene Manufacture- 1997</b>				
<b>Energy</b>	<b>Specific Energy<sup>e</sup> (Btu/lb)</b>	<b>Average Specific Energy (Btu/lb)</b>	<b>Total Energy Use<sup>f</sup> (10<sup>12</sup> Btu/lb)</b>	<b>Estimated Chemical Industry Use<sup>g</sup> (10<sup>12</sup> Btu/lb)</b>
<b>Net Electricity<sup>a</sup></b>	270 - 540	405	19.6	9.8
<b>Energy for Steam/Process Heat<sup>f</sup></b>				
<b>Fuel Oil and LPG<sup>b</sup></b>	154 - 308	231	11.2	5.6
<b>Natural Gas</b>	3,954 - 7,907	5,931	287.0	143.5
<b>Coal and Coke</b>	514 - 1,027	770	37.3	18.6
<b>Other<sup>c</sup></b>	514 - 1,027	770	37.3	18.6
<b>NET PROCESS ENERGY</b>	<b>5,405 - 10,809</b>	<b>8,107</b>	<b>392.4</b>	<b>196.2</b>
<b>Electricity Losses</b>	561 - 1,121	841	40.7	20.4
<b>Energy Export</b>	(3,927 - 8,215)	(6,071)	(293.8)	(146.9)
<b>TOTAL PROCESS ENERGY</b>	<b>2,039 - 3,715</b>	<b>2,877</b>	<b>139.3</b>	<b>69.6</b>
<b>Heat of Feedstock (<math>\Delta H_c</math>)<sup>d</sup></b>	31,414	31,414	1,520.4	760.2
<b>TOTAL PRIMARY ENERGY</b>	<b>33,453 - 35,129</b>	<b>34,291</b>	<b>1,659.7</b>	<b>829.8</b>
<b>Feedstock Process Energy</b>	329.00	329	15.9	8.0
<b>TOTAL ENERGY EMBODIED IN ETHYLENE MFG</b>	<b>33,782 - 35,458</b>	<b>34,620</b>	<b>1,675.6</b>	<b>837.8</b>

- a Does not include 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

<b>Table 2-2. Estimated Energy Use in Polyethylene Manufacture - 1997</b>			
<b>Energy</b>	<b>Specific Energy <sup>f</sup> (Btu/lb)</b>	<b>Average Specific Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>g</sup> (10<sup>12</sup> Btu)</b>
<b>Electricity<sup>a</sup></b>	473 - 1,278	876	23.6
<b>Energy for Steam/Process Heat <sup>f</sup></b>			
<b>Fuel Oil and LPG<sup>b</sup></b>	5 - 13	9	0.3
<b>Natural Gas</b>	127 - 339	233	6.3
<b>Coal and Coke</b>	17 - 44	30	0.8
<b>Other<sup>c</sup></b>	17 - 44	30	0.8
<b>NET PROCESS ENERGY</b>	<b>638 - 1,718</b>	<b>1,178</b>	<b>31.8</b>
<b>Electricity Losses</b>	982 - 2,654	1,818	49.1
<b>Energy Export</b>	0	0	0.0
<b>TOTAL PROCESS ENERGY</b>	<b>1,620</b>	<b>2,996</b>	<b>80.9</b>
<b>Heat of Feedstock (<math>\Delta H_c</math>) <sup>d</sup></b>	21,625	21,625	583.9
<b>TOTAL PRIMARY ENERGY</b>	<b>23,245 - 25,997</b>	<b>24,621</b>	<b>664.8</b>
<b>Feedstock Process Energy<sup>e</sup></b>	8,649	8,649	233.5
<b>TOTAL ENERGY EMBODIED IN POLYETHYLENE MFG</b>	<b>31,894 - 34,646</b>	<b>33,270</b>	<b>898.3</b>

- a Does not include 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) by 1997 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.

<b>Table 2-3. Estimated Energy Use in Ethylene Dichloride Manufacture - 1997</b>		
<b>Energy</b>	<b>Average Specific <sup>f</sup> Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>g</sup> (10<sup>12</sup> Btu)</b>
<b>Electricity<sup>a</sup></b>	341	6.9
<b>Energy for Steam/Process Heat <sup>f</sup></b>		
<b>Fuel Oil and LPG<sup>b</sup></b>	92	1.9
<b>Natural Gas</b>	2,363	47.7
<b>Coal and Coke</b>	307	6.2
<b>Other<sup>c</sup></b>	307	6.2
<b>NET PROCESS ENERGY</b>	<b>3,140</b>	<b>68.9</b>
<b>Electricity Losses</b>	708	14.3
<b>Energy Export</b>	0	0.0
<b>TOTAL PROCESS ENERGY</b>	<b>4,118</b>	<b>83.2</b>
<b>Heat of Feedstock (<math>\Delta H_c</math>) <sup>d</sup></b>	9,948	201.0
<b>TOTAL PRIMARY ENERGY</b>	<b>14,066</b>	<b>284.1</b>
<b>Feedstock Process Energy<sup>e</sup></b>	72,066	145.6
<b>TOTAL ENERGY EMBODIED IN ETHYLENE DICHLORIDE MFG</b>	<b>21,272</b>	<b>429.7</b>

- a Does not include 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) by 1997 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 remove nitrogen, which adds to energy costs and utility requirements. Most of the steam

<b>Table 2-4. Estimated Energy Use in Poly Vinyl Chloride Manufacture - 1997</b>		
<b>Energy</b>	<b>Average Specific <sup>f</sup> Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>g</sup> (10<sup>12</sup> Btu)</b>
Electricity <sup>a</sup>	256	3.6
<b>Energy for Steam/Process Heat <sup>f</sup></b>		
Fuel Oil and LPG <sup>b</sup>	30	0.4
Natural Gas	762	10.8
Coal and Coke	99	1.4
Other <sup>c</sup>	99	1.4
<b>NET PROCESS ENERGY</b>	<b>1,246</b>	<b>17.6</b>
Electricity Losses	532	7.5
Energy Export	0	0.0
<b>TOTAL PROCESS ENERGY</b>	<b>1,778</b>	<b>25.1</b>
Heat of Feedstock ( $\Delta H_c$ ) <sup>d</sup>	10,147	143.1
<b>TOTAL PRIMARY ENERGY</b>	<b>11,925</b>	<b>168.1</b>
Feedstock Process Energy <sup>e</sup>	7,350	103.6
<b>TOTAL ENERGY EMBODIED IN POLY VINYL CHLORIDE MFG</b>	<b>19,275</b>	<b>271.8</b>

- a Does not include 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) by 1997 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



<b>Table 2-5. Estimated Energy Use in Ethylene Oxide Manufacture - 1997</b>			
<b>Energy</b>	<b>Specific Energy <sup>f</sup> (Btu/lb)</b>	<b>Average Specific Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>g</sup> (10<sup>12</sup> Btu)</b>
<b>Electricity<sup>a</sup></b>	360 - 627	494	3.5
<b>Energy for Steam//Process Heat <sup>f</sup></b>			
<b>Fuel Oil and LPG<sup>b</sup></b>	27 - 46	37	0.3
<b>Natural Gas</b>	693 - 1,182	937	6.7
<b>Coal and Coke</b>	90 - 154	122	0.9
<b>Other<sup>c</sup></b>	90 - 154	122	0.9
<b>NET PROCESS ENERGY</b>	<b>1,260 - 2,162</b>	<b>1,711</b>	<b>12.2</b>
<b>Electricity Losses</b>	748 - 1,302	1,025	7.3
<b>Energy Export</b>	0	0	0.0
<b>TOTAL PROCESS ENERGY</b>	<b>2,008 - 3,464</b>	<b>2,736</b>	<b>19.4</b>
<b>Heat of Feedstock (<math>\Delta H_c</math>) <sup>d</sup></b>	19,463	19,463	138.2
<b>TOTAL PRIMARY ENERGY</b>	<b>21,471 - 22,927</b>	<b>22,199</b>	<b>157.6</b>
<b>Feedstock Process Energy<sup>e</sup></b>	8,891	8,891	63.1
<b>TOTAL ENERGY EMBODIED IN ETHYLENE OXIDE MFG</b>	<b>30,362 - 31,818</b>	<b>31,090</b>	<b>220.7</b>

- a Does not include 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) by 1997 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).

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

- a Does not include 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) by 1997 production values (5.6 billion lbs) (CMA 1998).

<b>Table 2-7. Estimated Energy Use in Polyester Manufacture - 1997</b>			
<b>Energy</b>	<b>Specific Energy <sup>f</sup> (Btu/lb)</b>	<b>Average Specific Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>g</sup> (10<sup>12</sup> Btu)</b>
<b>Electricity<sup>a</sup></b>	1,022 - 1,244	1,133	6.7
<b>Energy for Steam/Process Heat <sup>f</sup></b>			
<b>Fuel Oil and LPG<sup>b</sup></b>	298 - 362	330	2.0
<b>Natural Gas</b>	7,636 - 9,259	8,466	50.0
<b>Coal and Coke</b>	992 - 1,207	1,099	6.5
<b>Other<sup>c</sup></b>	992 - 1,207	1,099	6.5
<b>NET PROCESS ENERGY</b>	<b>10,939 - 13,316</b>	<b>12,128</b>	<b>71.6</b>
<b>Electricity Losses</b>	21,222 - 2,583	2,353	13.9
<b>Energy Export</b>	0	0	0.0
<b>TOTAL PROCESS ENERGY</b>	<b>13,061 - 15,899</b>	<b>14,480</b>	<b>85.4</b>
<b>Heat of Feedstock (<math>\Delta H_c</math>) <sup>d</sup></b>	22,448	22,448	132.4
<b>TOTAL PRIMARY ENERGY</b>	<b>35,509 - 38,347</b>	<b>36,928</b>	<b>217.9</b>
<b>Feedstock Process Energy<sup>e</sup></b>	4,863	4,863	28.7
<b>TOTAL ENERGY EMBODIED IN POLYESTER MFG</b>	<b>40,327 - 43,210</b>	<b>41,791</b>	<b>246.6</b>

- 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) by 1997 production values (5.9 billion lbs) (SPI 1998).

<b>Table 2-8 Estimated Energy Use in Polyester Fiber Melt Spinning and Drawing - 1997</b>		
<b>Energy</b>	<b>Average Specific <sup>c</sup> Energy (Btu/lb)</b>	<b>Chemical Industry Energy Use <sup>d</sup> (10<sup>12</sup> Btu)</b>
<b>Electricity<sup>a</sup></b>	826	4.9
<b>Steam<sup>b</sup></b>	1,776	10.6
<b>NET PROCESS ENERGY</b>	<b>2,602</b>	<b>15.5</b>
<b>Electricity Losses</b>	1,715	10.1
<b>TOTAL PRIMARY ENERGY</b>	<b>4,317</b>	<b>25.6</b>

- 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) by 1997 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.

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.

<b>Table 2-10 Air Emission Factors for Polyester Manufacture</b>				
<b>Emission Stream</b>	<b>Nonmethane VOCs<sup>a</sup> (grams/kg)</b>		<b>Particulate Emissions (grams/kg)</b>	
	<b>DMT Process</b>	<b>TPA Process</b>	<b>DMT Process</b>	<b>TPA Process</b>
<b>Raw Material Storage</b>	0.1	0.1	0.165	ND
<b>Mix Tanks</b>	N	N	ND	ND
<b>Methanol Recovery System</b>	0.3	NA	ND	NA
<b>Recovered Methanol Storage<sup>b</sup></b>	0.09	NA	ND	NA
<b>Esterification<sup>c</sup></b>	NA	0.04	ND	ND
<b>Prepolymerization Vacuum System</b>	0.009	0.009	ND	ND
<b>Polymerization Reactor Vacuum System</b>	0.005	0.005	ND	ND
<b>Cooling Tower<sup>d</sup></b>	0.2 3.4	0.2 3.4	ND	ND
<b>Ethylene Glycol Process Tanks</b>	0.0009	0.0009	ND	ND
<b>Ethylene Glycol Recovery Condenser</b>	0.01	NA	ND	NA
<b>Ethylene Glycol Recovery Vacuum System</b>	0.0005	0.0005	ND	ND
<b>Product Storage<sup>e</sup></b>	ND	ND	0.0003	0.0003
<b>Sludge Storage and Loading</b>	0.73	0.36	0.17	NED
<b>TOTAL PLANT<sup>d</sup></b>	3.9	3.6		

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.

<b>Table 2-11. Air Emission Factors for Melt Spinning of Polyester (lbs/1000 lbs fiber spun, including waste fiber)</b>		
<b>Type of Fiber</b>	<b>Nonmethane Volatile Organics</b>	<b>Particulates</b>
Staple	0.6 <sup>a</sup>	252 <sup>c</sup>
Yarn <sup>b</sup>	0.05 <sup>a</sup>	0.03 <sup>d</sup>

Source: EPA 1990.

- a Emitted in aerosol form, and uncontrolled
- b Factors for high viscosity industrial and tire yarn 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<sub>x</sub>, NO<sub>x</sub>, 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**

<b>Waste Classification</b>	<b>Description</b>	<b>Hazardous Constituents</b>
<b>K018</b>	Heavy ends from the fractionation column in ethyl chloride	1,2-dichloroethane, trichloroethylene, hexachlorobutadiene, hexachlorobenzene
<b>K019</b>	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
<b>K020</b>	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.

