ETHYLENE

1. Introduction

Ethylene [74-85-1] (ethene), $H_2C{=}CH_2$, is the largest volume building block for many petrochemicals. This olefin is used to produce many end products such as plastics, resins, fibers, etc. Ethylene is produced mainly from petroleum-based feedstocks by thermal cracking, although alternative methods are also gaining importance.

2. Physical Properties

Ethylene is the lightest olefin. It is a colorless, flammable gas with a slightly sweet odor. Physical and thermodynamic properties are given in many references (1–7), and are briefly summarized in Tables 1–3.

3. Chemical Properties

3.1. Structure. Ethylene is a planar molecule with a carbon–carbon bond distance of 0.134 nm, which is shorter than the C–C bond length of 0.153 nm found in ethane. The C–H bond distance is 0.110 nm, and the bond angles are $<$HCH $= 117.2^\circ$ and $<$HCC $= 121.4^\circ$ consistent with the sp^2 hybridized state.

3.2. Reactivity. Ethylene is a very reactive intermediate, and hence is involved in many chemical reactions. The ethylene double bond reacts readily to form saturated hydrocarbons, their derivatives, or polymers. Electrons in the π-bond are less tightly held and more easily polarized than electrons in a sigma bond. The carbon-carbon double-bond energy is 611 kJ/mol (146 kcal/mol), which is less than twice the C–C bond dissociation energy of 368 kJ/mol (88 kcal/mol) found in ethane. The C–H bond dissociation energy is 452 kJ/mol (108 kcal/mol), and approximate acidity as measured by K_a is 10^{-45}. Therefore, ethylene reacts with electrophilic reagents like strong acids (H^+), halogens, and oxidizing agents, but not with nucleophilic reagents such as Grignard reagents and bases. Some of the reactions have commercial significance and others have only academic interest. For fundamental mechanisms of these reactions see References 8 and 9.

The principal reactions with commercial significance include polymerization, oxidation, and addition including halogenation, alkylation, oligomerization, hydration, and hydroformylation.

3.3. Polymerization. Very high purity ethylene ($>$99.9% plus) is polymerized under specific conditions of temperature and pressure in the presence of an initiator or catalyst.

$$n\,CH_2{=}CH_2 \longrightarrow -\!\!\left(CH_2-CH_2\right)\!\!-_n$$

This is an exothermic reaction, and both homogeneous (radical or cationic) and heterogeneous (solid catalyst) initiators are used. The products range in

Table 1. **Physical Properties of Ethylene**

Property	Value
mol wt	28.0536
triple point	
temperature, °C	−169.164
pressure, kPa[a]	0.12252
latent heat of fusion, kJ/mol[b]	3.353
normal freezing point	
temperature, °C	−169.15
latent latent heat of fusion, kJ/mol[b]	3.353
normal boiling point	
temperature °C	−103.71
latent heat of vaporization, kJ/mol[b]	13.548
density of liquid	
mol/L	20.27
d_4^{-104}	0.566
specific heat of liquid, J/(mol · K)[b]	67.4
viscosity of the liquid, mPa · s (= cP)	0.161
surface tension of the liquid, mN/m (= dyn/cm)	16.4
specific heat of ideal gas at 25°C, J/(mol · K)[b]	42.84
critical point	
temperature, °C	9.194
pressure, kPa[a]	5040.8
density, mol/L	7.635
compressibility factor	0.2812
gross heat of combustion of gas at 25°C, MJ/mol[b]	1.411
limits of flammability at atmospheric pressure and 25°C	
lower limit in air, mol%	2.7
upper limit in air, mol%	36.0
autoignition temperature in air at atmospheric pressure, °C	490.0
Pitzer's accentric factor	0.278
standard enthalpy of formation at 25°C, kJ/mol[b]	52.3
standard Gibbs energy of formation at 25°C for ideal gas at atmospheric pressure, kJ/mol[b]	68.26
solubility in water at 0°C and 101 kPa[a], mL/mL H_2O	0.226
speed of sound at 0°C and 409.681 kPa[a], m/s	224.979
standard entropy of formation, J/(mol · K)[b]	219.28
standard heat capacity, J/(mol · K)[b]	42.86

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

molecular weight from below 1000 to a few million (see OLEFIN POLYMERS). Reaction mechanisms and reactor designs have been extensively discussed (10–12).

There are four types of reaction systems for the production of polyethylene of commercial importance:

1. High pressure (60–350 MPa) free-radical polymerization using oxygen, peroxide, or other strong oxidizers as initiators at temperatures of up to 350°C to produce low density polyethylene (LDPE), a highly branched polymer, with densities from 0.91 to 0.94 g/cm^3.
2. Low pressure (0.1 to 20 MPa) and temperatures of 50 to 300°C using heterogeneous catalysts such as molybdenum oxide or chromium oxide

Table 2. **Thermodynamic and Transport Properties of Gaseous Ethylene**

Temperature, °C	Specific volume, L/kg	Viscosity, mPa · s (=cP)	Thermal cond, $\frac{\text{MW}}{(\text{m} \cdot \text{K})}$	Heat capacity, C_p, J/(mol · K)[a]
		Pressure = 100 *kPa*[b]		
0°C	803.50	0.00941		40.90
25°C	878.63	0.01027	20.3	43.11
50°C	953.52	0.01108	23.3	45.48
75°C	1028.20	0.01180	26.7	47.95
100°C	1102.90	0.01260	30.2	50.43
		Pressure = 5000 *kPa*[b]		
25°C	11.10	0.01404	31.5	92.8
50°C	14.33	0.01310	30.3	67.2
75°C	16.82	0.01314	31.7	61.5
100°C	19.02	0.01395	34.9	60.0

[a] To convert J to cal, divide by 4.184.
[b] To convert kPa to psi, multiply by 0.145.

supported on inorganic carriers to produce high density polyethylene (HDPE), which is more linear in nature, with densities of 0.94 to 0.97 g/cm^3.

3. Low pressure polymerization via ionic catalysts, using Ziegler catalysts (aluminum alkyls and titanium halides).
4. Low pressure polymerization with Ziegler catalysts supported on inorganic carriers.

A more recent development in ethylene polymerization is the simplified low pressure LDPE process. The pressure range is 0.7–2.1 MPa with temperatures less than 100°C. The reaction takes place in the gas phase instead of liquid phase as in the conventional LDPE technology. These new technologies demand ultra high purity ethylene.

In order to improve the physical properties of HDPE and LDPE, copolymers of ethylene and small amounts of other monomers such as higher olefins, ethyl

Table 3. **Thermodynamic and Transport Properties of Liquid Ethylene**

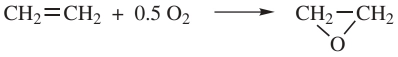
Temperature, °C	Vapor pressure, kPa[a]	Density, mol/L	Viscosity, mPa·s (=cP)	Thermal conductivity, W/(m·K)	Heat capacities C_p, J/(mol·K)[b]	Heat capacities C_v, J/(mol·K)[b]
−165°C	0.249	23.16	0.600	0.252		44.75
−150°C	2.040	22.47	0.387	0.237	70.66	45.55
−125°C	23.76	21.29	0.229	0.214	66.76	39.54
−100°C	126.0	20.05	0.160	0.191	67.44	37.55
−75°C	422.4	18.70		0.166	70.68	37.13
−50°C	1063	17.15		0.140	77.15	37.39
−25°C	2219	15.20		0.113	92.57	38.44
0°C	4100	12.20		0.080	185.00	41.82

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert J to cal, divide by 4.184.

acrylate, maleic anhydride, vinyl acetate, or acrylic acid are added to the polyethylene. For example, linear low density polyethylene (LLDPE), although linear, has a significant number of branches introduced by using comonomers such as 1-butene or 1-octene. The linearity provides strength, whereas branching provides toughness.

Ethylene–propylene elastomers exhibit a high resistance to oxygen, ozone, and heat, and are used in motor parts because of their excellent low temperature flexibility. Two types of elastomers that are manufactured are copolymers (EPR) formed by polymerizing ethylene and propylene, and terpolymers (EPDM) formed by polymerizing ethylene, propylene, and a small amount of a termonomer like a diene or triene, eg, 1,4-hexadiene (see ELASTOMERS, SYNTHETIC–ETHYLENE–PROPYLENE–DIENE RUBBER).

3.4. Oxidation. Ethylene oxide (qv) is produced by oxidizing ethylene.



The reaction is carried out over a supported metallic silver catalyst at 250–300°C and 1–2 MPa (10–20 bar). A few parts per million (ppm) of 1,2-dichloroethane are added to the ethylene to inhibit further oxidation to carbon dioxide and water. This results in chlorine generation, which deactivates the surface of the catalyst. Chem Systems of the United States has developed a process that produces ethylene glycol monoacetate as an intermediate, which on thermal decomposition yields ethylene oxide [75-21-8].

About 60% of the ethylene oxide produced is converted to ethylene glycol by reaction of ethylene oxide in the presence of excess water and an acidic catalyst at 50–70°C. This is followed by hydrolysis at relatively high temperatures (140–230°C) and 2–4 MPa (20–40 bar) (see GLYCOLS, ETHYLENE GLYCOL). When the water concentration is lowered, poly(ethylene glycol) is obtained.

Acetaldehyde [75-07-0] can be obtained by the Wacker process, in which a homogeneous $CuCl_2$–$PdCl_2$ system is used for the oxidation.

$$CH_2{=}CH_2 + 0.5\ O_2 \longrightarrow CH_3CHO$$

The reaction is carried out in a bubble column at 120–130°C and 0.3 MPa (3 bar). Palladium chloride is reduced to palladium during the reaction, and then is reoxidized by cupric chloride. Oxygen converts the reduced cuprous chloride to cupric chloride.

Vinyl acetate [108-05-4] is obtained by vapor-phase oxidation of ethylene with acetic acid. Acetic acid is obtained by oxidation of acetaldehyde.

$$CH_2{=}CH_2 + CH_3COOH + 0.5\ O_2 \longrightarrow CH_2{=}CH{-}OOCCH_3 + H_2O$$

This process employs a palladium on carbon, alumina, or silica–alumina catalyst at 175–200°C and 0.4 to 1.0 MPa (58–145 psi).

3.5. Addition.

Addition reactions of ethylene have considerable importance and lead to the production of ethylene dichloride, ethylene dibromide, and ethyl chloride by halogenation–hydrohalogenation; ethylbenzene, ethyltoluene, and aluminum alkyls by alkylation; α-olefins by oligomerization; ethanol by hydration; and propionaldehyde by hydroformylation.

Halogenation–Hydrohalogenation. The most important intermediate is ethylene dichloride [107-06-2] (EDC) which is produced from ethylene either by direct chlorination or by oxychlorination. Direct chlorination is carried out in the liquid or vapor phase over catalysts of iron, aluminum, copper, or antimony chlorides, and at conditions of 60°C. Oxychlorination is carried out in a fixed or fluidized bed at 220°C with a suitable solid chloride catalyst.

$$CH_2{=\!=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl$$

$$CH_2{=\!=}CH_2 + O_2 + 4\,HCl \longrightarrow 2\,ClCH_2CH_2Cl + 2\,H_2O$$

By similar methods, ethylene dibromide [106-93-4] can also be obtained. This compound is used in gasoline as an antiknocking additive.

The leading derivative of ethylene dichloride is vinyl chloride [75-01-4] monomer (VCM), which is subsequently used to produce poly(vinyl chloride) and chlorinated hydrocarbons. Vinyl chloride is obtained by dehydrochlorination of ethylene dichloride in the gas phase (500–600°C and 2.5–3.5 MPa).

$$ClCH_2CH_2Cl \longrightarrow CH_2{=\!=}CHCl + HCl$$

Trichloro- and tetrachloroethylene are important organic solvents. These are produced by further chlorination of 1,2-dichloroethylene in the gas phase with simultaneous dehydrochlorination in the presence of a suitable chloride catalyst (see CHLOROCARBONS AND CHLOROHYDROCARBONS).

Ethyl chloride [25-00-3] is obtained by reaction of ethylene with hydrogen chloride in the presence of $AlCl_3$ or $FeCl_3$ at 300–500 kPa (3–5 bar) and 30–90°C (liquid phase), or at 130–250°C (vapor phase).

$$CH_2{=\!=}CH_2 + HCl \longrightarrow CH_3CH_2Cl$$

Alkylation. Ethylbenzene [100-41-4], the precursor of styrene, is produced from benzene and ethylene. The ethylation of benzene is conducted either in the liquid phase in the presence of a Friedel-Crafts catalyst ($AlCl_3$, BF_3, $FeCl_3$) or in the vapor phase with a suitable catalyst. The Monsanto/Lummus process uses an aluminum chloride catalyst that yields more than 99% ethylbenzene (13). More recently, Lummus and Union Oil commercialized a zeolite catalyst process for liquid-phase alkylation (14). Badger and Mobil also have a vapor-phase alkylation process using zeolite catalysts (15). Almost all ethylbenzene produced is used for the manufacture of styrene [100-42-5], which is obtained by dehydrogenation in the presence of a suitable catalyst at 550–640°C and relatively low pressure, <0.1 MPa (<1 atm).

Toluene also reacts with ethylene to produce *p*-ethyltoluene [622-96-8] or *p*-methylethylbenzene, which can be dehydrogenated to give *p*-methylstyrene.

The polymer (PMS), has a high glass-transition point and better flow properties, and has gained significant commercial importance in recent years.

Alkylation of aluminum with ethylene yields products that find application as initiators and starter compounds in the production of α-olefins and linear primary alcohols, as polymerization catalysts, and in the synthesis of some monomers like 1,4-hexadiene. Triethylaluminum [97-93-8], $Al(C_2H_5)_3$, is the most important of the ethylene-derived aluminum alkyls.

In the production of α-olefins, ethylene reacts with an aluminum alkyl at relatively low temperature to produce a higher alkylaluminum. This is then subjected to a displacement reaction with ethylene at high temperatures to yield a mixture of α-olefins and triethylaluminum. In an alternative process, both reactions are combined at high temperatures and pressures where triethylaluminum functions as a catalyst in the polymerization process.

Hydration. Ethanol [64-17-5] is manufactured from ethylene by direct catalytic hydration over a $H_3PO_4{-}SiO_2$ catalyst at process conditions of 300°C and 7.0 MPa (1015 psi). Diethyl ether is also formed as a by-product.

$$CH_2{=\!=}CH_2 + H_2O \longrightarrow C_2H_5OH$$

In another process, ethylene is absorbed in 90–98% sulfuric acid at 50–85°C and 1.0–1.4 MPa (145–200 psi) to give a mixture of ethyl sulfates. These can be hydrolyzed to ethanol and dilute sulfuric acid.

Hydroformylation. In hydroformylation, the oxo reaction, ethylene reacts with synthesis gas ($CO + H_2$) over a cobalt catalyst at 60–200°C and 4–35 MPa (39–345 atm) to form propionaldehyde [123-38-6] (see OXO PROCESS). This reaction is usually carried out in an organic liquid phase where inert diluents are used as liquids (16).

3.6. Other Reactions. Comprehensive discussions of the following reactions, which are primarily of academic interest, are provided in various references (10,17). Ethylene may be hydrogenated to ethane under a variety of conditions. For example, hydrogenation is feasible for systems utilizing finely divided platinum or palladium at room temperature and atmospheric pressure, or utilizing nickel at 150–300°C and elevated pressure. These reactions are mainly used in research work.

Acyl halides may also be added to ethylene in the presence of aluminum chloride to form halogenated ketones. At low temperatures, ethylene reacts with halogens to yield dihaloethanes. At high temperatures, trichloroethylene and perchloroethylene are formed. The most profitable route for chloroethylene is via ethylene dichloride (see CHLOROCARBONS AND CHLOROHYDROCARBONS).

4. Biological Properties

Ethylene is slightly more potent as an anesthetic than nitrous oxide, and the smell of ethylene causes choking. Diffusion through the alveolar membrane is sufficiently rapid for equilibrium to be established between the alveolar and the pulmonary capillary blood with a single exposure. Ethylene is held both in cells and in plasma in simple physical solution. The lipoid stroma of the red blood cells absorb ethylene, but it does not combine with hemoglobin. The concentration in the blood is 1.4 mg/mL when ethylene is used by itself for anesthesia. However, in the 1990s it is not used as an anesthetic agent. Ethylene is eliminated from the body unchanged, primarily by the lungs, and most elimination is complete within three minutes of administration.

The controlled ripening of various fruits and vegetables by ethylene is of considerable importance. Ethylene was identified as one of the volatiles emitted by ripening fruits as early as the 1930s, and its biological use had been mentioned as early as 1901. A few ppm of ethylene (<10 ppm) is often used for ripening bananas and other fruits. However, the ethylene concentration varies with the type of fruit and environmental conditions. Ethylene can also have adverse effects on plants. It causes the bleaching of green tissue, gives rise to foliar abscission, suppresses certain types of dormancy, and promotes cellular swelling. For further information on this subject, consult Reference 10.

5. Manufacture by Thermal Cracking

Although ethylene is produced by various methods as follows, only a few are commercially proven: thermal cracking of hydrocarbons, catalytic pyrolysis, membrane dehydrogenation of ethane, oxydehydrogenation of ethane, oxidative coupling of methane, methanol to ethylene, dehydration of ethanol, ethylene from coal, disproportionation of propylene, and ethylene as a by-product.

Thermal cracking of hydrocarbons is the principal route for the industrial production of ethylene. The chemistry and engineering of thermal cracking has been reviewed (17–19). In thermal cracking, valuable by-products including propylene, butadiene, and benzene are also produced. Commercially less valuable methane and fuel oil are also produced in significant proportions. An important parameter in the design of commercial thermal cracking furnaces is the selectivity to produce the desired products.

5.1. Mechanism.

The thermal cracking of hydrocarbons proceeds via a free-radical mechanism (20). Since that discovery, many reaction schemes have been proposed for various hydrocarbon feeds (21–24). Since radicals are neutral species with a short life, their concentrations under reaction conditions are extremely small. Therefore, the integration of continuity equations involving radical and molecular species requires special integration algorithms (25). An approximate method known as pseudo steady-state approximation has been used in chemical kinetics for many years (26,27). The errors associated with various approximations in predicting the product distribution have been given (28).

The free-radical mechanism involves initiation, propagation, and termination steps. During *initiation* two radicals are produced for every paraffin molecule.

$$C_2H_6 \longrightarrow 2\,CH_3^{\bullet}$$

Only a small fraction of reactant is involved in this step. When naphthenes are involved, diradicals are produced. For aromatics with side chains, $H^{\bullet}$ radicals are produced.

In *propagation* many types of reactions are involved including H abstraction, addition, radical decomposition, and radical isomerization.

In H abstraction, a hydrogen radical reacts with a molecule (primarily a paraffin) and produces a hydrogen molecule and a radical. In the same way, a methyl radical reacts to produce a radical and methane. Similar reactions with other radicals (ethyl and propyl) can also occur. In addition, some radicals like $H^\bullet$, $CH_3^\bullet$, etc, are added to olefins to form heavier radicals.

Radical decomposition is one of the most important types of reactions. In this case, a larger radical decomposes to an olefin and a smaller radical. Radicals usually decompose at the beta position of the radical center where the C−C bond is the weakest. In the case of naphthenes and aromatics this may not be the case, and C−H bond may be the weakest. Radical isomerization frequently occurs for large radicals, and explains to a large extent the observed product distribution.

Radical termination is the reverse of initiation.

5.2. Conversion. The terms severity or conversion are used to measure the extent of cracking. Conversion can easily be measured for a single component (C) feed and is defined as follows, where the quantities are measured in weight units.

$$\text{conversion} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}}$$

When a mixture is cracked, one or more components in the feed may also be formed as products. For example, in the cocracking of ethane and propane, ethane is formed as a product of propane cracking and propane is formed as a product of ethane cracking. Therefore, the “out” term in the above equation contains the contribution or formation from other feed components and hence does not represent true conversion. For simple mixtures, the product formation can be accounted for, and approximate true conversions can be calculated (29). For liquid feeds like naphtha, it is impractical if not impossible to calculate the true conversion. Based on measured feed components, one can calculate a weighted average conversion (X) (30):

$$X = \Sigma W_i X_i$$

where X_i is the conversion for the ith feed component, and W_i is the weighting factor (weight or mole fraction, usually).

As a practical method, designers have employed other methods such as n-pentane conversion as a key component, kinetic severity factor (31), or molecular collision parameter (32) to represent severity. Alternatively, molecular weight of the complete product distribution has been used to define conversion (X) for liquid feeds.

$$X = \frac{[(\text{MW}_f/\text{MW}_e) - 1]}{[(\text{MW}_f/24.5) - 1]}$$

In the equation, MW_f and MW_e are the molecular weight of the feed and of the dry (steam-free) effluent, respectively. Instead of molecular weight, hydrogen content in the C_5-plus product is also used.

Instead of conversion, some producers prefer to use other identifications of severity, including coil outlet temperature, propylene to methane ratio, propylene to ethylene ratio, or cracking severity index (33). Of course, all these definitions are somewhat dependent on feed properties, and most also depend on the operating conditions.

When simple liquids like naphtha are cracked, it may be possible to determine the feed components by gas chromatography combined with mass spectrometry (GC/MS) (30). However, when gas oil is cracked, complete analysis of the feed may not be possible. Therefore, some simple definitions are used to characterize the feed. When available, paraffins, olefins, naphthenes, and aromatics (PONA) content serves as a key property. When PONA is not available, the Bureau of Mines Correlation Index (BMCI) is used. Other properties like specific gravity, ASTM distillation, viscosity, refractive index. Conradson Carbon, and Bromine Number are also used to characterize the feed. In recent years even nuclear magnetic resonance spectroscopy has been used to characterize heavy feedstocks.

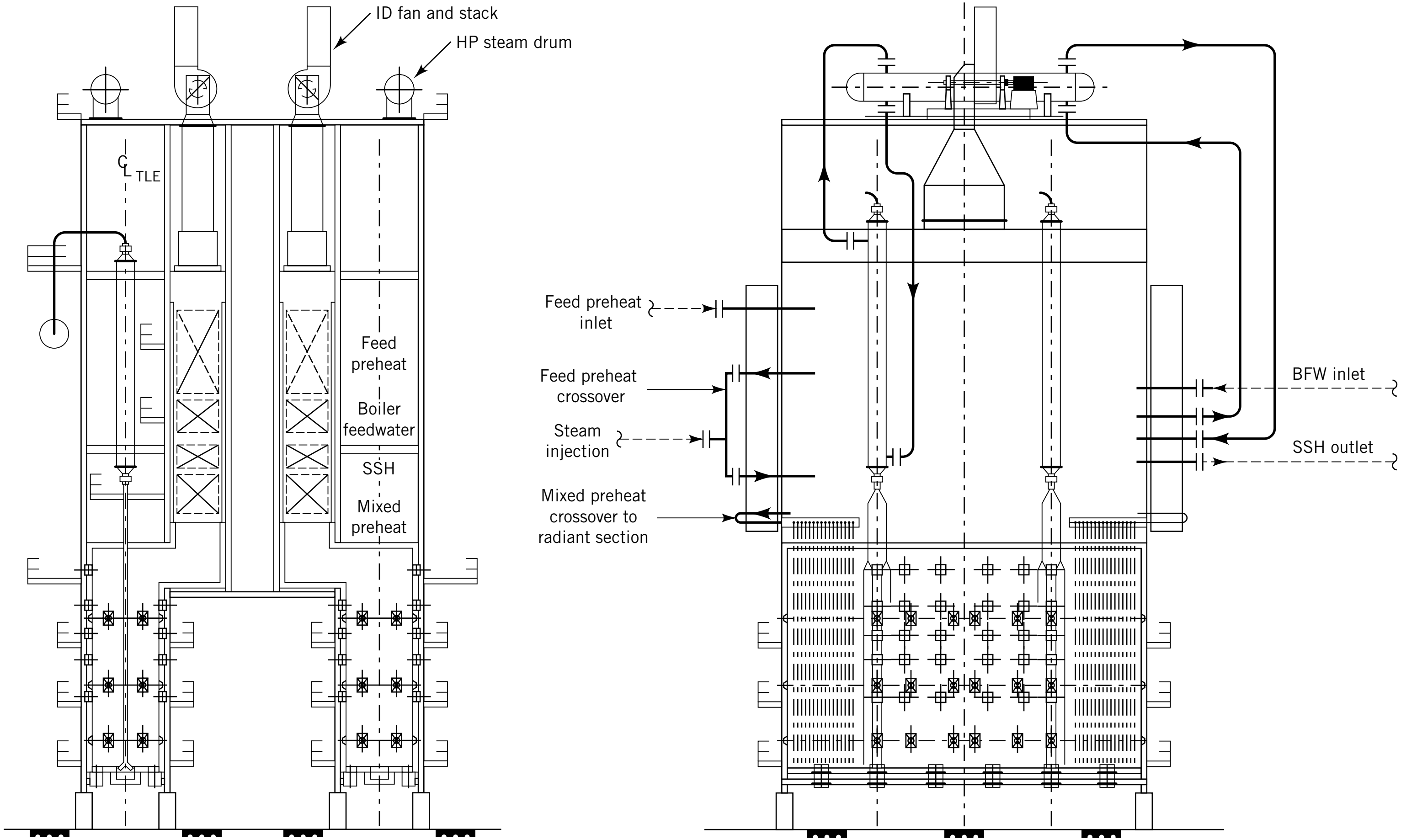
5.3. Industrial Furnaces.

Thermal cracking of hydrocarbons is accomplished in tubular reactors commonly known as cracking furnaces, crackers, cracking heaters, etc. Several engineering contractors including ABB Lummus Global, Stone and Webster, Kellogg-Braun & Root, Linde, and KTI offer cracking furnace technology. Usually two cracking furnaces share a common stack, and the height of the heater may vary from 30 to 50 m. Before the 1960s, the cracking tubes were arranged in horizontal rows in a radiant chamber leading to low ethylene capacity ($<20,000$ t/yr). Modern designs use tubes arranged in vertical rows, providing superior mechanical performance and higher capacity. The capacity of a single furnace is well over 130,000 t/yr. A typical sketch of such a furnace is shown in Figure 1.

Reaction. The reaction proceeds in the pyrolysis coils of the radiant section of the furnace. Since coke is also formed during pyrolysis, steam is added as a diluent to the feed. The steam minimizes the side reaction forming coke, and improves selectivity to produce the desired olefins by lowering hydrocarbon partial pressure. The temperature of the hydrocarbon and steam mixture entering the radiant chamber (known as the crossover temperature) is 500 to 700°C. Lower temperatures are used for heavy feeds like atmospheric gas oil (AGO) and vacuum gas oils (VGO), and higher temperatures are used for light gases like ethane and propane. Some cracking can start as low as 400°C. However, for light gases incipient conversion is quite low. Depending on the residence time and required feed severity, the coil outlet temperature is typically maintained between 775 and 950°C.

The combination of low residence time and low partial pressure produces high selectivity to olefins at a constant feed conversion. In the 1960s, the residence time was 0.5 to 0.8 seconds, whereas in the late 1980s, residence time was typically 0.1 to 0.15 seconds. Typical pyrolysis heater characteristics are given in Table 4. Temperature, pressure, conversion, and residence time profiles across the reactor for naphtha cracking are illustrated in Figure 2.

Cracking reactions are endothermic, 1.6–2.8 MJ/kg (700–1200 BTU/lb) of hydrocarbon converted, with heat supplied by firing fuel gas and/or fuel oil in side-wall or floor burners. Side-wall burners usually give uniform heat



End elevation

Side elevation

Fig. 1. Typical heater configuration. BFW = boiler feed water; SSH = super high pressure steam; HP = high pressure; and ID = induced draft.

Table 4. **Pyrolysis Heater Characteristics**

Single heater characteristics	Range
number of coils	2–176
coil length, m	9–80
inside coil diameter, mm	30–200
process gas outlet temperature, °C	750–950
clean coil metal temperature, °C	900–1,080
max metal temperature, °C	1,040–1,150
average heat absorption, kW/m^2 ext. area	50–110
bulk residence time, s	0.1–0.6
coil outlet pressure, kPa[a]	150–275
clean coil pressure drop, kPa[a]	10–200
ethylene capacity, t/yr	20,000–200,000

[a] To convert kPa to bar, divide by 100.

distribution, but the capacity of each burner is limited (0.1–1 MW) and hence 40 to 200 burners are required in a single furnace. With modern floor burners, also called hearth burners, uniform heat flux distribution can be obtained for coils as high as 10 m, and these are extensively used in newer designs. The capacity of these burners vary considerably (1–10 MW), and hence only a few burners are required. The selection of burners depends on the type of fuel (gas and/or liquid), source of combustion air (ambient, preheated, or gas turbine exhaust), and required NO_x levels.

The reaction mixture exiting the furnace is quickly cooled in quench coolers also called transferline exchangers (TLE). In earlier designs, direct quenching with oil or water was used for most liquid feeds. Almost all modern designs employ indirect quenching, by which valuable high pressure steam is generated. Direct quenching is only used for very heavy feeds.

Single-stage or two-stage cooling is used to achieve the desired degree of cooling. These alternatives achieve the same thermal efficiency, but offer different approaches to low pressure drop operation and mechanical design.

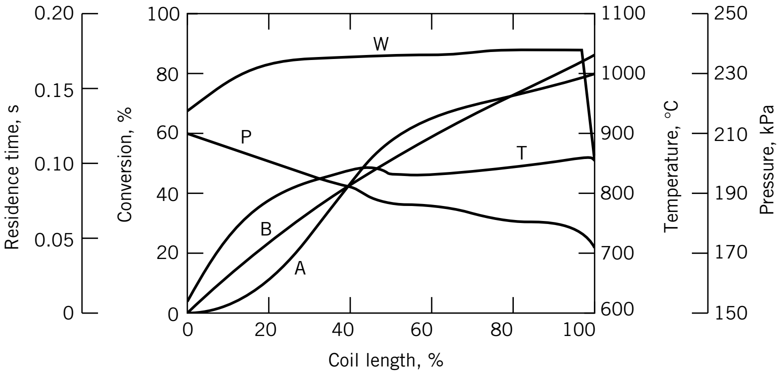


Fig. 2. Profiles of conversion, A, having pressure P and gas temperature T along the reactor length. Residence time, B, where W=maximum wall temperature. To convert kPa to bar, divide by 100.

In the first stage, the process gas is cooled in a double-pipe exchanger or in a shell and tube exchanger. In the second stage, a shell and tube exchanger is used to generate additional steam and sometimes to preheat the feed and dilution steam. The outlet gas temperature from the transferline exchanger varies from 350 to 650°C depending on the feedstock and the design. If the reaction mixture is not cooled quickly, olefin selectivity is reduced because of the many side reactions taking place in this zone. After the transferline exchanger, further cooling is achieved by spraying the furnace effluent with quench oil. The oil and water phases are then separated from the gas phase. The cooled furnace effluent then proceeds to the recovery section for further separation.

Efficiency. Since only 35 to 50% of fired duty is absorbed in the radiant section, the flue gas leaving the radiant chamber contains considerable energy that can be extracted efficiently in the convection section of the furnace. In the convection section, the feed is preheated along with dilution steam to the desired crossover temperature. Residual heat is recovered by generating steam. The overall thermal efficiency of modern furnaces exceeds 93%, and a value of 95% is not uncommon.

The convection section is a series of cross-flow exchangers with flue gas on one side and process fluids on the other (tube) side. Since mainly gas-to-gas heat transfer is involved, fin tubes are employed to improve the heat-transfer rate where practical. The metallurgy of the tubes vary from carbon steel to high temperature alloy depending on the service. When high overall efficiency is desired, condensation of acidic flue gases must be taken into account in the selection of materials. Fouling of heat-transfer surfaces both inside and outside is unavoidable. Outside fouling is cleaned by steam lancing, and inside fouling is usually handled by burning.

In new plant designs, cogeneration of electricity and steam has become economically attractive. Depending on the plant capacity, gas turbines (15–50 MW) are used to generate electric power. These turbines usually burn fuel gas with 200%+ excess air. Therefore, the exhaust gas is not only hot, but also rich in oxygen. Instead of directly generating steam from the exhaust gas by using waste heat boilers, the gas is fed to the cracking heaters as a source of combustion oxygen. Typically, the exhaust gas temperature is 400 to 590°C with an oxygen content of 14 mol% or more. Typical energy savings of 10 to 30% are reported (34,35). Using hot combustion air requires special ducting, and hence the investment cost of the heater is slightly higher.

Instead of gas turbine exhaust, air preheat has been used in some plants to reduce fuel consumption. Flue gas leaving the furnace stack passes through an air preheater, and the preheated air is supplied to the burners. By using mostly hearth burners, the duct work and the investment cost can be minimized with air preheat and gas turbine exhaust. It is also possible with 100% wall-fired furnaces, and has been proven in commercial operation (34).

Environmental. Stringent environmental laws require that nitrogen oxides (NO_x) and sulfur oxides emission from furnaces be drastically reduced. In many parts of the world, regulations require that NO_x be reduced to 70 vol ppm or lower on a wet basis. Conventional burners usually produce 100 to 120 vol ppm of NO_x. Many vendors (McGill, John Zink, Callidus, Selas and North American) are supplying low NO_x burners.

Table 5. **Product Distribution Obtained in a Short Residence Time Coil at 172 kPa**[a]

Property	C_2H_6	C_3H_8	n-C_4H_{10}	Light naphtha	Light AGO	HVGO[b]
sp gr				0.662	0.8191	0.852
boiling range, °C				35–150	185–335	360–540
mol wt	30.0	44.0	58.0	81.0	205.0	425.0
feed H_2, wt%	20.10	18.29	17.34	16.00	13.93	14.20
steam/HC, wt/wt	0.30	0.30	0.40	0.50	0.75	0.75
severity/conv,%	65	95	96	[c]	[c]	[c]
yields, wt%						
H_2	3.93	1.56	1.17	1.00	0.63	0.65
CH_4	3.82	25.30	21.70	18.00	11.20	12.60
C_2H_2	0.43	0.64	0.78	0.95	0.47	0.33
C_2H_4	53.00	39.04	39.20	34.30	26.50	29.00
C_2H_6	35.00	3.94	3.02	3.80	3.40	3.70
C_3H_4	0.06	0.53	1.15	1.02	0.80	0.95
C_3H_6	0.89	11.34	15.34	14.10	13.40	13.10
C_3H_8	0.17	5.00	0.16	0.35	0.25	0.24
C_4H_6	1.19	4.50	4.08	4.45	5.00	5.00
C_4H_8	0.18	0.80	1.69	3.70	3.70	3.40
C_4H_{10}	0.22	0.09	4.00	0.20	0.10	0.07
C_5	0.27	1.61	1.38	2.10	2.75	1.90
C_6–C_8[d]	0.39	0.31	1.45	0.80	1.20	1.40
benzene	0.37	2.74	2.48	6.40	6.90	7.30
toluene	0.08	0.67	0.52	2.30	3.20	3.65
xylene + ethylbenzene	0.00	0.09	0.20	0.21	1.30	1.10
styrene	0.00	0.51	0.23	0.75	0.79	0.65
C_9–205°C	0.00	0.93	0.87	1.40	2.96	2.90
fuel oil	0.00	0.40	0.58	4.17	15.45	12.06
Total	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*

[a] Absolute = 1.72 bar.
[b] Hydrocracked vacuum gas oil.
[c] Maximized ethylene product.
[d] Nonaromatic.

Since NO_x production depends on the flame temperature and quantity of excess air, achieving required limits may not be possible through burner design alone. Therefore, many new designs incorporate DENOX units that employ catalytic methods to reduce the NO_x limit. Platinum-containing monolithic catalysts are used (36). Each catalyst performs optimally for a specific temperature range, and most of them work properly around 400°C.

Product Distribution. In addition to ethylene, many by-products are also formed. Typical product distributions for various feeds from a typical short residence time furnace are shown in Table 5. The product distribution is strongly influenced by residence time, hydrocarbon partial pressure, steam-to-oil ratio, and coil outlet pressure.

Table 6 shows the effect of varying coil outlet pressure and steam-to-oil ratio for a typical naphtha feed on the product distribution. Although in these tables, the severity is defined as maximum, in a realistic sense they are not maximum. It is theoretically possible that one can further increase the severity and thus increase the ethylene yield. Based on experience, however, increasing the

Table 6. **Product Distribution, wt%, as a Function of Severity and Selectivity for a Naphtha Feed**[a,b,c]

Product	Max C_3H_6	Max olefin	Max C_2H_4	Max C_2H_4[d]	Max C_2H_4[e]
H_2	0.75	0.86	0.91	0.91	0.91
CH_4	12.60	14.65	15.70	15.95	15.30
C_2H_2	0.43	0.66	0.78	0.66	0.95
C_2H_4	25.50	29.00	30.80	29.95	32.20
C_2H_6	4.30	4.10	3.30	3.62	2.80
C_3H_4	0.56	0.80	1.00	0.91	1.15
C_3H_6	17.00	15.90	14.00	13.70	14.40
C_3H_8	0.45	0.34	0.28	0.32	0.22
C_4H_6	4.50	4.75	4.70	4.55	4.90
C_4H_8	6.50	4.15	3.80	3.80	3.81
C_4H_{10}	0.80	0.30	0.20	0.20	0.20
C_5	4.95	3.20	2.93	2.78	3.10
C_6–C_8 non-aromatic	6.40	2.60	1.80	1.55	2.20
benzene	4.00	6.00	6.70	7.15	5.95
toluene	3.80	3.93	4.00	4.10	3.90
xylene + ethylbenzene	2.20	1.57	1.30	1.34	1.24
styrene	0.65	0.78	0.82	0.87	0.75
C_9–205°C	2.16	1.90	1.82	1.89	1.72
fuel oil	2.45	4.51	5.16	5.75	4.30
Total	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*

[a] Specific gravity = 0.7260.

[b] Coil outlet pressure (COP) = 172 kPa unless otherwise noted.

[c] Steam/HC, wt/wt = 0.5 unless otherwise noted.

[d] COP = 207 kPa.

[e] Steam/HC, wt/wt = 0.75.

severity above these practical values produces significantly more fuel oil and methane with a severe reduction in propylene yield. The run length of the heater is also significantly reduced. Therefore, this is an arbitrary maximum, and if economic conditions justify, one can operate the commercial coils above the so-called maximum severity. However, after a certain severity level, the ethylene yield drops further, and it is not advisable to operate near or beyond this point because of extremely severe coking.

Kinetic Models Used for Designs. Numerous free-radical reactions occur during cracking; therefore, many simplified models have been used. For example, the reaction order for overall feed decomposition based on simple reactions for alkanes has been generalized (37).

Many researchers have correlated the overall decomposition as an nth order reaction, with most paraffins following the first order and most olefins following a higher order. In general, isoparaffin rate constants are lower than normal paraffin rate constants. The rate constants are somewhat dependent on conversion due to inhibition effects; that is, the rate constant often decreases with increasing conversion, and the order of conversion is not affected. This has been explained by considering the formation of allyl radicals (38). To predict the product distribution, yields are often correlated as a function of conversion or other severity parameters (39).

Instead of radical reactions, models based on molecular reactions have been proposed for the cracking of simple alkanes and liquid feeds like naphtha and gas oil (40–42). However, the validity of these models is limited, and cannot be extrapolated outside the range with confidence. With sophisticated algorithms and high speed computers available, this molecular reaction approach is not recommended.

With the introduction of Gear's algorithm (25) for integration of stiff differential equations, the complete set of continuity equations describing the evolution of radical and molecular species can be solved even with a personal computer. Many models incorporating radical reactions have been published. For the cracking of light hydrocarbons at low temperatures, one study (22) used more than 300 reactions, and another (21), 133 reactions. The estimation of frequency factors and activation energies of these elementary reactions from other thermodynamic data has been outlined (43). Properties of various radicals are available (2,44–47). A more detailed model for the cracking of hydrocarbons has been published (24). Unfortunately, these models assume pseudo steady state for the radicals, at least for a small portion of the furnace if not over the complete furnace. This integration is inferior to Gear's algorithm which does not assume steady state. For example, calculations generated for propane cracking in a non-isothermal pilot reactor with Gear's algorithm, show clearly that many radicals do not attain steady state (21).

Run Length. Coke is produced as a side product that deposits on the radiant tube walls. This limits the heat transfer to the tubes, and increases the pressure drop across the coil. The coke deposition not only limits the heat transfer, but also reduces the olefin selectivity. Periodically, the heater has to be shut down and cleaned. Typical run lengths are 40 to 100 days between decokings. Prediction of run length of a commercial furnace is still an art, and various mechanisms are postulated in the literature. Coke also deposits in transferline exchangers. Mechanisms for coking in radiant coils and transferline exchangers appears to be different for different feeds.

Over 25 years ago the coking factor of the radiant coil was empirically correlated to operating conditions (48). It has been assumed that the mass transfer of coke precursors from the bulk of the gas to the walls was controlling the rate of deposition (39). Kinetic models (24,49,50) were developed based on the chemical reaction at the wall as a controlling step. Bench-scale data (51–53) appear to indicate that a chemical reaction controls. However, flow regimes of bench-scale reactors are so different from the commercial furnaces that scale-up of bench-scale results cannot be confidently applied to commercial furnaces. For example, Figure 3 shows the coke deposited on a controlled cylindrical specimen in a continuous stirred tank reactor (CSTR) and the rate of coke deposition. The deposition rate decreases with time and attains a pseudo steady value. Though this is achieved in a matter of minutes in bench-scale reactors, it takes a few days in a commercial furnace.

Transferline exchanger (TLE) coking is different from coking of the radiant coil. Condensation of coke precursors contained in the heavier fractions of the cracked gas has been claimed to account for TLE fouling (54). Mass transfer of precursors to the film is assumed to be the controlling factor. Others have assumed (55,56) that a chemical reaction is the controlling mechanism, and a

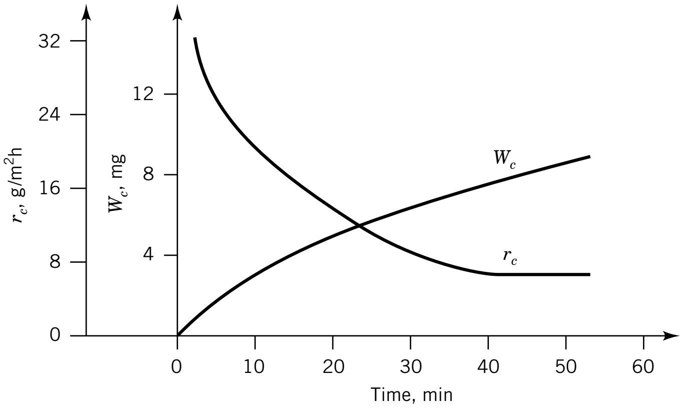


Fig. 3. Weight of coke formed (W_c) and coking rate (r_c) in ethane cracking as a function of time (51).

polymerization mechanism similar to the Ziegler-Natta mechanism has been proposed. Both models work well within the data range. Based on commercial experience with a hydrocracked vacuum gas oil (HVGO) (57), it appears that more than polymerization or condensation occurs in a TLE, at least for this feedstock. By way of example typical outlet gas temperatures as a function of on-stream time are shown in Figure 4.

TLE fouling for gaseous feedstocks is different from that for liquid feedstocks. With gas cracking (especially with ethane), coke deposits on the TLE inlet tubesheet, but does not significantly build up inside the tubes. With time, enough coke builds up and tubes are partially or fully blocked and the heat-transfer surface is reduced. This gives rise to higher outlet temperatures and high pressure drop. Now, larger tubes are used to prevent plugging. Generally, only a small temperature rise is observed from start to end of run.

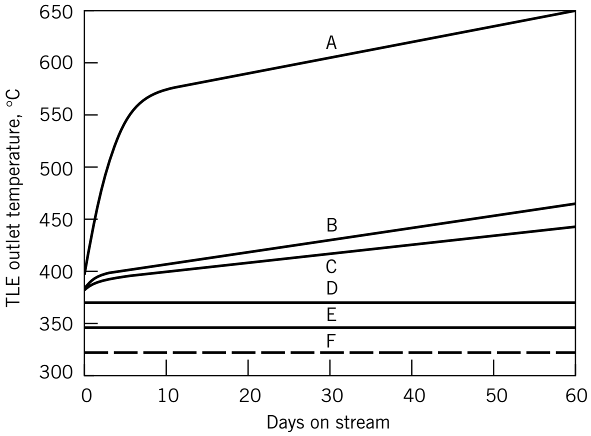


Fig. 4. Typical TLE outlet temperatures as a function of time on stream for various feedstocks: A, HVGO high severity; B, naphtha high severity; C, naphtha moderate severity; D, n-butane; E, ethane; and F, steam.

Only a few commercial vendors manufacture high pressure shell and tube transferline exchangers. Notably, Schmidtsche Heissdamp GmbH of Germany, Borsig of Germany, Mitsubishi of Japan, Mitsui of Japan, Babcock-Hitachi of Japan, and Struthers-Wells of the United States manufacture these TLEs. There are, however, many vendors who build low pressure TLEs.

Both Mitsubishi and Mitsui TLEs differ drastically from other designs. Mitsubishi offers a TLE with an integral steam drum and cyclone for vapor–liquid separation. The pyrolysis gas flows in the shell side, and is claimed to accomplish the decoking of the furnace and the transferline exchanger in one operation. The Mitsui quench cooler uses three concentric tubes as the tube element, and requires steam–air decoking to clean the TLE (58,59).

During radiant coil decoking, the TLE is also partially decoked (at least for ethane cracking, in which most of the coke is deposited on the inlet tubesheet). For complete decoking, the furnace is usually cooled down and the TLEs are separated from the coil and hydrojetted with high pressure water. In some cases, the coke in the TLEs can also be burnt off, and hence no mechanical cleaning is required (60). The radiant coil is always cleaned by burning the coke with steam and air in different proportions and at different temperatures for 12 to 48 hours. Since hydrogen burns off very rapidly, the initial concentration of oxygen is kept low to avoid temperature overshoot. Usually, all coils in a given heater are decoked, and the effluent of decoking is sent to a decoking pot or to a firebox for burning. One patent claims single-coil decoking, while other coils in the same heater are cracking hydrocarbons which is true on-line decoking. Unfortunately, the decoking effluent contains CO, CO_2, and carbon particles that affect the downstream units, so widespread use of this method is limited. Usually the shorter the cracking time, the shorter is the decoking time for the same feedstock and cracking severity.

The inside of the convection tubes rarely foul, but occasionally the liquid unsaturates in feedstocks tend to polymerize and stick to the walls and thus reduce the heat transfer. This soft coke is normally removed by mechanical means. In limited cases, the coke can also be burnt off with air and steam. Normally, the outside surface of the convection section fouls due to dust and particles in the flue gas. Periodically (6 to 36 months), the outside surface is cleaned by steam lancing. With liquid fuel firing, the surface may require more frequent cleaning.

6. Coke Suppression Technologies

Several companies are engaged in finding an additive or modifying the radiant coil surface to suppress coke deposition (119,120). In place of sulfur, or sometimes in addition to sulfur, coke suppressing additives are added to the hydrocarbon / dilution steam mixture before entering the coil. It is claimed that these additives reduce the CO formation and prolong the run length by a factor of two to four. Some additives are used successfully in commercial gas cracking furnaces. The effectiveness of these additives to liquids cracking has yet to be proven. The cost of these chemicals needs to be evaluated considering the benefits of longer run lengths. Instead of adding a chemical, some vendors have modified the radiant coil surface with a suitable coating. This reduces the catalytic coking, which is predominant at start-of-run, and reduces the adherence of gas phase coke, a dominant factor after a few days of operation. Again, bench scale experiments show as high as ten-fold reduction in coking rate. However, commercial experiments show only a two-fold increase in run length for gas cracking. Currently, the coating is expensive and the life of the coating is not yet fully established.

6.1. Recovery and Purification.

The pyrolysis gas leaves the transferline exchanger at 300 to 400°C for gaseous and light naphtha feeds, and at 550 to 650°C for heavy liquid feeds. The lowest temperature is at the beginning of an operating cycle when the exchangers are clean. In order to minimize any further cracking for liquid feeds, the temperature must be quickly reduced. This is achieved by spraying quench oil directly into the effluent. For naphtha-based plants, quenching is performed before primary fractionation. In gas oil plants, quenching is done immediately after the transferline exchanger, resulting in two-phase flow in the transferline.

For all feeds the effluent is separated into desired products by compression in conjunction with condensation and fractionation at gradually lower temperatures.

Figure 5 represents a typical flow diagram of an ethylene plant for a naphtha feedstock. The quenched effluent enters the gasoline fractionator where the heavy fuel oil cuts are separated from the bulk of the effluent stream. The function of the fractionator is to make a sharp separation between the pyrolysis gasoline and pyrolysis fuel oil. The quench oil is cooled to 185°C by generating dilution or low pressure steam. The bottom temperature of the fractionator has to be critically controlled, since at high temperatures the quench material is unstable. Carbon (asphaltenes) is deposited, and the viscosity of the fluid increases. When light feeds are cracked, the fuel oil content is low, and therefore higher concentrations of unstable material are present. When gas oil is cracked, though the fuel oil content is high, it is mainly unconverted feed; hence the concentration of unstable material is low, and a higher bottom temperature can be tolerated.

Because of the small temperature difference between the hot quench oil and the steam generators, and the large amount of heat to be removed from the pyrolysis gas, quench oil flow has to be large and is typically in the range of 15 to 25 times the flow of feedstock to the heaters. Because of coke particles in the quench oil, specially designed pumps are used. The dilution steam generator is one of the largest exchangers in the plant consisting of multiple shells. In addition, spare pumps and exchangers are needed because of severe fouling. This optimization problem has been analyzed (61,62) in detail.

The quench tower in essence operates as a partial condenser for the gasoline fractionator, condensing practically all of the steam and most of the pyrolysis gasoline components. In some designs, the quench tower and gasoline fractionator are combined into a single structure. Separation of the water phase from the gasoline phase occurs in a quench water drum. Hot quench water is used as a process heat source for the recovery section. A portion of the gasoline phase is refluxed for the gasoline fractionator, while the remainder is sent to the gasoline

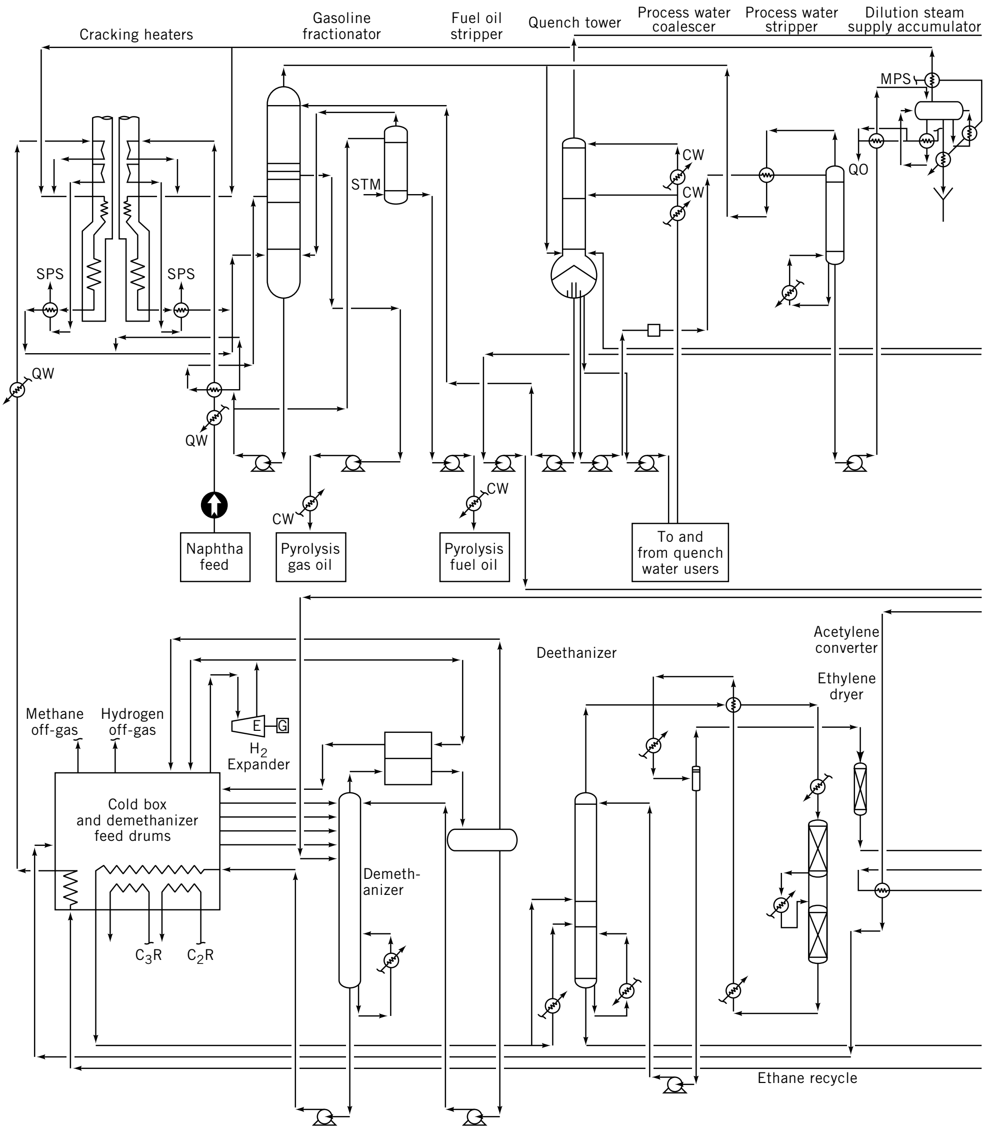


Fig. 5. Schematic flow diagram of an ethylene plant using naphtha feedstock. CW = cooling water; QW = quench water; QO = quench oil; LPS = low pressure steam; MPS = medium pressure steam; SPS = super high pressure steam; C_3R = propylene refrigerant; and C_2R = ethylene refrigerant.

stripper for stabilization. This gasoline has an octane number (RON) of 95 to 99, and is usually blended with other gasoline products.

The pyrolysis gas leaving the quench tower is compressed to 3.5 MPa (35 atm) in a four- or five-stage centrifugal compressor. The number of stages is determined by the maximum temperature permissible for the material of construction and the fouling tendency of the pyrolysis gas. The compressor consists

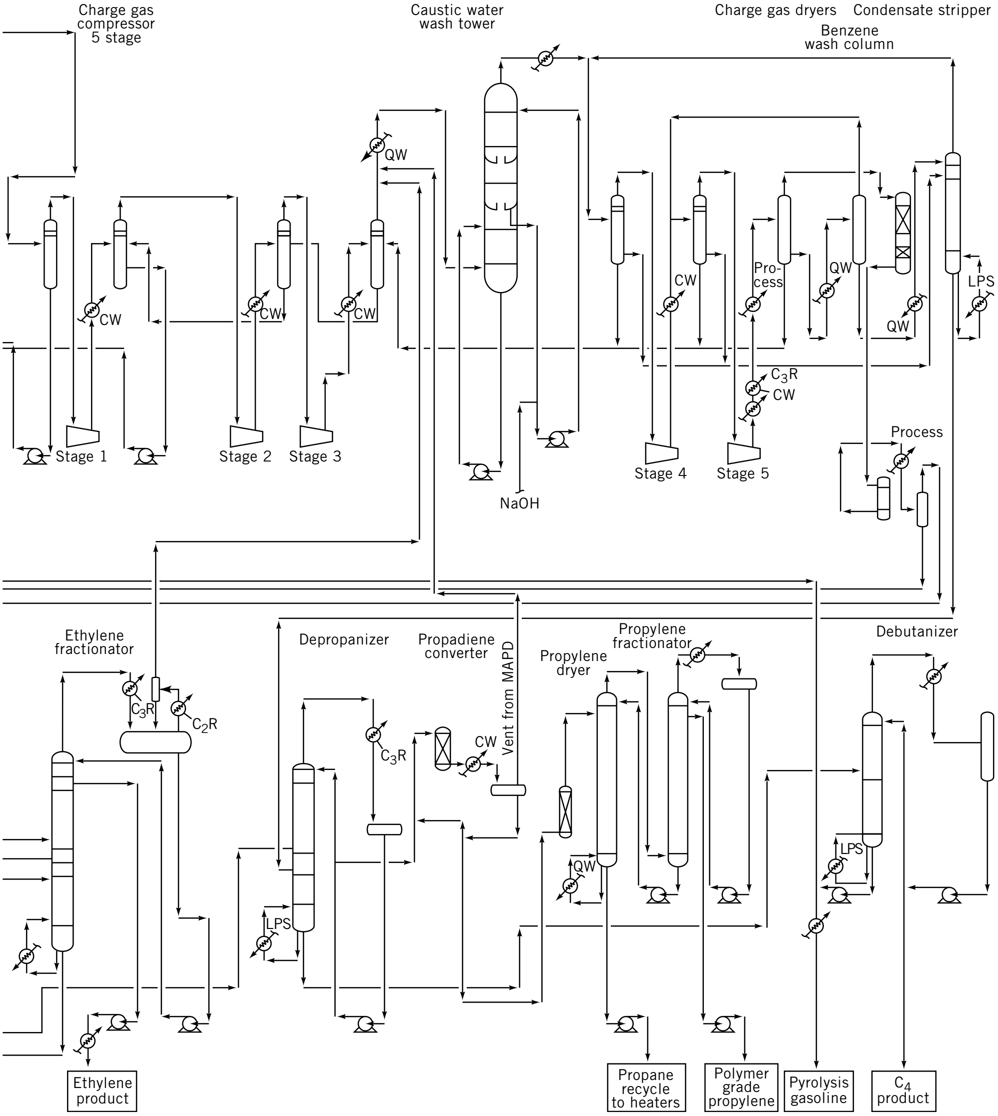


Fig. 5. *Continued*

of two or three compressor casings driven by a single extraction/condensing turbine. For large plants two turbines may be used. Water and hydrocarbons are separated from the pyrolysis gas between stages and recycled.

Acid gases (CO_2 and H_2S) are removed after the third or fourth compression stage. This is an optimum location since the gas volume has been reduced significantly in the previous stages and the acid gases have not contaminated any final products. When the sulfur content of the feed is low as for naphtha feeds, scrubbing with a dilute caustic soda solution is economical. Typically 4 to 12% free caustic solution is used. Relatively weak solutions are preferred to avoid the precipitation of sodium salts and to minimize the formation of sodium complexes and "yellow oil." The pyrolysis gas leaving the scrubber contains less than 1 ppm of acid gases, and is further treated by a water wash to remove any hydroxide carryover. A detailed analysis has been given (63). Plants designed to process high sulfur content feeds, eg, higher than 500 ppm, often contain a regenerative acid gas removal system upstream of the caustic scrubber. These systems may employ monoethanolamine, diethanolamine, or alkazid as solvents with a standard absorber–desorber design. Disposal of the spent caustic solution can be a troublesome environmental problem. Depending on the plant location, acid gases are either sent to a fired heater or treated in a Claus unit for conversion of hydrogen sulfide to elemental sulfur.

Complete removal of water from the pyrolysis gas is achieved with molecular sieve dryers. Typically, there are two dryers; one is in normal operation while the other is being regenerated. The dryers are designed for 24 to 48 hours between successive regenerations and high pressure methane heated with steam at 225°C is the preferred regeneration medium. Activated alumina was used in older plants, but it is less selective than molecular sieves.

After acid gas removal the pyrolysis gas from the last stage of compression is cooled by propylene refrigerant and sent to a condensate stripper. This tower separates the C_3 and heavier products, which exit the bottom, from the C_2 and lighter components.

The pyrolysis gas is partially condensed at essentially constant pressure over the stages of the cascade refrigeration system to about -165 °C where only the hydrogen remains in the vapor state. The stage condensates (only one is shown in Fig. 5) are fed to the appropriate trays of the demethanizer. Hydrogen (95 mol%) is withdrawn from the lowest temperature stage separator. The demethanizer is designed for complete separation of methane from ethylene and heavier components and operates at 0.7 MPa (7 atm). Condensing propylene refrigerant supplies heat to the reboilers and vaporizing refrigerant condenses the reflux. The demethanizer overhead consists of methane (95 mol%) with some minor impurities of hydrogen, carbon monoxide, and traces of ethylene. Brazed aluminum plate-fin exchangers are used for the multipass cryogenic heat-transfer services, and are installed in a cylindrical or rectangular carbon steel container, commonly known as a cold box. This unit is filled with perlite or rockwool for insulation.

The system just described is for the so-called low pressure demethanizer. Some licensors offer a high pressure demethanizer design (3.5 MPa), combined with either front-end deethanization or depropanization.

The demethanizer bottoms, consisting of ethylene and heavier components, are sent to the deethanizer, a conventional tray-type fractionator operating at a pressure of 2.4 to 2.8 MPa (~25 atm). An overhead stream containing C_2 hydrocarbons and a bottoms product of C_3 and heavier hydrocarbons are produced. Since acetylene is not usually recovered, the deethanizer overhead is heated to 20–100°C and hydrogen is added. The mixture is passed over a fixed bed of palladium catalyst. Because of the exothermicity of the acetylene hydrogenation, multiple beds with intermediate cooling are preferred. The acetylene hydrogenation reactor effluent contains less than 1 ppm of acetylene, but contains traces of methane and hydrogen. This is known as rear-end acetylene hydrogenation, and is preferred to front-end hydrogenation because of higher selectivity and precise temperature control.

Front-end hydrogenation is also possible. This approach uses a different type of catalyst, and the reactor is located upstream of the demethanizer. For this design, a deethanizer or depropanizer tower is located upstream of the demethanizer to remove heavy fractions. This approach has been utilized by some licensors with some success.

During acetylene hydrogenation, there is a net gain of ethylene since, under normal conditions, more acetylene is hydrogenated to ethylene than ethylene is hydrogenated to ethane. In most designs, traces of carbon monoxide are used to control the selectivity of hydrogenation. The catalyst is deactivated over time due to coke and green oil (a polymer formed as a result of side reactions) production, and is therefore regenerated periodically (3 to 6 months). The kinetics of this reaction has been discussed (64,65). New catalysts do not require CO addition.

When acetylene is recovered, absorption–desorption towers are used. In the first tower, acetylene is absorbed in acetone, dimethylformamide, or methylpyrollidinone (66,67). In the second tower, absorbed ethylene and ethane are rejected. In the third tower, acetylene is desorbed. Since acetylene decomposition can result at certain conditions of temperature, pressure, and composition, for safety reasons, the design of this unit is critical. The handling of pure acetylene streams requires specific design considerations such as the use of flame arrestors.

After acetylene hydrogenation, the dried gas enters an ethylene–ethane separator known as an ethylene fractionator. This column contains 80 to 150 trays, and a reflux ratio of 2.5 to 4.0 is typical depending on feed composition. A pasteurizing section is usually provided at the top of the fractionator for removal of residual hydrogen, carbon monoxide, and methane. The conditions of the reboiler and overhead condenser are ideal for the use of a closed heat pump (68), with propylene refrigerant as the working fluid. Condensing refrigerant vapor supplies heat to the reboiler, and the refrigerant boiling under low pressure generates the cooling required in the overhead condenser. An open heat pump can be used with the integration of the ethylene–ethane fractionator into the ethylene refrigeration system. The ethane withdrawn from the tower bottom is recycled to the heaters and cracked to extinction.

The condensate stripper bottoms and the deethanizer bottoms are processed in the depropanizer for a sharp separation of C_3 hydrocarbons and C_4 and heavier hydrocarbons. The reboiler and tower internals are routinely fouled by rubberlike polymers, and require periodic mechanical cleaning. To minimize this problem, two types of designs are used. In the first design, the bottoms temperature is set low, which results in an operating pressure requiring propylene refrigerant instead of cooling water for the condensation of the overhead product. In the second design, cooling water is used, and a high bottom temperature is required. The latter requires a full spare tower and reboiler for continuous operation while the former requires only a spare reboiler. A two-tower system is also used to provide the benefits of both approaches, ie, low fouling and low refrigeration, but this option is somewhat more costly.

The depropanizer bottoms are further processed in the debutanizer for separation of C_4 product from light pyrolysis gasoline. The debutanizer operates at a moderate pressure of 0.4 to 0.5 MPa, and is a conventional fractionator with steam heated reboilers and water cooled condensers.

The overhead of the depropanizer is sent to the propylene fractionator. The methylacetylene (MA) and propadiene (PD) are usually hydrogenated before entering the tower. An MAPD converter is similar to an acetylene converter, but operates at a lower temperature and in the liquid phase. Due to recent advances in catalysis, the hydrogenation is performed at low temperatures (50–90°C) in trickle bed reactors (69). Only rarely are methylacetylene and propadiene recovered.

Because of the low relative volatility, fractionation of propylene and propane is even more difficult than the fractionation of ethylene and ethane. The propylene fractionator operates at a pressure of 1.8 to 2.0 MPa with more than 160 trays required for a high purity propylene product. Often a two-tower design is employed when polymer grade (99.5%+) is required. A pasteurization section may also be used when high purity is required. The bottoms product contains mainly propane that can be recycled to the cracking heaters or used as fuel. Typical tower dimensions and internals for a 450,000 t/yr ethylene plant with naphtha feed are summarized in Table 7.

6.2. Energy Efficiency Improvement.

Modern plants are more energy efficient than those designed in the 1980s. Reduction in energy consumption was made possible by improvements in cracking coil technology and improvements in

Table 7. **Characteristics of Towers in an Ethylene Plant**[a]

Service	Diameter, m	Height, m	Type, tray/pack	Design temp, °C	Design pressure, kPa[b]
gasoline fractionator	7.1	35.6	pall ring	340	450
pyrolysis fuel oil stripper	1.5–3.2	14.3	valve	340	450
quench tower	7.2–14.4	32.8	packed	340	450
process water stripper	3.0–11.0	32.8	valve	210	450
caustic/water wash tower	3.6	38	bubb/pack	85	1270
condensate stripper	1.5	26.4	valve	95	1300
demethanizer[c]	2.0–3.0	64.7	pall ring	−142	880
deethanizer	2.7	39.7	valve	−45/85	2450
ethylene fractionator	3.7	84.3	valve	−45	2040
depropanizer	2.3	22–32	valve	100	2020
propylene fractionator	4.1	47.9	valve	75	2190
debutanizer	2.4	34.3	valve	140	760
acetylene absorber	2.1	51.9	valve	−35/110	2200
acetylene stabilizer	6.5–22.5	9–29	pall ring	−35/110	1600
acetylene stripper	1.2–2.1	26.6	pall ring	200	1400
depentanizer	1.5	37.1	valve	150	450
BTX tower	2.6	23.2	valve	180	450
H_2S stripper	1.1	22	valve	195	9300

[a] Ethylene capacity = 450,000 t/yr; tower material is carbon steel.
[b] To convert kPa to atm, divide by 101.3.
[c] Tower material is stainless steel.

recovery section design. Some improvements may not only reduce energy, but can also increase the capacity of an existing plant.

Quench Oil Viscosity Control. Increasing the bottoms temperature of the gasoline fractionator increases the viscosity, and flux oil is often added to reduce the viscosity. Effluents from ethane cracking can be used as a viscosity control stripping medium, allowing a temperature of 195°C in the gasoline fractionator bottom. This reduces the quench oil pumping power, eliminates the flux oil addition (69), and improves energy efficiency.

Feed Saturation. When gas feeds like ethane and propane are cracked, dilution steam can be added via direct humidification in towers known as feed saturators. This design reduces the load on the dilution steam system and/or medium pressure (MP) steam level.

Predemethanization. The conventional design employs a single-step multiple feed tower. Utilization of a second tower upstream of the existing primary tower reduces the load on the primary tower. This reduces the propylene refrigeration power and reduces the propylene chilling loads. This approach is typically uneconomical with low pressure demethanizers, but has been combined with high pressure demethanizer systems by some licensors.

Demethanizer Overhead Expander and Multifeed Fractionation. Incorporation of an expander into the conventional high pressure demethanizer system eliminates bottlenecks in the refrigeration system, the demethanizer condenser, and charge gas compressor. It reduces the cost by lowering the refrigeration power. Multiple feed deethanization and ethylene fractionation debottlenecks the deethanizer, ethylene fractionator, and the refrigeration systems, thereby reducing power consumption.

Tower Internals and Equipment Modification. Tower capacity expansion can be achieved through the use of random or structured packing, or through the use of higher capacity trays such as the UOP multiple downcomer tray. Packing has been used in the gasoline fractionator, water quench tower, caustic and amine towers, demethanizer, the upper zone of the deethanizer, debutanizer, and condensate strippers. Packing reduces the pressure drop and increases the capacity.

Improved and redesigned rotors of modern compressors save considerable power. The ethylene fractionator and the propylene refrigeration condensers can be replaced with extended surface tube bundles instead of conventional tube bundles.

Dephlegmaters. Dephlegmaters accomplish feed gas separation while maintaining simplicity of process design, fabrication, and operation. Cryogenic dephlegmaters are brazed aluminum (plate-fin or core) heat exchangers specially designed to operate as mass-transfer devices. Depending on the feed composition, 5 to 15 theoretical stages can be obtained for one dephlegmater. Application of dephlegmaters to ethylene plants has been discussed (70,71).

7. Catalytic Distillation

It is not surprising to see the hydrogenation and fractionation steps involved in the purification of olefins combined. In an ethylene plant, catalytic distillation can be applied to MAPD hydrogenation, selective hydrogenation of C4 and C5 acetylenes and dienes, and to total hydrogenation of C3/C4/C5 olefins and dienes (121). Catalytic distillation accomplishes both the hydrogenation and the separation in one step and there is a capital saving with this technology. Usually, a catalyst bed replaces a portion of the trays in the distillation tower. Since the reflux required for the distillation passes through the catalyst bed, oligomers formed in the bed are continuously washed. It is claimed that this washing effect increases the catalyst life and the selectivity to olefins. The hydrocarbon and the hydrogen enter the reaction zone as a two-phase mixture. Since the reaction takes place in the liquid phase, the potential for runaway associated with high exothermicity of hydrogenation is also reduced. The proper selection of the catalyst is crucial, since a highly active catalyst will also saturate the valuable propylene.

8. Binary Refrigeration

The low-pressure demethanizer has utilized a methane refrigeration system to provide lowest level cooling to the cracked gas and the reflux to the demethanizer. This system results in investment and operating cost advantages compared to a high-pressure demethanizer system utilizing lowest level ethylene refrigeration. The latest developments further simplify this system by combining the ethylene and methane refrigeration, a binary refrigeration system. It is a closed loop, constant composition mixed refrigeration system and provides refrigeration typically at four temperature levels, from -60°C to -140°C.

9. Other Routes to Ethylene Production

In addition to conventional thermal cracking in tubular furnaces, other thermal methods and catalytic methods to produce ethylene have been developed. None of these are as yet commercialized.

9.1. Advanced Cracking Reactor. The selectivity to olefins is increased by reducing the residence time. This requires high temperature or reduction of the hydrocarbon partial pressure. An advanced cracking reactor (ACR) was developed jointly by Union Carbide with Kureha Chemical Industry and Chiyoda Chemical Construction Co. (72). A schematic of this reactor is shown in Figure 6. The key to this process is high temperature, short residence time, and low hydrocarbon partial pressure. Superheated steam is used as the heat carrier to provide the heat of reaction. The burning of fuel (H_2 and CH_4) with pure oxygen generates temperatures of 2000°C, and the cracking reaction is carried out at 950 to 1050°C (73–75) with a residence time of less than 10 milliseconds. Since the residence time in the reactor is so low, a specially designed Ozaki quench cooler for rapid quenching is required. A prototype was in operation for over 18 months during the 1980s. Unfortunately, all very high temperature processes produce high amounts of acetylene (>2 wt%). Acetylene hydrogenation is a significant cost factor if acetylene has no market.

9.2. Adiabatic Cracking Reactor. This principle is based on the injection of hydrocarbon feedstock into the flue gas at elevated temperatures. Because

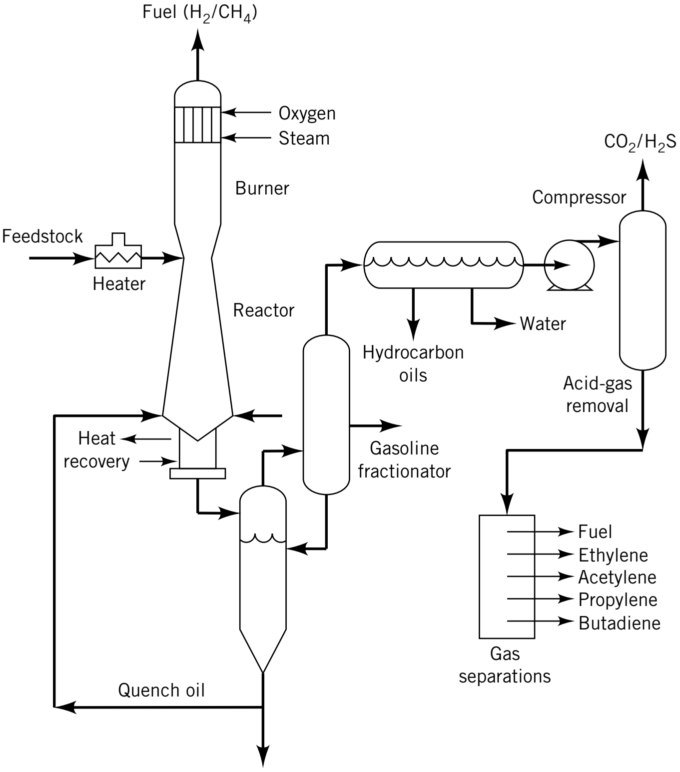


Fig. 6. Sketch of an advanced cracking reactor (73).

of the high initial temperature (1200°C), the feed can be instantaneously vaporized, and a very high rate of decomposition can be obtained. The temperature of the flue gas can be controlled by varying the oxygen/fuel ratio at the combustion chamber, and by the injection of steam in the combustion chamber. The endothermic nature of the cracking process causes the temperature to drop rapidly after the injection of the feed. A substantial increase (over 10 wt%) in olefin yield can be expected, but quenching the reaction to desired conditions is still a problem. In addition, the economics of the process are still not profitable. This route to ethylene production has been analyzed (76,77) using mathematical models. Instead of hydrocarbon, hydrogen has also been used as fuel that generates *in situ* dilution steam.

9.3. Fluidized-Bed Cracking. Since many fractions of crude oil are used individually as feedstocks in conventional cracking furnaces, logically many researchers aimed at cracking crude oil directly. This cannot be done in conventional coils because of severe fouling in the convection section and radiant coils, and in the transferline exchangers. Therefore, various types of fluid-bed processes have been developed. Notably, Lurgi developed the sand cracker (78) using sand as the heat carrier, whereas BASF used coke particles as the fluidizing medium (79). Ube (80) used inorganic oxide as a heat carrier, and the Kunugi and Kunii process (81) used fluidized bed with coke as a heat carrier. Thermal regenerative cracking jointly developed by Gulf Chemical (now Chevron) and Stone and Webster (82) uses solid heat carriers in the fluid bed. A semicommercial unit operated for over two years in Texas in the early 1980s. Other thermal process have also been discussed (83).

9.4. Catalytic Pyrolysis. This should not be confused with fluid catalytic cracking, which is used in petroleum refining (see CATALYSTS, REGENERATION). Catalytic pyrolysis is aimed at producing primarily ethylene. There are many patents and research articles covering the last 20 years (84–89). Catalytic research until 1988 has been summarized (86). Almost all catalysts produce higher amounts of CO and CO_2 than normally obtained with conventional pyrolysis. This indicates that the water gas reaction is also very active with these catalysts, and usually this leads to some deterioration of the olefin yield. Significant amounts of coke have been found in these catalysts, and thus there is a further reduction in olefin yield with on-stream time. Most of these catalysts are based on low surface area alumina catalysts (86). A notable exception is the catalyst developed in the former USSR (89). This catalyst primarily contains vanadium as the active material on pumice (89), and is claimed to produce low levels of carbon oxides.

Cracking temperatures are somewhat less than those observed with thermal pyrolysis. Most of these catalysts affect the initiation of pyrolysis reactions and increase the overall reaction rate of feed decomposition (85). Applicability of this process to ethane cracking is questionable since equilibrium of ethane to ethylene and hydrogen is not altered by a catalyst, and hence selectivity to olefins at lower catalyst temperatures may be inferior to that of conventional thermal cracking. Suitability of this process for heavy feeds like condensates and gas oils has yet to be demonstrated.

9.5. Membrane Reactor. Another area of current activity uses membranes in ethane dehydrogenation to shift the ethane to ethylene equilibrium. The use of membranes is not new, and has been used in many separation processes. However, these membranes, which are mostly biomembranes, are not suitable for dehydrogenation reactions that require high temperatures. Technology has improved to produce ceramic and other inorganic (90) membranes that can be used at high temperatures (600°C and above). In addition, the suitable catalysts can be coated without blocking the pores of the membrane. Therefore, catalyst-coated membranes can be used for reaction and separation.

As an example the use of ceramic membranes for ethane dehydrogenation has been discussed (91). The construction of a commercial reactor, however, is difficult, and a sweep gas is required to shift the product composition away from equilibrium values. The achievable conversion also depends on the permeability of the membrane. Figure 7 shows the equilibrium conversion and the conversion that can be obtained from a membrane reactor by selectively removing 80% of the hydrogen produced. Another way to use membranes is only for separation and not for reaction. In this method, a conventional, multiple, fixed-bed catalytic reactor is used for the dehydrogenation. After each bed, the hydrogen is partially separated using membranes to shift the equilibrium. Since separation is independent of reaction, reaction temperature can be optimized for superior performance. Both concepts have been proven in bench-scale units, but are yet to be demonstrated in commercial reactors.

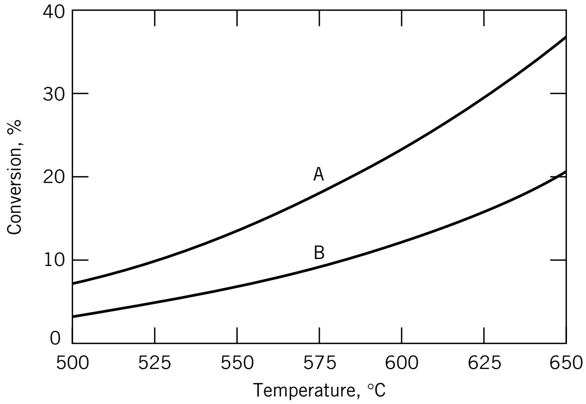


Fig. 7. Equilibrium conversion of ethane versus temperature at 210 kPa in a membrane reactor. The effect of hydrogen removal on ethane conversion is shown: A, 80% H_2 removal; B, 0% removal.

9.6. Dehydrogenation. The dehydrogenation of paraffins is equilibrium-limited and hence requires high temperatures. Using this approach and conventional separation methods, both Houdry and UOP have commercialized the dehydrogenation of propane to propylene (92). A similar concept is possible for ethane dehydrogenation, but an economically attractive commercial reactor has not been built.

9.7. Oxydehydrogenation. Because of the limitations of ethane dehydrogenation equilibrium, research has focused on ways to remove one of the products, namely hydrogen, by chemical methods. In this way, hydrogen is oxidized to water and there is no equilibrium limitation.

$$C_2H_6 + 0.5\ O_2 \longrightarrow C_2H_4 + H_2O$$

However, the same oxygen also oxidizes ethane and ethylene to CO_2 and other oxygenated products. Therefore, selectivity to olefins is a serious consideration. Literature citations (93,94) claim development of low temperature, highly selective oxydehydrogenation catalysts. Although this process has not yet been commercialized, it seems promising.

9.8. Oxidative Coupling of Methane. The most stable paraffin is methane, where it is difficult to break the C–H bond. During the 1980s, new catalysts were developed to activate methane, producing methyl radicals. These methyl radicals combine to give ethane, which further undergoes pyrolysis reactions. This has been discussed in detail (95,96). Recently, Eindhoven University Research Group (97) has proposed incentives for commercialization of this process. It has been shown that very high selectivity to ethylene can be obtained with lanthanum-based catalysts (98). The economics of this process have been discussed (95). According to these sources, this process is not economical when conventional feedstocks (naphtha, LPG, etc) are inexpensive. The process could be economical when methane is available in abundance at extremely low cost, such as in Saudi Arabia and other geographic locations. Since this process does not depend on crude oil for raw feed, research has continued in many countries, and it is possible that it may soon be commercialized.

9.9. Methanol to Ethylene. Methanol to ethylene economics track the economics of methane to ethylene. Methanol to gasoline has been fully developed and, during this development, specific catalysts to produce ethylene were discovered. The economics of this process have been discussed, and a catalyst (Ni/SAPO 34) with almost 95% selectivity to ethylene has been claimed (99). Methanol is converted to dimethyl ether, which decomposes to ethylene and water; the method of preparation of the catalyst rather than the active ingredient of the catalyst has made the significant improvement in yield (100). By optimizing the catalyst and process conditions, it is claimed that yields of ethylene, propylene, or both are maximized. This is still in the bench-scale stage.

9.10. Ethanol to Ethylene. The economics of this process depend on the availability and price of ethanol. High volume production of ethylene from ethanol, which is derived from fermentable raw materials, cannot normally compete with ethylene produced in large hydrocarbon-based olefin units. This process, however, offers several advantages to a country with abundant fermentation materials but limited hydrocarbon resources (102).

Activated alumina and phosphoric acid on a suitable support have become the choices for an industrial process. Zinc oxide with alumina has also been claimed to be a good catalyst. The actual mechanism of dehydration is not known. In industrial production, the ethylene yield is 94 to 99% of the theoretical value depending on the processing scheme. Traces of aldehyde, acids, higher hydrocarbons, and carbon oxides, as well as water, have to be removed. Fixed-bed processes developed at the beginning of this century have been commercialized in many countries, and small-scale industries are still in operation in Brazil and India. New fluid-bed processes have been developed to reduce the plant investment and operating costs (102,103). Commercially available processes include the Lummus processes (fixed and fluidized-bed processes), Halcon/Scientific Design process, NIKK/JGC process, and the Petrobras process. In all these processes, typical ethylene yield is between 94 and 99%.

9.11. Ethylene from Coal. There are several possible routes to ethylene from coal based on both conventional and emerging technologies. Synthesis gas derived from coal gasification can be converted to hydrocarbons by the Fischer-Tropsch (FT) process. The conventional FT process produces high molecular weight saturated and olefinic hydrocarbons and oxygenated compounds. Ethylene can be recovered directly or after pyrolyzing the ethane and naphtha produced. In general this is not an economical process; however, there is a plant based on this route in South Africa (104). Some of the new FT catalysts recently developed maximize ethylene and propylene yield (105). However, in Mobil's MTG (methanol to gasoline) or MTO (methanol to olefins), zeolite catalysts are used and high yields of olefins are reported (106).

9.12. Propylene Disproportionation. A commercial plant utilizing the disproportionation of propylene to ethylene was built in 1966 by Gulf Oil of Canada Ltd. utilizing technology developed by Phillips.

$$2\ C_3H_6 \rightleftarrows C_2H_4 + C_4H_8$$

Since the above reaction is reversible, it can be used to produce either propylene or ethylene and butenes depending on relative prices. For example, when propylene is inexpensive, ethylene and butenes are produced. When ethylene is inexpensive and there is a high demand for propylene, ethylene is dimerized to butene and then the reverse reaction is utilized. A commercial plant based on the reverse reaction has been built on the Gulf Coast.

9.13. Ethylene as a By-Product. The contribution to world ethylene production is small, but not zero. In petroleum refining fluid catalytic cracking (FCC) units, small amounts of ethylene are produced but generally not recovered, except in a few locations where large FCC units are adjacent to petrochemical facilities.

10. Advanced Computer Control Systems and Training Simulators

An ethylene plant contains more than 300 equipment items. Traditionally, operators were trained at the site alongside experienced co-workers. With the advent of modern computers, the plant operation can be simulated on a real-time basis, and the results displayed on monitors (107). Computers are used in a modern plant to control the entire operation, eg, they are used to control the heaters and the recovery section (108). A well-controlled plant is much more profitable than a poorly controlled plant. For the heaters, a model-based control system is gaining importance (109). Instead of simply controlling the coil outlet temperature (COT), severity is actually controlled. The measurement of severity (either C_3H_6/C_2H_4 or C_3H_6/CH_4 ratio) requires on-line effluent analysis using chromatographs. However, these chromatographs have significant lag time. To overcome this lag time, sophisticated kinetic models are used to predict the severity for a given COT and compare it against the actual measurement as it becomes available. Although COT is used as the set point, severity is the control variable (108). This also provides a means to optimally adjust severity as fouling in the radiant coil and in the transferline exchanger occurs.

11. Shipment and Storage

In 1989, over 500,000 t/yr of ethylene were traded internationally. The principal exporting countries were in the Middle East, and the principal importing countries were in Western Europe and Asia/Pacific. The tanker fleet that transported the ethylene numbered approximately 30 vessels with capacities ranging from 2000–6500 t (110). These tankers are of the semi-refrigerated type, and transport liquid ethylene at atmospheric pressure and −104°C. The tankers include reliquefaction plants on board since it is too expensive to vent ethylene. To accommodate the increase in international trade of ethylene, ethylene terminals have been built in the United States, Far East, Western Europe, and the Middle East with capacities of 35,000 t, 300,000 t, and 70,000 t, respectively (110).

The quantity of ethylene transported by international tankers accounts for only 1% of production. The majority of ethylene produced in the United States and Western Europe is moved by integrated pipeline systems.

In the United States, the Gulf Coast produces and consumes the majority of the U.S. ethylene production. The plants are located along the Texas southeast coast extending into Louisiana (111). The plants are served by a system of pipelines connecting the production and consuming plants. In 1989 there were 10 producers, 38 consumers, and 15 combined producers and consumers at the same site. The ethylene is transported as a gas at very high pressures of 5–5.7 MPa (49–56 atm) (112). Since the critical temperature for ethylene is 9.2°C, the ethylene remains as a gas at the elevated pressures. The pipelines are buried approximately 3–5 m below the ground so the surrounding ground temperature rarely approaches the critical temperature.

Western Europe also operates an integrated pipeline system. The system links the large producers and consumers in Germany, Holland, France, and Belgium. The pipeline system is being expanded both in terms of ethylene and the addition of propylene. Expansion of the pipeline is being instituted to phase out the use of rail tankers to transport the ethylene. Producers feel that pipeline transport offers superior specification guarantees that rail or barge tankers cannot offer since the operation is not directly under the user's control (113).

Very little data exists on the costs of transport via pipeline. In mid-1990, the cost of transport in Western Europe was approximately \$24/t regardless of distance plus \$0.12/km (113).

Inside operating plants a certain amount of storage is provided to smooth out operational upsets. The capacity stored can range from a few hours to a few days of production depending on the owner's operating philosophy. Small amounts of ethylene are stored as a liquid in pressure tanks and held at the required temperature by refrigeration available from the operating unit. This method of storage is only appropriate for a few hours of production, since the tanks must be expensive, heavy, thick-walled vessels. For larger amounts of ethylene, cryogenic/low pressure storage is used. Cryogenic storage allows use of thinner-walled tanks that are less expensive (112). The ethylene is kept below its critical temperature, and therefore lower pressure can be used. To keep the ethylene below its boiling point (−103.7°C), some ethylene is vaporized and then passed to a refrigeration plant for recovery (112). Cryogenic storage tanks employ an outer and an inner wall with the interspace filled with an insulating material (114).

For storage of very large quantities, underground caverns or jugs leached out of underground salt domes are used. As the ethylene is pumped into the cavern it displaces a pool of brine. The pool of brine exerts pressure on the ethylene, keeping it in the cavern. The ethylene is removed by returning brine to the cavern. Since the caverns are located a few hundred meters below ground level, temperatures are fairly constant and always above the critical temperature of ethylene (112).

12. Specification and Analysis

Polyethylene is the predominant derivative of ethylene requiring very high purity (99.9% plus). A typical polymer-grade specification is given in Table 8. Almost all ethylene plants use gas chromatography or gas chromatography combined

Table 8. **Specification for Polymer-Grade Ethylene**

Component	Value
ethylene, mol%, min	99.95
methane + ethane	balance
other impurities, mol ppm, max	
hydrogen	5.0
acetylene	1.0
oxygen	1.0
carbon monoxide	1.0
carbon dioxide	1.0
propylene	10.0
C_4+	10.0
water	2.0
total sulfur	2.0
methanol	5.0
total chlorine	2.0
DMF	1.0
other compounds	5.0

with mass spectrometry for analysis. For specific impurities like sulfur, water, and other hydrocarbons and elements, ASTM standard tests are recommended (D2504-67, D2505-67, 2785-70, E203-75).

13. Economic Aspects

In 1996, world capacity for the production of ethylene was approximately 84×10^6 t. The United States production capacity accounted for almost 28% of the world capacity, or approximately 17×10^6 t, followed by Western Europe with almost 24% or 20×10^6 t (115).

Although the United States and Western Europe account for half of the world's production capacity, the most rapid growth in capacity has been occurring in the developing areas of the world. Table 9 shows the projected worldwide

Table 9. **Ethylene Capacity and Projected Growth Rate**[a]

Region	1991	1996	Projected growth rate, %/year 1996–2001
North America	24.84	28.70	5.1
Western Europe	17.50	20.13	1.6
Asia	12.68	19.33	9.9
Middle East	3.12	4.82	12.0
South & Central America	2.16	3.29	10.5
Eastern Europe	6.52	6.20	1.4
Africa	0.86	1.12	7.6
Oceania	0.47	0.47	0
Total	68.14	84.16	6.1

[a] Capacity in 10^6 t/yr (115). World operating rate is 86% in 1996.

Table 10. **Prices[a] for Ethylene and Propylene in the United States, $/t**

Year	Ethylene	Propylene
1984	415	420
1985	330	370
1986	330	260
1987	330	360
1988	630	460
1989	660	450
1990	550	390
1991	500	420
1992	420	330

[a] Refs. (111,117), and 118.

increase in capacity through 2001. Growth in capacity in the developing countries is almost twice that of North America and Western Europe. However, demand for ethylene is not expected to increase at the same high rate, leading to a shift in exports and imports.

Ethylene is first in total market value among petrochemicals. Based on 1996 production capacity of 84×10^6 t, the total potential market value would be approximately $\$42 \times 10^9$ based on an ethylene price of $500/t.

Table 10 shows the historical sales price for ethylene and propylene in the United States. The economics for an ethylene plant are strongly affected by the prices for the propylene co-product. During most of the early 1980s, the price of ethylene was depressed, leading to a reluctance on the part of producers to install new capacity. By the late 1980s, the demand for ethylene had increased to such an extent that the existing capacity could only barely keep up with demand. Between 1987 and 1988 the price for ethylene almost doubled, encouraging producers to increase capacity. As the new capacity became available, the market price for ethylene began to drop. This trend of lower prices for ethylene will continue until surplus capacity is used up, forcing an increase in price.

The economics for the production of ethylene depends to a large extent on the prices for feedstocks and co-products. In the United States the feedstocks of choice have been the lighter feeds of ethane and propane, as opposed to Western Europe and the Far East which favor naphtha (116). Table 11 shows the percentage of ethylene produced from the various feedstocks in the United States since 1984. Approximately 70% of U.S. ethylene production is from ethane, propane, and butane. This percentage has remained fairly constant throughout the 1980s and it is assumed it will remain at this level. During the same time frame the use of naphtha as a feedstock has more than doubled, supplanting the use of gas oil as a feedstock.

Ethane feed gives the lowest cost of production and the lowest capital investment. As the feeds become successively heavier, cost of production increases as well as the capital investment required. Depending on the cost of feedstock and the value of the co-products, processing heavier feedstocks can lead to lower returns on investment. Table 12 shows the effect on capital investment for various feedstocks as well as for a range of capacities.

Table 11. **U.S. Ethylene Produced from Various Feedstocks, %[a]**

Year	Ethane/propane/ butane	Naphtha	Gas oil
1984	70	10	20
1985	77	10	13
1986	71	16	13
1987	74	15	11
1988	70	25	5
1989	69	26	5
1990	68	27	5
1991	71	24	5
1992	71	24	5
1996	76	20	4

[a] Refs. (115,116 and 118).

Another significant factor affecting capital investment is plant capacity. Prior to 1970, ethylene plant capacity was rarely greater than 300,000 t/yr. During the 1970s and 1980s, technological advances resulted in plants being built with capacities of 500,000–700,000 t/yr. The incentive to build these larger plants was the economic advantages of scale resulting from the reduction in capital requirements per ton of ethylene.

By 1990 it was theoretically possible to build a single-train (no duplication of compressors or other equipment except for cracking heaters) ethylene plant with a capacity of approximately 1,000,000 t/yr. The limitation above this capacity becomes the suction volume to the charge gas compressor. There are reports of two plants operating at 1,200,000 t/yr and one being built in North America with as yet no limitation. Other factors limiting the size of ethylene

Table 12. **Ethylene Plant Investment and Cost of Production as a Function of Feedstock and Plant Capacity[a]**

Plant capacity, t/yr	Ethane	Propane	Butane	Naphtha	Gas oil
		Relative plant investment			
300,000	1.17	1.35	1.40	1.70	1.93
400,000	1.06	1.22	1.27	1.54	1.75
500,000	1.00	1.15	1.20	1.45	1.55
600,000	0.96	1.10	1.15	1.39	1.58
700,000	0.89	1.02	1.07	1.29	1.47
800,000	0.84	0.97	1.01	1.22	1.39
		Relative cost of production			
300,000	1.05	1.15	1.16	1.15	1.48
400,000	1.02	1.11	1.13	1.11	1.43
500,000	1.00	1.09	1.11	1.08	1.40
600,000	0.99	1.08	1.09	1.06	1.38
700,000	0.97	1.07	1.08	1.05	1.37
800,000	0.96	1.06	1.07	1.04	1.35

[a] Factors are per ton of ethylene produced.

plants are that larger equipment items require more costly field fabrication as opposed to shop fabrication, limiting potential savings in investment and increased risk resulting from large initial capital outlay and changing market conditions.

14. Health and Safety Factors

Although ethylene is a colorless gas with a mild odor that is not irritating to the eyes or respiratory system, it is a hydrocarbon and therefore a flammable gas. All vessels must be designed for handling the liquids and gases during operation at the temperatures and pressures that exist, and safety and depressuring valves must be provided to relieve excessive pressure. Releasing of hydrocarbons into the air in large amounts must be avoided because of health and fire hazards. If hydrocarbons must be released into the air, it is done under a blanket of steam. To protect the plant and personnel in case of fire, a complete fire fighting system is provided with tanks grouped to minimize fire and provided with foam makers and deluge systems. Reviews at various stages of a project assure safety is given constant attention in the plant design (see HAZARD ANALYSIS AND RISK ASSESSMENT). An ethylene plant produces liquid, gaseous, and solid wastes that must be disposed of in an environmentally safe manner. Liquid wastes generated within the complex consist of wastewater streams of relatively low organic content, and process wastes of high organic content. Wastewater from various units and operations are segregated according to the wastewater characteristics, such as type of contaminants, concentration, special treatment, or pretreatment requirements. A segregated sewer system allows for the most efficient treatment of the wastewaters.

Atmospheric emissions from the facility are either controlled or fugitive in nature. Controlled emissions are released from process venting, waste incineration, decoking operations, and heater firing. Fugitive emissions occur from product loading and storage and equipment and valve leaks. In general, all continuous process vents are flared or combusted in the furnaces. If required, the process vents are scrubbed prior to flaring to minimize acid gas emissions. Flow monitors are installed in major branches in the flare collection header to monitor process venting. A smokeless flare has a normal destruction efficiency of over 98%.

Solid wastes are treated in a solid waste disposal area to reduce their volume and or toxicity prior to final disposal in a secured landfill. Combustible wastes can be incinerated in a slagging rotary kiln to reduce volume and toxicity.

15. Uses

Almost all ethylene produced is consumed as feedstock for manufacturing other petrochemicals. Only a very small amount has been used in the agricultural industry for ripening fruits. Table 13 lists the principal ethylene derivatives and capacities.

Table 13. **Ethylene Derivatives and World Consumption**[a]

	Actual		Projected avg growth, %/yr
	1991	1996	1996–2001
polyethylene			
LDPE/LLDPE	19250	23026	4.8
HDPE	12618	16928	5.0
ethylene dichloride	8766	9935	4.7
ethylbenzene–styrene	4213	5013	4.9
ethylene oxide	6952	8686	5.6
ethanol	729	687	1.2
EPDM rubber	347	464	1.7
Oligomers	1406	1789	3.2
Vinyl acetate	925	1673	8.5
Acetaldehyde	997	960	−.7
Others	1872	1673	8.5
Total	58075	70245	4.9

[a] Worldwide consumption as ethylene equivalent in 1000 t/yr (115).

Although some ethylene is shipped across the oceans in large quantities, the preference is to ship first-generation products such as polyethylene, ethylbenzene, etc.

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