# Ethylene

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

**Heinz Zimmermann,** Linde Engineering Division, Pullach, Germany

**Roland Walzl,** Linde Engineering Division, Pullach, Germany

## 1. Introduction

Ethylene [*74-85-1*], ethene, $H_2C{=}CH_2$, $M_r$ 28.52, as one of the great building blocks in chemistry is a large-volume petrochemical with a production of approximately 120 × $10^6$ t/a [1–3] in 2008. It has been recovered from coke-oven gas and other sources in Europe since 1930 [4]. Ethylene emerged as a large-volume intermediate in the 1940s when U.S. oil and chemical companies began separating it from refinery waste gas and producing it from ethane obtained from refinery byproduct streams and from natural gas. Since then, ethylene has almost completely replaced acetylene for many syntheses. Ethylene is produced mainly by thermal cracking of hydrocarbons in the presence of steam, and by recovery from refinery cracked gas.

In 2005 total worldwide ethylene production capacity was 112.9 × $10^6$ t, with an actual demand of ca. 105 × $10^6$ t/a [2], which has growth projections of 3.7 to 4.3 % per year worldwide for the period of 2005–2010 [5–7].

The production of ethylene today is based on feedstocks derived from crude oil (→ Oil Refining) or from natural or associated gas (→ Natural Gas). The leading technology applied for production of ethylene is steam cracking, a high temperature pyrolysis in the presence of steam, which has been developed in the 1960s, but the principles have not been changed. Recent developments have been made to increase size and scale of the plants and to improve overall economics. Today's plants can produce up to 1.5 × $10^6$ t/a of ethylene in a single-train plant. Alternatives have been developed such as methanol to olefins, in which methanol derived from

DOI: 10.1002/14356007.a10_045.pub3

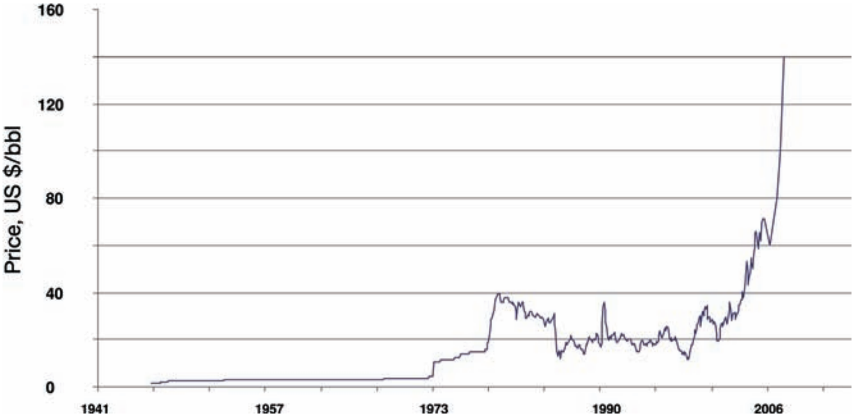


**Figure 1.** Crude-oil price development [8–10]

natural gas (→ Gas Production, 5. Examples of Complex Gas Production Plants, Chap. 1) is converted finally into ethylene. However, none of the alternative technologies has the economics to be a challenge for the well-established steam-cracking process until today.

With the development of the prices for crude oil in 2007 and especially 2008, when prices increased from approximately 60 US$/bbl to 140 US $/bbl [8–10] (Fig. 1), alternative technologies for production of ethylene have to been re-evaluated. A second aspect that could trigger a significant change is the $CO_2$ aspect, as the production of ethylene produces significant amounts of $CO_2$ and will be subject to $CO_2$ trading schemes in the future in several areas.

These recent changes have started several developments in the petrochemical industry, such as shift of huge production capacities to areas with advantaged feedstocks (Middle East, South America, Central Asia, etc.) but also fuelled the search for alternative production routes for commercial-scale ethylene production. One of the most promising routes is the dehydration of ethanol, a reaction known for quite some time, but historically not used for large-scale ethylene production, due to economics and availability of raw materials. However, due to the dramatically increasing production of bioethanol worldwide, this route has to be reconsidered as an alternative to conventional ethylene production from fossil raw materials. In addition, the dependence of the ethylene value chain on crude-oil price developments could be interrupted as bioethanol offers a production from renewable raw materials.

More than half of the production of ethylene is used for the production of polyethylene (→ Polyethylene), one of the most important plastic materials today. The market grows continuously with an average rate of 4 % worldwide and can be related to the gross national product growth in an area or a certain country.

In steam crackers, per ton of ethylene significant amounts of $CO_2$ are produced, which range from 1 – 1.6 t/t, depending on the raw material used for cracking. The annual growth of the worldwide ethylene production is typically in the range of $5 - 6 \times 10^6$ t/a, which translates into additional $CO_2$ emissions of $5 - 9 \times 10^6$ t/a. In addition, due to the high temperature pyrolisis $NO_x$ emissions are produced when using the conventional technology.

Besides the major industrial applications of ethylene, a small portion is converted into ethanol by hydration and has been a source of synthetic ethanol for quite some time. However, with the increase in oil prices and consequently the increase of raw material costs for ethylene production, the reverse reaction has become of significant interest.

Ethylene units are centers of petrochemical complexes in which ethylene is transferred into transportable intermediates or semifinished products with ethylene capacities of up to $1.5 \times 10^6$ t/a and significant amounts of high-value byproducts. These sizes are required in order to utilize the economy of scale for production of ethylene. In a world-scale plant of such scale, ethylene can be produced at much lower specific costs than in smaller units.

Small-scale ethylene production in quantities of 100 × $10^3$ – 200 × $10^3$ t/a is in most cases not economical as many of the byproducts are produced in quantities to small for marketing. However, world-scale plants for EDC/PVC require ethylene in quantities of 100 × $10^3$ – 200 × $10^3$ t/a only and ethylene supply from standalone crackers of this size is not feasible in most cases.

## 2. Physical Properties

Ethylene is a colorless flammable gas with a sweet odor. The physical properties of ethylene are as follows:

| | |
|---|---|
| *mp* | −169.15 °C |
| *bp* | −103.71 °C |
| Critical temperature, $T_c$ | 9.90 °C |
| Critical pressure, $P_c$ | 5.117 MPa |
| Critical density | 0.21 g/$cm^3$ |
| Density | |
| at *bp* | 0.57 g/$cm^3$ |
| at 0 °C | 0.34 g/$cm^3$ |
| Gas density at STP | 1.2603 g/L |
| Density relative to air | 0.9686 |
| Molar volume at STP | 22.258 L |
| Surface tension | |
| at *bp* | 16.5 mN/m |
| at 0 °C | 1.1 mN/m |
| Heat of fusion | 119.5 kJ/kg |
| Heat of combustion | 47.183 MJ/kg |
| Heat of vaporization | |
| at *bp* | 488 kJ/kg |
| at 0 °C | 191 kJ/kg |
| Specific heat | |
| of liquid at *bp* | 2.63 kJ $kg^{-1}$ $K^{-1}$ |
| of gas at $T_c$ | 1.55 kJ $kg^{-1}$ $K^{-1}$ |
| Enthalpy of formation | 52.32 kJ/mol |
| Entropy | 0.220 kJ $mol^{-1}$ $K^{-1}$ |
| Thermal conductivity | |
| at 0 °C | $177 \times 10^{-4}$ W $m^{-1}$ $K^{-1}$ |
| at 100 °C | $294 \times 10^{-4}$ W $m^{-1}$ $K^{-1}$ |
| at 400 °C | $805 \times 10^{-4}$ W $m^{-1}$ $K^{-1}$ |
| Viscosity of liquid | |
| at *mp* | 0.73 mPa · s |
| at *bp* | 0.17 mPa · s |
| at 0 °C | 0.07 mPa · s |
| of gas | |
| at *mp* | $36 \times 10^{-4}$ mPa · s |
| at 0 °C | $93 \times 10^{-4}$ mPa · s |
| at 150 °C | $143 \times 10^{-4}$ mPa · s |
| Vapor pressure | |
| at −150 °C | 0.002 MPa |
| at *bp* | 0.102 MPa |
| at −50 °C | 1.10 MPa |
| at 0° | 4.27 MPa |
| Explosive limits in air at 0.1 MPa and 20 °C | |
| lower (LEL) | 2.75 vol% or 34.6 g/$cm^3$ |
| upper (UEL) | 28.6 vol% or 360.1 g/$cm^3$ |
| Ignition temperature | 425–527 °C |

## 3. Chemical Properties

The chemical properties of ethylene result from the carbon–carbon double bond, with a bond length of 0.134 nm and a planar structure. Ethylene is a very reactive intermediate, which can undergo all typical reactions of a short-chain olefin. Due to its reactivity ethylene gained importance as a chemical building block. The complex product mixtures that have to be separated during the production of ethylene are also due to the reactivity of ethylene.

Ethylene can be converted to saturated hydrocarbons, oligomers, polymers, and derivatives thereof. Chemical reactions of ethylene with commercial importance are: addition, alkylation, halogenation, hydroformylation, hydration (see Section 5.4), oligomerization, oxidation, and polymerization.

The following industrial processes are listed in order of their 2000 worldwide ethylene consumption [11]:

1. Polymerization to low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE)
2. Polymerization to high-density polyethylene (HDPE)
3. Addition of chlorine to form 1,2-dichloroethane
4. Oxidation to oxirane [*75-21-8*] (ethylene oxide) over a silver catalyst
5. Reaction with benzene to form ethylbenzene [*100-41-4*], which is dehydrogenated to styrene [*100-42-5*]
6. Oxidation to acetaldehyde
7. Hydration to ethanol (Section 5.4)
8. Reaction with acetic acid and oxygen to form vinyl acetate
9. Other uses, including production of linear alcohols, linear olefins, and ethylchloride [*75-00-3*], and copolymerization with propene to make ethylene–propylene (EP) and ethylene–propylene–diene (EPDM) rubber

**Table 1.** Raw materials for ethylene production (as a percentage of total ethylene produced)

| Raw material | USA 1979 | USA 1995 | Western Europe 1981 | Western Europe 1995 | Japan 1981 | Japan 1993 |
|---|---|---|---|---|---|---|
| Refinery gas | 1 | 4 |  | 3 |  |  |
| LPG, NGL | 65 | 76 | 4* | 17 | 10* | 3* |
| Naphtha | 14 | 11 | 80 | 71 | 90 | 97 |
| Gas oil | 20 | 9 | 16 | 9 | 0 | 0 |

*Including refinery gas

## 4. Raw Materials

Table 1 lists the percentage of ethylene produced worldwide from various feedstocks for 1981 and 1992 [12]. In Western Europe and Japan, over 80 % of ethylene is produced from naphthas — the principal ethylene raw materials.

A shift in feedstocks occurred for the period from 1980 to 1991. In the United States and Europe larger amounts of light feedstocks(liquefied petroleum gas LPG: propane + butanes) and NGL (natural gas liquids: ethane, propane, butane) are used for ethylene production, whereas in Japan more naphtha was used in 1995 compared to 1981. The use of gas oils for ethylene production decreased slightly during the 1980s. Since 2000 a huge amount of new capacities have been installed in the Middle East based on ethane as feedstock, increasing the share of ethane-based production significantly (see Fig. 2 and Table 2). This trend will continue in the coming years due to favorable production costs for ethane-based crackers. As a result the production of propene from new crackers will decrease requiring different ways of production of this cracker coproduct.

Ethane [*74-84-0*] is obtained from wet natural gases and refinery waste gases. It may be cracked alone or as a mixture with propane. Propane [*74-98-6*] is obtained from wet natural gases, natural gasolines, and refinery waste gases. Butanes are obtained from natural gasolines and refinery waste gases.

Naphthas, which are the most important feedstocks for ethylene production, are mixtures of hydrocarbons in the boiling range of 30–200 °C. Processing of light naphthas (boiling range 30–90 °C, full range (FR) naphthas (30–200 °C) and special cuts ($C_6$–$C_8$ raffinates) as feedstocks is typical for naphtha crackers.

A natural-cut full-range naphtha contains more than 100 individual components, which can be detected individually by gas chromatography (GC). Depending on the origin naphtha quality can vary over a wide range, which necessitates quality control of the complex feed mixtures. Characterization is typically based on boiling range; density; and content of paraffins (*n*-alkanes), isoalkanes, olefins, naphthenes, and aromatics ( PIONA analysis) by carbon number. This characterization can be carried out by GC analysis or by a newly developed infrared method [13]. Full characterization of feedstocks is even more important when production is based on varying feedstocks, e.g. feedstocks of different origins purchased on spot markets.

The quality of a feedstock is depending on the potential to produce the target products (ethylene and propylene). Simple yield correlations for these products can be used to express the quality

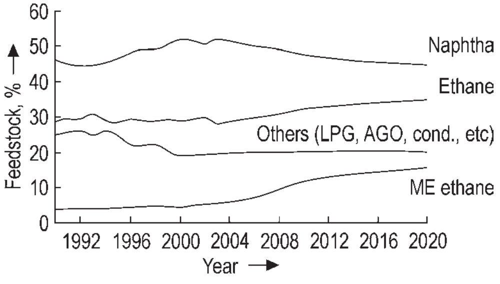


**Figure 2.** Feedstocks used for ethylene production

**Table 2.** World consumption of feedstocks for ethylene production in 2002 (as percentage of total ethylene produced) [11]

| | |
|---|---|
| Ethane | 29 |
| Propane | 8 |
| Butane | 3 |
| Naphtha | 53 |
| Gas oil | 6 |
| Others | 1 |

of a feedstock in a simple figure, the quality factor, which indicates whether yields of the target products are high or low, with aromatic feedstocks being poor and saturated feedstocks being good feedstocks.

Quality characterization factors for naphthas have been developed, which indicate the aromatics content by empirical correlation. Since aromatics contribute little to ethylene yields in naphtha cracking, a rough quality estimate can be made for naphthas with a typical weight ratio of *n*- to isoparaffins of 1–1.1. The *K* factor is defined as [14]:

$$K = \frac{(1.8T_\mathrm{k})^{1/3}}{d}$$

where $T_\mathrm{k}$ is the molal average boiling point in K. Naphthas with a *K* factor of 12 or higher are considered saturated; those below 12 are considered naphthenic or aromatic. The *K* factor does not differentiate between iso- and *n*-alkanes. The U.S. Bureau of Mines Correlation Index (BMCI) [15] can also be used as a rough quality measure of naphthas:

$$\mathrm{BMCI} = 48640/T + 473.7d - 456.8$$

where *T* is the molal average boiling point in K and *d* is the relative density $d^{15.6}_{15.6}$. A high value of BMCI indicates a highly aromatic naphtha; a low value, a highly saturated naphtha.

Gas condensates are very similar to naphthas in composition with the main difference of having no sharp boiling endpoint. A typical boiling curve of gas condensates is shown in Figure 3. Gas condensates gain importance as raw material for ethylene production because they are cheaper than naphtha.

Gas oils are feedstocks that are gaining importance in several areas of the world. Gas oils used for ethylene production are crude oil fractions in the boiling range of 180–350 °C (atmospheric gas oils, AGO) and 350–600 °C (vacuum gas oils, VGO). In contrast to naphtha and lighter gas feeds, these feedstocks can not be characterized by individual components.

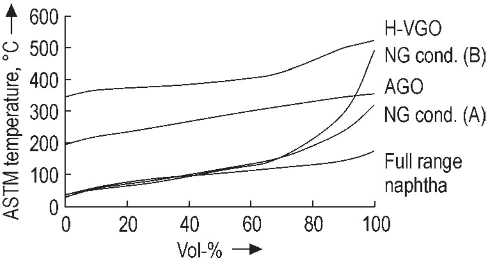


**Figure 3.** Boiling curves of liquid cracker feedstocks VGO = Vacuum gas oil; AGO = Atmospheric gas oil

Gas chromatography coupled with mass spectrometry (GC–MS) or high performance liquid chromatography (HPLC) allow the analysis of structural groups, i.e., the percentage of paraffins, naphthenes, olefins, monoaromatics, and polyaromatics in the gas oil, and can be used to determine the quality of the hydrocarbon fraction. If this information is used together with data such as hydrogen content, boiling range, refractive index, etc., the quality can be determined quite accurately. A rough estimate of feed quality can be made by using the BMCI or the calculated cetane number of a gas oil. The cetane number, normally used to calculate the performance of diesel fuels, is an excellent quality measure, since it is very sensitive to the *n*-paraffin content, which is one of the key parameters for the ethylene yield. The cetane number CN is calculated as follows [16]:

$$\mathrm{CN} = 12.822 + 0.1164\,\mathrm{CI} + 0.012976\,\mathrm{CI}^2$$

where $\mathrm{CI} = 0.9187 \quad (T_{50} \quad /10)^{1.26687} (n_\mathrm{D}^{20}/100)^{1.44227}$, where $T_{50}$ is the volume average boiling point in°C and $n_\mathrm{D}^{20}$ the refractive index at 20 °C

# 5. Production

## 5.1. Ethylene from Pyrolysis of Hydrocarbons

The bulk of the worldwide annual commercial production of ethylene is based on thermal cracking of petroleum hydrocarbons with steam; the process is commonly called pyrolysis or steam cracking. The principal arrangement of such a cracking reactor is shown in Figure 4, a photograph of the furnace section of a modern ethylene plant in Figure 5. The technology has been applied for more than 50 years with permanent improvements in details.

A hydrocarbon stream is heated by heat exchange against flue gas in the convection section, mixed with steam, and further heated to incipient cracking temperature (500–680 °C,

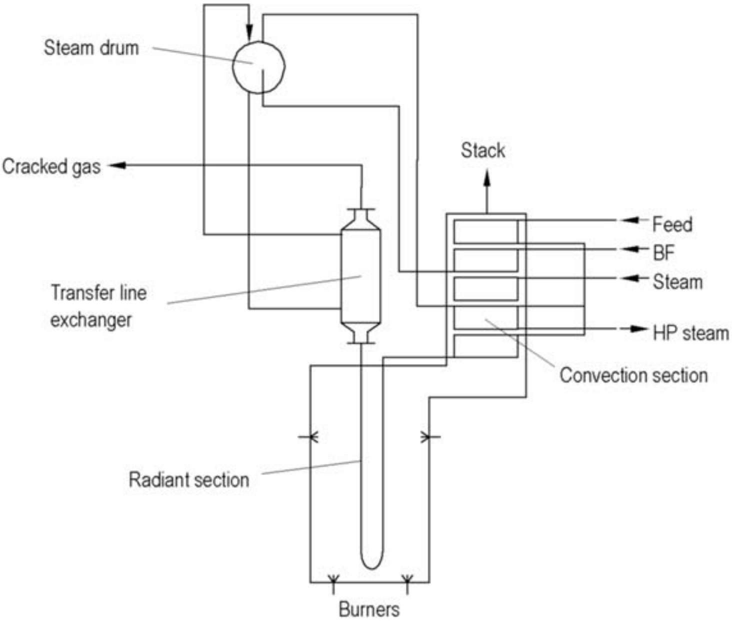


**Figure 4.** Principal arrangement of a cracking furnace

depending on the feedstock). The stream then enters a fired tubular reactor (radiant tube or radiant coil) where, under controlled residence time, temperature profile, and partial pressure, it is heated from 500–650 to 750–875 °C for 0.1–0.5 s. During this short reaction time hydrocarbons in the feedstock are cracked into smaller molecules; ethylene, other olefins, and diolefins are the major products. Since the conversion of saturated hydrocarbons to olefins in the radiant tube is highly endothermic, high energy input rates are needed. The reaction products leaving the radiant tube at 800–850 °C are cooled to 550–650 °C within 0.02–0.1 s to prevent degradation of the highly reactive products by secondary reactions.

**Figure 5.** Furnace section of a modern ethylene plant

The resulting product mixtures, which can vary widely, depending on feedstock and severity of the cracking operation, are then separated into the desired products by using a complex sequence of separation and chemical-treatment steps.

The cooling of the cracked gas in the transfer-line exchanger is carried out by vaporization of high-pressure boiler feed water (BFW, $p = 6$–12 MPa), which is separated in the steam drum and subsequently superheated in the convection section to high-pressure superheated steam (HPSS, 6–12 MPa).

### 5.1.1. Cracking Conditions

Commercial pyrolysis of hydrocarbons to ethylene is performed almost exclusively in fired tubular reactors, as shown schematically in Figure 4. These furnaces can be used for all feedstocks from ethane to gas oil, with a limitation in the end point of the feedstock of 600 °C. Higher boiling materials can not be vaporized under the operating condition of a cracking furnace.

Increasing availability of heavy gas oil fractions, due to a shift in demand to lighter fractions, offers cost advantages for processing heavy feedstocks in some areas of the world. Furthermore, the availability of large quantities of residual oil have led some companies to investigate crude oil and residual oils as ethylene sources. Such feedstocks cannot be cracked in conventional tubular reactors. Various techniques employing fluidized beds, molten salts, recuperators, and high-temperature steam have been investigated, but none of these have attained commercial significance [17]. Recently cracking of gas condensates instead of naphthas has gained importance, as some gas condensates offer yield and cost advantages compared to naphthas. Some gas condensates are contaminated with Hg or As, which need to be removed prior to cracking, as these contaminants could lead to corrosion (Hg) of aluminum heat exchangers used in the separation section or to poisoning (As) of hydrogenation catalysts [18].

Pyrolysis of hydrocarbons has been studied for years. Much effort has been devoted to mathematical models of pyrolysis reactions for use in designing furnaces and predicting the products obtained from various feedstocks under different furnace conditions. Three major types of model are used: empirical or regression, molecular, and mechanistic models [19].

Today, mechanistic computer models, which are available from various companies, are used for design, optimization and operation of modern olefin plants. Sophisticated regression models are also used, mainly by operators, and offer the advantage of a much lower computer performance requirements than mechanistic models.

The regression models are based on a data set, which can consist of historical data or calculated data. Depending on the quality of the data base the empirical regression models can be of sufficient accuracy for most operating problems, within the range of the data field. These models can be run on small computers and are well suited for process computer control and optimization.

Molecular kinetic models that use only apparent global molecular reactions and thus describe the main products as a function of feedstock consumption have been applied with some success to the pyrolysis of simple compounds such as ethane, propane, and butanes.

For example, cracking of propane can be described as

$$C_3H_8 \rightarrow a\,H_2 + b\,CH_4 + c\,C_2H_4 + d\,C_3H_6 + e\,C_4H_8 + f\,C_{5+}$$

where $a$, $b$, $c$, $d$, $e$, $f$ are empirical factors depending on the conversion of propane.

Gross oversimplification is required if these models are applied to complex mixtures such as naphthas or gas oils, but some success has been attained even with these materials.

Advances have been made in mechanistic modeling of pyrolysis, facilitated by the availability of more accurate thermochemical kinetic and pyrolysis data and of high-speed computers. The major breakthrough in this area, however, has been the development of methods to integrate large systems of differential equations [20–22].

Mechanistic models need less experimental data and can be extrapolated. The accuracy of these models is very good for most components, but they require permanent tuning of the kinetic parameters, especially for computing the cracked-gas composition for ultrashort residence times. The main application for mechanistic models is the design of cracking furnaces and complete ethylene plants. The accuracy of the models has been improved, driven by the competition between the contractors for ethylene plants. A number of mechanistic models are used today in the ethylene industry, describing the very complex kinetics with hundreds of kinetic equations [23–25].

To demonstrate the complexity of the chemical reactions, the cracking of ethane to ethylene is discussed here in detail. A simple reaction equation for ethane cracking is:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (1)$$

If this were the only reaction, the product at 100 % conversion would consist solely of ethylene and hydrogen; at lower conversion, ethylene, hydrogen and ethane would be present. In fact, the cracked gas also contains methane, acetylene, propene, propane, butanes, butenes, benzene, toluene, and heavier components. This reaction (Eq. 1) is clearly not the only reaction occurring.

In the 1930s, the free-radical mechanism for the decomposition of hydrocarbons was established [26]. Although the free-radical treatment does not explain the complete product distribution, even for a compound as simple as ethane, it has been extremely useful. Ethane cracking represents the simplest application of the free-radical mechanism. Ethane is split into two methyl radicals in the chain initiation step (Eq. 2). The methyl radical reacts with an ethane molecule to produce an ethyl radical (Eq. 3), which decomposes to ethylene and a hydrogen atom (Eq. 4). The hydrogen atom reacts with another ethane molecule to give a molecule of hydrogen and a new ethyl radical (Eq. 5).

*Initiation*

$$C_2H_6 \rightarrow CH_3^{\bullet} + CH_3^{\bullet} \tag{2}$$

*Propagation*

$$CH_3^{\bullet} + C_2H_6 \rightarrow CH_4 + C_2H_5^{\bullet} \tag{3}$$

$$C_2H_5^{\bullet} \rightarrow C_2H_4 + H^{\bullet} \tag{4}$$

$$H^{\bullet} + C_2H_6 \rightarrow H_2 + C_2H_5^{\bullet} \tag{5}$$

If reactions (4) and (5) proceed uninterrupted, the molecular reaction in Equation (1) results. If only reactions (3)–(5) occurred, the cracked gas would contain traces of methane (Eq. 3) and equimolar quantities of ethylene and hydrogen with unreacted ethane. This is not observed.

Reactions (3) and (4) terminate if either an ethyl radical or a hydrogen atom reacts with another radical or atom by reactions such as:

*Termination*

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \tag{6}$$

$$CH_3^{\bullet} + H^{\bullet} \rightarrow CH_4 \tag{7}$$

$$H^{\bullet} + C_2H_5^{\bullet} \rightarrow C_2H_6 \tag{8}$$

$$C_2H_5^{\bullet} + CH_3^{\bullet} \rightarrow C_3H_8 \tag{9}$$

$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10} \tag{10}$$

On termination of chain propagation, new methyl or ethyl radicals or a new hydrogen atom must be generated (Eqs. 2–4) to start a new chain. Thus, every time a new chain is initiated, a molecule of methane is formed (Eq. 3) and a molecule of ethylene is produced (Eq. 4). Other normal and branched-chain alkanes decompose by a similar, but more complex, free-radical mechanism [27]. The number of possible free radicals and reactions increases rapidly as chain length increases.

The free-radical mechanism is generally accepted to explain hydrocarbon pyrolysis at low conversion [26]. As conversion and concentrations of olefins and other products increase, secondary reactions become more significant. Partial pressures of olefins and diolefins increase, favoring condensation reactions to produce cyclodiolefins and aromatics. The cracking of heavy feed, such as naphthas or gas oils, often proceeds far enough to exhaust most of the crackable material in the feedstock.

The reaction scheme with heavier feeds is much more complex than with gaseous feedstocks, due to the fact the hundreds of reactants (feed components) react in parallel and some of those components are formed as reaction products during the reaction. Since the radicals involved are relatively short lived, their concentration in the reaction products is rather low.

Radical decomposition is one of the most important types of reaction and it directly produces ethylene according to the following scheme:

*Radical decomposition*

$$RCH_2CH_2CH_2^{\bullet} \rightarrow RCH_2^{\bullet} + C_2H_4 \tag{11}$$

This β-scission reaction produces a shorter radical ($RCH_2^{\bullet}$) and ethylene. Radicals normally decompose in the β-position, where the C–C bond is weaker due to electronic effects. Large radicals are more stable than smaller ones and can therefore undergo isomerization.

*Radical isomerization*

$$RCH_2CH_2CH_2^{\bullet} \rightarrow RCH_2\dot{C}HCH_3 \tag{12}$$

The free-radical decomposition of *n*-butane (Eqs. 12–14) results in the molecular equation (Eq. 15):

$$n\text{-}C_4H_{10} + H^{\bullet} \rightarrow n\text{-}C_4H_9^{\bullet} + H_2 \tag{14}$$

$$n\text{-}C_4H_9^{\bullet} \rightarrow C_2H_4 + C_2H_5^{\bullet} \tag{15}$$

$$C_2H_5^{\bullet} \rightarrow C_2H_4 + H^{\bullet} \qquad (16)$$

$$n\text{-}C_4H_{10} \rightarrow 2\,C_2H_4 + H_2 \qquad (17)$$

Reactions like (1) and (15) are highly endothermic. Reported values of $\Delta H$ at 827 °C are $+144.53$ kJ/mol for Equation (1) and $+232.244$ kJ/mol for Equation (15).

The mathematical description of these complex systems requires special integration algorithms [28]. Based on the pseudo steady state approximation, the chemical reactions can be integrated and the concentration of all components at each location of the reactor (cracking coil) can be computed [29, 30].

In a generalized and very simplified form the complex kinetics of cracking of hydrocarbons (ethane to gas oil) in steam crackers can be summarized as follows:

| Primary reactions | | Secondary reactions |
|---|---|---|
| Feedstock | ~ ethylene | ~ $C_4$ products |
| /steam | propene | $C_5$ products |
| | acetylene | $C_6$ products |
| | hydrogen | aromatics |
| | methane | $C_7$ products |
| | etc. | heavier products |

The fundamentals of furnace design and the main influences of the different parameters can be understood even with this simplified mechanism:

- Residence time: From the above scheme it is clear that a long residence time favors the secondary reactions, whereas a short residence time increases the yields of the primary products, such as ethylene and propylene.
- Partial pressure: Since most of the secondary products result from reactions in which the number of molecules decreases, increasing the pressure favors the secondary products. One function of the steam present in the system is to reduce the hydrocarbon partial pressure and thus favor the formation of primary products.
- Temperature and temperature profiles: The oligomerization reactions involved in the formation of secondary products are favored by lower temperatures; therefore, special temperature profiles are applied along the cracking coil to avoid long residence times at low temperatures.

Most commercial pyrolysis to produce ethylene is carried out in fired tubular reactors in which the temperature of the reactant increases continuously from the inlet to the outlet. Typical inlet temperatures are 500–680 °C, depending on the material being processed. Typical outlet temperatures are 775–875 °C.

Modern cracking furnaces are designed for rapid heating at the radiant coil inlet, where reaction rate constants are low because of the low temperature. Most of the heat transferred simply raises the reactant from the inlet temperature to the necessary reaction temperature. In the middle of the coil, the rate of temperature rise is lower, but cracking rates are appreciable. In this section,the endothermic reaction absorbs most of the heat transferred to the mixture. At the coil outlet, the rate of temperature rise again increases but never becomes as rapid as at the inlet.

The designers of cracking coils try to optimize the temperature and pressure profiles along the radiant coils to maximize the yield of valuable products yields by special coil design that allows rapid temperature increase in the inlet section and low pressure drops in the outlet section of the cracking coils.

Typical process gas temperature profiles along the radiant coil of modern ethylene furnaces are shown in Figure 6 for ethane, propane, butane, and naphtha cracking.

The quantity of steam used, generally expressed as steam ratio (kilograms of steam per kilogram of hydrocarbon), varies with feedstock, cracking severity, and design of the cracking coil. Typical steam ratios used at a coil outlet pressure of 165–225 kPa (1.65–2.25 bar) for various feedstocks are:

| | |
|---|---|
| Ethane | 0.25–0.35 |
| Propane | 0.30–0.40 |
| Naphthas | 0.40–0.50 |
| Gas condensates | 0.40–0.60 |
| Atmospheric gas oils (cut: 180–350 °C) | 0.60–0.70 |
| Hydrocracker bottoms (cut: 350–600 °C) | 0.70–0.85 |

Steam dilution lowers the hydrocarbon partial pressure, thereby enhancing olefin yield. It also

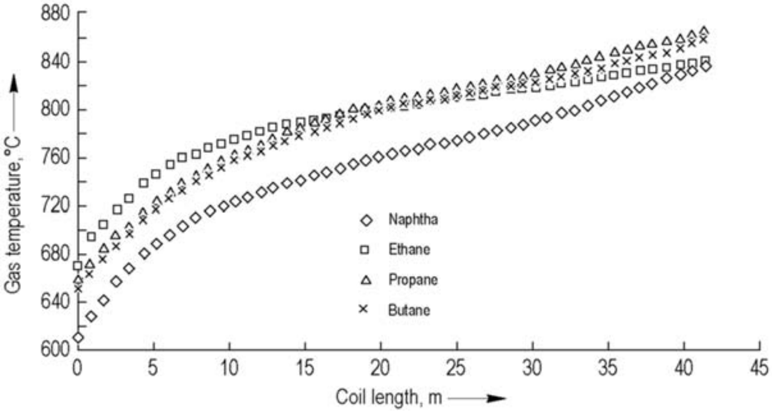


**Figure 6.** Process gas temperatures along radiant coils

reduces the partial pressure of high-boiling, high-molecular-mass aromatics and heavy tarry materials, reducing their tendency to deposit and form coke in the radiant tubes and to foul quench-exchanger tubes. Steam reduces the fouling of the radiant tubes by reacting with deposited coke to form carbon monoxide, carbon dioxide, and hydrogen in a water gas reaction, but as can be seen from the concentration of carbon monoxide in the cracked gas (normally ca. 100 ppm), only to a limited extent.

The sulfur content of the feed is important, since sulfur passivates active Ni sites of the cracking coil material by forming nickel sulfides, which do not catalyze coke gasification, in contrast to nickel metal and nickel oxides. This explains why CO production is high (up to 1 % in the cracked gas) if the feedstock is free of sulfur. To prevent this effect, ca. 20 ppm of sulfur (e.g., as dimethyl sulfide) are added to sulfur-free feedstocks.

Feedstock composition is another important consideration in commercial production of ethylene. Ethylene-plant feedstocks generally contain straight- and branched-chain alkanes, olefins, naphthenes, and aromatics. Ethylene and other olefins are formed primarily from alkanes and naphthenes in the feed. *n*-Alkanes are the preferred component for high ethylene yields, and those containing an even number of carbon atoms give slightly better ethylene yields than odd-numbered ones. *n*-Alkanes also produce propene, whose yield decreases with increasing chain length.

Isoalkanes, in general, produce much smaller yields of ethylene and propene than *n*-alkanes. They give higher yields of hydrogen and methane, and of $C_4$ and higher olefins. Isoalkanes tend to produce more propene than ethylene compared to *n*-alkanes.

Olefin and diolefin yields from cyclopentane, methylcyclopentane, and cyclohexane have been reported [27]; methylcyclopentane and cyclohexane give substantial amounts of butadiene.

Simple and condensed ring aromatics produce no ethylene. Benzene is stable under normal cracking conditions. It is formed during cracking and remains unchanged in the feed. Other aromatics yield primarily higher molecular mass components. Aromatics with long side chains, such as dodecylbenzene, yield ethylene and other olefins by side-chain cracking. The aromatic nucleus still, however, generally produces pyrolysis fuel oil and tar.

In summary, maximum ethylene production requires:

- A highly saturated feedstock
- High coil outlet temperature
- Low hydrocarbon partial pressure
- Short residence time in the radiant coil
- Rapid quenching of the cracked gases

These conditions maximize the yield of olefins and minimize the yield of methane and high molecular mass aromatic components.

Cracking conditions and yield structure are often optimized for economic reasons in plant design and operation; even small changes in cracked gas composition influence the overall plant economics dramatically.

The dilution steam ratio is in most cases at the minimum of the range for the specified feedstock, due to the contribution of the dilution steam to the production costs.

### 5.1.2. Heat Requirements for Hydrocarbon Pyrolysis

Primary hydrocarbon pyrolysis reactions are endothermic; heat requirements are determined by feedstock and cracking conditions. The temperature required to attain a given reaction rate decreases as the carbon chain length in the feedstock increases. Thus, the enthalpy required to reach cracking temperature depends on feedstock and cracking conditions.

Heat requirements for hydrocarbon pyrolysis can be divided into three components:

1. The enthalpy required to heat the feedstock, including the latent heat of vaporization of liquids
2. The endothermic heat of cracking
3. The enthalpy required to heat the cracked gas from the radiant-coil inlet temperature to the radiant-coil outlet temperature

The first is accomplished in the convection section of the furnace; the last two, in the radiant section. Enthalpies (1) and (3) can be calculated from standard heat-capacity data; they represent 25–60 % of total process heat input in the furnace as the feedstock changes from ethane to gas oils [27].

A typical heat balance for a modern naphtha furnace including the transfer-line exchanger (TLE) is shown in Figure 7.

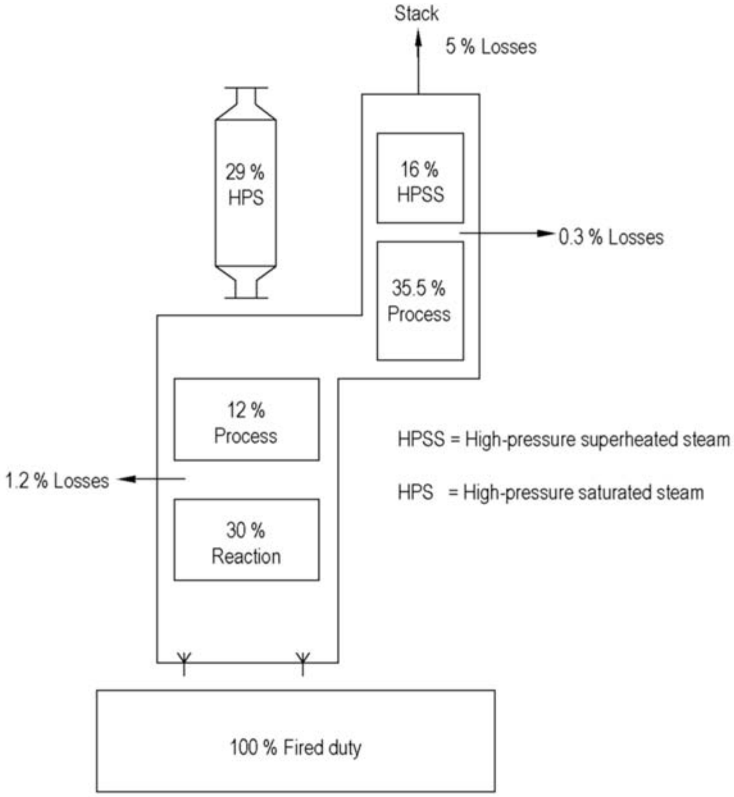


**Figure 7.** Heat balance of a naphtha cracking furnace

The endothermic heat of cracking is most simply calculated from heats of formation by the following equation:

$$\Delta H_r = \Delta H_p - \Delta H_f$$

where $\Delta H_r$ = endothermic heat of cracking, kJ/kg; $\Delta H_p$ = heat of formation of the cracked products, kJ/kg; and $\Delta H_f$ = heat of formation of the feed, kJ/kg.

Heats of formation for some alkanes, olefins, naphthenes, and aromatics are as follows (in kJ/kg) [31]:

| | |
|---|---|
| Hydrogen | 0.0 |
| Methane | −5646.3 |
| Ethane | −3548.1 |
| Ethylene | 1345.3 |
| Acetylene | 8540.7 |
| Propane | −2949.9 |
| Propene | −17.9 |
| Methylacetylene | 4317.1 |
| Propadiene | 4496.8 |
| *n*-Butane | −2694.4 |
| Isobutane | −2827.5 |
| 1-Butene | −459.4 |
| *cis*-2-Butene | −649.5 |
| *trans*-2-Butene | −668.2 |
| Isobutene | −746.5 |
| Ethylacetylene | 2720.4 |
| 1,3-Butadiene | 1721.8 |
| Benzene | 783.6 |
| Toluene | 243.4 |
| Cyclopentane | −1611.3 |
| Methylcyclopentane | −1722.6 |
| Cyclohexane | −1846.4 |
| Methylcyclohexane | −1890.3 |

As the alkane chain length increases, the heat of formation approaches 1800 kJ/kg asymptotically. Ethane, the most refractory alkane besides methane, has the most endothermic heat of cracking, +4893 kJ/kg. The corresponding figure for propane is +4295 kJ/kg and for a high-molecular-mass *n*-alkane, ca. 1364 kJ/kg.

Endothermic heat of cracking increases with degree of saturation of the feed; as conversion increases, secondary condensation products increase. These products have less negative heats of formation than alkanes, or positive heats of formation.

### 5.1.3. Commercial Cracking Yields

Determining the complete yield patterns (gas and liquid products) for a commercial cracking furnace requires a standardized procedure, especially if the feedstock is changed from ethane to naphtha and gas oil. A homogeneous sample is withdrawn from the furnace effluent, quenched, and separated into gaseous and liquid fractions. These are analyzed separately and then combined to give a complete cracked-gas analysis.

The material balance is obtained by matching the hydrogen, carbon, and sulfur content of the feedstock with that of the cracked gas. This type of analysis is time-consuming. In a faster system, gas–liquid separation is eliminated [32] or only a gas-phase analysis is taken. Due to many sources of errors, series of samples have to be taken and analyzed. Statistical methods are used to check the quality of the results.

For gas feedstocks, conversion is used as a measure of the severity of cracking:

$$\text{Conversion} = (C_{n,\text{in}} - C_{n,\text{out}}/C_{n,\text{in}})$$

where $C_{n,\text{in}}$ = quantity of component *n* at inlet in kg/h and $C_{n,\text{out}}$ = quantity of component *n* at outlet in kg/h.

For liquid feedstocks the severity is defined as the ratio of propylene to ethylene (on weight basis) P/E or as ratio of methane to propylene M/P. Both ratios P/E and M/P are a linear function of temperature over a wide range and can be measured with much higher accuracy than the apparent bulk coil outlet temperature of a cracking furnace. The use of P/E and M/P ratios for severity definition is accepted in industry.

**Ethane.** Ethane is cracked commercially in all types of furnaces, from long residence time to short residence time. However, since ethane is a very stable paraffin, cracking temperatures at the coil inlet typically are higher than for other hydrocarbons. For ethane the coil inlet temperatures are in the range of 650–680 °C. Typical conversion ranges of commercial furnaces are 60–75 %, with 67–70% conversion being a typical figure for modern designs.

Table 3 lists yields for ethane cracking at various residence times. There is a slight increase in yield at short residence times. However, as the run length of short-residence-time ethane furnaces is low (Fig. 8) and yield improvement is moderate, application of short-residence-time furnaces for ethane cracking is not feasible in most cases. In certain economic scenarios with limited quantity of feedstock the application of

**Table 3.** Yields from ethane cracking with various residence times

| | | | | | |
|---|---|---|---|---|---|
| Conversion, kg/kg | | 65.01 | 64.97 | 65.01 | 65.01 |
| Steam dilution, kg/kg | | 0.3 | 0.3 | 0.3 | 0.3 |
| Residence time, s | | 0.4607 | 0.3451 | 0.186 | 0.1133 |
| $H_2$ | wt % | 4.04 | 4.05 | 4.09 | 4.12 |
| CO | wt % | 0.04 | 0.04 | 0.03 | 0.03 |
| $CO_2$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $H_2S$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $CH_4$ | wt % | 3.75 | 3.52 | 3.19 | 2.84 |
| $C_2H_2$ | wt % | 0.44 | 0.47 | 0.54 | 0.75 |
| $C_2H_4$ | wt % | 51.88 | 52.31 | 52.85 | 53.43 |
| $C_2H_6$ | wt % | 34.99 | 35.03 | 34.99 | 34.99 |
| $C_3H_4$ | wt % | 0.02 | 0.02 | 0.02 | 0.02 |
| $C_3H_6$ | wt % | 1.22 | 1.13 | 1.06 | 0.97 |
| $C_3H_8$ | wt % | 0.12 | 0.12 | 0.12 | 0.13 |
| $C_4H_4$ | wt % | 0.05 | 0.05 | 0.05 | 0.06 |
| $C_4H_6$ | wt % | 1.80 | 1.80 | 1.79 | 1.65 |
| $C_4H_8$ | wt % | 0.19 | 0.19 | 0.18 | 0.16 |
| $C_4H_{10}$ | wt % | 0.21 | 0.21 | 0.21 | 0.22 |
| Benzene | wt % | 0.55 | 0.47 | 0.38 | 0.26 |
| Toluene | wt % | 0.08 | 0.07 | 0.06 | 0.04 |
| Xylenes | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| Ethylbenzene | wt % | 0.01 | 0.00 | 0.00 | 0.00 |
| Styrene | wt % | 0.03 | 0.02 | 0.02 | 0.01 |
| Pyrolysis gasoline | wt % | 0.35 | 0.32 | 0.29 | 0.24 |
| Pyrolysis fuel oil | wt % | 0.21 | 0.16 | 0.11 | 0.06 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

short-residence-time coils can make sense, because additional ethylene is produced in a short-residence-time coil if a limited amount of feedstock is available. In such scenarios residence times in the range of 0.25 s are applied in order to give the advantage of high yield and sufficient run length.

In naphtha plants the ethane contained in the cracked gas is separated and recycled to a segregated ethane-cracking furnace, in which cracking is carried out under typical ethane-cracking conditions. In case the capacity of the ethane furnace is not sufficient to crack all the ethane, co-cracking of ethane with naphtha is performed, with ethane conversions of 40–50 %. Due to the build up of large recycle streams in such operations, co-cracking should be avoided wherever possible.

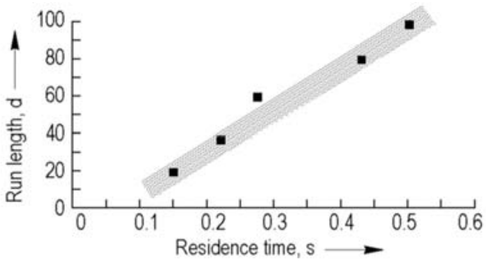


**Figure 8.** Run length versus residence time for ethane cracking

**Propane** is cracked in all types of furnaces at typical conversions of 90–93 %. The application of short-residence-time furnaces for propane cracking has to be evaluated carefully, due to the reduction in run length between successive decokings. In many naphtha plants with propane recycle, propane is co-cracked together with naphtha, without a dramatic drop in propane conversion.

Typical yields for propane cracking for various residence times are listed in Table 4. For very mild propane cracking conditions (70 % conversion) yields of propylene show a maximum at 18–19 wt % based on propane feed.

**Butane.** All types of furnaces can be used for butane cracking, which typically is performed at 94–96 % conversion. Yields for *n*-butane and isobutane differ widely. For *n*-butane, ethylene yields in the range of 40 % are typical (Table 5), whereas for isobutane only 15 wt %

**Table 4.** Yields from propane cracking with various residence times

| | | | | | |
|---|---|---|---|---|---|
| Conversion, kg/kg | | 90.020 | 90.035 | 89.926 | 89.983 |
| Steam dilution, kg/kg | | 0.3 | 0.3 | 0.3 | 0.3 |
| Residence time, s | | 0.4450 | 0.3337 | 0.1761 | 0.1099 |
| $H_2$ | wt % | 1.51 | 1.55 | 1.61 | 1.68 |
| CO | wt % | 0.04 | 0.04 | 0.03 | 0.04 |
| $CO_2$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $H_2S$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $CH_4$ | wt % | 23.43 | 23.27 | 22.82 | 22.40 |
| $C_2H_2$ | wt % | 0.46 | 0.51 | 0.59 | 0.82 |
| $C_2H_4$ | wt % | 37.15 | 37.51 | 38.05 | 38.59 |
| $C_2H_6$ | wt % | 3.06 | 2.80 | 2.37 | 1.96 |
| $C_3H_4$ | wt % | 0.52 | 0.57 | 0.65 | 0.89 |
| $C_3H_6$ | wt % | 14.81 | 14.82 | 15.01 | 15.27 |
| $C_3H_8$ | wt % | 9.97 | 9.96 | 10.07 | 10.01 |
| $C_4H_4$ | wt % | 0.08 | 0.08 | 0.09 | 0.11 |
| $C_4H_6$ | wt % | 2.85 | 2.9 | 2.98 | 2.99 |
| $C_4H_8$ | wt % | 1.00 | 1 | 1.02 | 1.09 |
| $C_4H_{10}$ | wt % | 0.04 | 0.04 | 0.05 | 0.05 |
| Benzene | wt % | 2.15 | 2.12 | 2.02 | 1.80 |
| Toluene | wt % | 0.43 | 0.4 | 0.36 | 0.28 |
| Xylenes | wt % | 0.05 | 0.05 | 0.04 | 0.03 |
| Ethylbenzene | wt % | 0.01 | 0.01 | 0.01 | 0.00 |
| Styrene | wt % | 0.21 | 0.2 | 0.18 | 0.15 |
| Pyrolysis gasoline | wt % | 1.27 | 1.26 | 1.27 | 1.24 |
| Pyrolysis fuel oil | wt % | 0.94 | 0.89 | 0.76 | 0.58 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

**Table 5.** Yields from butane cracking with various residence times

| | | | | | |
|---|---|---|---|---|---|
| Conversion, kg/kg | | 93.95 | 93.43 | 93.44 | 93.92 |
| Steam dilution, kg/kg | | 0.35 | 0.35 | 0.35 | 0.35 |
| Residence time, s | | 0.4775 | 0.3440 | 0.1781 | 0.1117 |
| $H_2$ | wt % | 1.05 | 1.09 | 1.16 | 1.22 |
| CO | wt % | 0.04 | 0.04 | 0.03 | 0.04 |
| $CO_2$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $H_2S$ | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| $CH_4$ | wt % | 20.48 | 20.29 | 19.85 | 19.33 |
| $C_2H_2$ | wt % | 0.37 | 0.42 | 0.51 | 0.71 |
| $C_2H_4$ | wt % | 35.03 | 35.81 | 37.25 | 38.36 |
| $C_2H_6$ | wt % | 4.57 | 4.16 | 3.47 | 3.02 |
| $C_3H_4$ | wt % | 0.87 | 0.93 | 1.04 | 1.32 |
| $C_3H_6$ | wt % | 17.37 | 17.24 | 17.03 | 16.99 |
| $C_3H_8$ | wt % | 0.37 | 0.35 | 0.33 | 0.33 |
| $C_4H_4$ | wt % | 0.09 | 0.1 | 0.11 | 0.13 |
| $C_4H_6$ | wt % | 3.98 | 4.08 | 4.27 | 4.38 |
| $C_4H_8$ | wt % | 2.85 | 2.83 | 2.78 | 2.85 |
| $C_4H_{10}$ | wt % | 6.05 | 6.07 | 6.06 | 6.08 |
| Benzene | wt % | 2.78 | 2.69 | 2.52 | 2.18 |
| Toluene | wt % | 0.83 | 0.77 | 0.66 | 0.49 |
| Xylenes | wt % | 0.12 | 0.11 | 0.09 | 0.06 |
| Ethylbenzene | wt % | 0.01 | 0.01 | 0.01 | 0.01 |
| Styrene | wt % | 0.25 | 0.24 | 0.22 | 0.18 |
| Pyrolysis gasoline | wt % | 1.85 | 1.81 | 1.80 | 1.72 |
| Pyrolysis fuel oil | wt % | 1.02 | 0.94 | 0.79 | 0.58 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

ethylene yield is achieved. Due to the poor ethylene yield from isobutane, other applications such as dehydrogenation, oligomerization, and alkylation seem to be more feasible than cracking isobutane to produce ethylene. However, mild cracking at 70 % conversion and high pressures has been claimed to yield isobutene as primary product [33].

**Naphtha.** Naphtha, the refinery hydrocarbon fraction with the boiling range of 35–180 °C, can vary in composition and boiling range, depending on source and refinery conditions. Today naphtha cuts from 35 to 90 °C (light naphtha), 90–180 °C (heavy naphtha) and 35–180 °C (full-range naphtha) are processed. In Europe and Asia/ Pacific naphtha is the primary raw material for ethylene cracking, with full range naphthas being processed most.

The properties of the naphtha feedstock used to generate the yield patterns given in Tables 6, 7, and 8 are as follows:

| | |
|---|---|
| Density at 20 °C | 0.692 g/mL |
| S content | 55 mg/kg |
| H content | 15.17 wt % |
| C content | 84.80 wt % |
| Average molar mass | 92 g/mol |
| *Boiling curve (ASTM D 86)* | |
| *initial boiling point* | 26 °C |
| 5 vol % | 49 °C |
| 10 vol % | 53 °C |
| 20 vol % | 58 °C |
| 30 vol % | 64 °C |
| 40 vol % | 70 °C |
| 50 vol % | 77 °C |
| 60 vol % | 86 °C |
| 70 vol % | 99 °C |
| 80 vol % | 116 °C |
| 90 vol % | 138 °C |
| 95 vol % | 152 °C |
| *final boiling point* | 183 °C |
| *PIONA analysis* | |
| *n*-Paraffins | 36.13 wt % |
| Isoparaffins | 36.62 wt % |
| Olefins | 0.21 wt % |
| Napthenes | 21.06 wt % |
| Aromatics | 5.98 wt % |

**Table 6.** Yields from low-severity naphtha cracking

| | | | | | |
|---|---|---|---|---|---|
| P/E *, kg/kg | | 0.65 | 0.65 | 0.65 | 0.65 |
| Steam dilution, kg/kg | | 0.4 | 0.4 | 0.4 | 0.4 |
| Residence time, s | | 0.4836 | 0.3526 | 0.1784 | 0.1096 |
| $H_2$ | wt % | 0.82 | 0.83 | 0.85 | 0.86 |
| CO | wt % | 0.03 | 0.02 | 0.02 | 0.02 |
| $CO_2$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $H_2S$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $CH_4$ | wt % | 13.56 | 13.2 | 12.44 | 11.83 |
| $C_2H_2$ | wt % | 0.32 | 0.34 | 0.36 | 0.45 |
| $C_2H_4$ | wt % | 25.23 | 25.6 | 26.08 | 26.43 |
| $C_2H_6$ | wt % | 4.76 | 4.36 | 3.62 | 3.16 |
| $C_3H_4$ | wt % | 0.59 | 0.63 | 0.70 | 0.92 |
| $C_3H_6$ | wt % | 16.42 | 16.63 | 16.97 | 17.18 |
| $C_3H_8$ | wt % | 0.68 | 0.65 | 0.61 | 0.60 |
| $C_4H_4$ | wt % | 0.09 | 0.09 | 0.10 | 0.12 |
| $C_4H_6$ | wt % | 4.63 | 4.86 | 5.27 | 5.68 |
| $C_4H_8$ | wt % | 5.76 | 5.94 | 6.34 | 6.69 |
| $C_4H_{10}$ | wt % | 0.72 | 0.75 | 0.80 | 0.85 |
| Benzene | wt % | 6.37 | 5.98 | 5.18 | 4.47 |
| Toluene | wt % | 3.08 | 2.9 | 2.60 | 2.26 |
| Xylenes | wt % | 1.17 | 1.15 | 1.09 | 0.96 |
| Ethylbenzene | wt % | 0.79 | 0.8 | 0.83 | 0.85 |
| Styrene | wt % | 1.08 | 1.01 | 0.87 | 0.77 |
| Pyrolysis gasoline | wt % | 11.25 | 11.81 | 13.19 | 14.09 |
| Pyrolysis fuel oil | wt % | 2.65 | 2.45 | 2.08 | 1.81 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

* Propene to ethylene ratio, a measure of severity.

**Table 7.** Yields from medium-severity naphtha cracking

| | | | | | |
|---|---|---|---|---|---|
| P/E *, kg/kg | | 0.55 | 0.55 | 0.55 | 0.55 |
| Steam dilution, kg/kg | | 0.45 | 0.45 | 0.45 | 0.45 |
| Residence time, s | | 0.4840 | 0.3572 | 0.1828 | 0.1132 |
| $H_2$ | wt % | 0.90 | 0.92 | 0.94 | 0.96 |
| CO | wt % | 0.04 | 0.04 | 0.03 | 0.04 |
| $CO_2$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $H_2S$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $CH_4$ | wt % | 15.23 | 14.91 | 14.31 | 13.82 |
| $C_2H_2$ | wt % | 0.44 | 0.47 | 0.53 | 0.71 |
| $C_2H_4$ | wt % | 27.95 | 28.45 | 29.24 | 29.87 |
| $C_2H_6$ | wt % | 4.59 | 4.23 | 3.57 | 3.14 |
| $C_3H_4$ | wt % | 0.71 | 0.76 | 0.87 | 1.21 |
| $C_3H_6$ | wt % | 15.38 | 15.64 | 16.09 | 16.43 |
| $C_3H_8$ | wt % | 0.53 | 0.51 | 0.48 | 0.47 |
| $C_4H_4$ | wt % | 0.12 | 0.13 | 0.16 | 0.20 |
| $C_4H_6$ | wt % | 4.54 | 4.79 | 5.28 | 5.79 |
| $C_4H_8$ | wt % | 4.41 | 4.52 | 4.75 | 4.95 |
| $C_4H_{10}$ | wt % | 0.42 | 0.44 | 0.47 | 0.49 |
| Benzene | wt % | 7.45 | 7.12 | 6.5 | 5.85 |
| Toluene | wt % | 3.26 | 3.10 | 2.82 | 2.46 |
| Xylenes | wt % | 1.18 | 1.16 | 1.12 | 0.97 |
| Ethylbenzene | wt % | 0.62 | 0.62 | 0.64 | 0.63 |
| Styrene | wt % | 1.21 | 1.14 | 1.00 | 0.88 |
| Pyrolysis gasoline | wt % | 7.70 | 7.96 | 8.52 | 8.79 |
| Pyrolysis fuel oil | wt % | 3.32 | 3.09 | 2.68 | 2.34 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

* Propene to ethylene ratio, a measure of severity.

**Table 8.** Yields from high-severity naphtha cracking

| | | | | | |
|---|---|---|---|---|---|
| P/E *, kg/kg | | 0.45 | 0.45 | 0.45 | 0.45 |
| Steam dilution, kg/kg | | 0.5 | 0.5 | 0.5 | 0.5 |
| Residence time, s | | 0.4930 | 0.3640 | 0.1897 | 0.1170 |
| $H_2$ | wt % | 0.9 | 1.00 | 1.03 | 1.06 |
| CO | wt % | 0.06 | 0.06 | 0.05 | 0.06 |
| $CO_2$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $H_2S$ | wt % | 0.00 | 0.00 | 0.00 | 0.00 |
| $CH_4$ | wt % | 16.9 | 16.61 | 16.10 | 15.74 |
| $C_2H_2$ | wt % | 0.64 | 0.69 | 0.80 | 1.14 |
| $C_2H_4$ | wt % | 30.25 | 30.81 | 31.74 | 32.38 |
| $C_2H_6$ | wt % | 4.32 | 4.00 | 3.43 | 3.00 |
| $C_3H_4$ | wt % | 0.81 | 0.88 | 1.02 | 1.48 |
| $C_3H_6$ | wt % | 13.63 | 13.88 | 14.29 | 14.55 |
| $C_3H_8$ | wt % | 0.37 | 0.35 | 0.33 | 0.32 |
| $C_4H_4$ | wt % | 0.18 | 0.2 | 0.24 | 0.32 |
| $C_4H_6$ | wt % | 4.20 | 4.45 | 4.90 | 5.39 |
| $C_4H_8$ | wt % | 3.11 | 3.17 | 3.26 | 3.28 |
| $C_4H_{10}$ | wt % | 0.17 | 0.18 | 0.19 | 0.18 |
| Benzene | wt % | 8.32 | 8.06 | 7.63 | 7.15 |
| Toluene | wt % | 3.40 | 3.26 | 3.00 | 2.63 |
| Xylenes | wt % | 1.14 | 1.12 | 1.09 | 0.95 |
| Ethylbenzene | wt % | 0.44 | 0.44 | 0.44 | 0.40 |
| Styrene | wt % | 1.44 | 1.37 | 1.24 | 1.12 |
| Pyrolysis gasoline | wt % | 5.25 | 5.35 | 5.55 | 5.57 |
| Pyrolysis fuel oil | wt % | 4.38 | 4.12 | 3.67 | 3.28 |
| **Sum** | **wt %** | 100.00 | 100.00 | 100.00 | 100.00 |

* Propene to ethylene ratio, a measure of severity.

The yield increases with decreasing residence time. The maximum benefit of a selective cracking coil is achieved in high-severity cracking, in which a 5 % feedstock saving can be achieved by using short residence times. However, careful analysis is required since, similar to gas cracking, shorter run lengths are typical for short-residence-time cracking. Maximum annual furnace productivity is achieved with a combination of short residence time and long run length.

**Gas Oil (AGO; Boiling Range 180–350 °C).** Compositions and boiling ranges of gas oils vary greatly with source and refinery conditions. Saturated gas oils may have BMCI values as low as 20, whereas aromatic gas-oil BMCI values can exceed 45. Typical yield distributions are shown in Table 9 for an AGO with properties as listed in Table 10.

Gas oils produce much more $C_{5+}$ material than the above feedstocks because they contain large amounts of condensed polynuclear aromatics. These components resist cracking and may remain unchanged or condense to higher molecular mass materials.

**Table 9.** Yields for AGO and HCR cracking

| | | AGO | HCR |
|---|---|---|---|
| P/E *, kg/kg | | 0.54 | 0.53 |
| Steam dilution, kg/kg | | 0.8 | 1 |
| Residence time, s | | 0.32 | 0.3 |
| $H_2$ | wt % | 0.71 | 0.68 |
| CO | wt % | 0.01 | 0.01 |
| $CO_2$ | wt % | 0.01 | 0.01 |
| $H_2S$ | wt % | 0.00 | 0.00 |
| $CH_4$ | wt % | 10.58 | 11.08 |
| $C_2H_2$ | wt % | 0.38 | 0.60 |
| $C_2H_4$ | wt % | 25.93 | 25.98 |
| $C_2H_6$ | wt % | 2.82 | 2.81 |
| $C_3H_4$ | wt % | 0.63 | 0.97 |
| $C_3H_6$ | wt % | 14.07 | 16.02 |
| $C_3H_8$ | wt % | 0.37 | 0.42 |
| $C_4H_4$ | wt % | 0.12 | 0.04 |
| $C_4H_6$ | wt % | 5.73 | 8.03 |
| $C_4H_8$ | wt % | 3.61 | 4.14 |
| $C_4H_{10}$ | wt % | 0.05 | 0.06 |
| Benzene | wt % | 5.44 | 5.64 |
| Toluene | wt % | 3.49 | 2.73 |
| Xylenes | wt % | 0.92 | 0.46 |
| Ethylbenzene | wt % | 0.37 | 0.34 |
| Styrene | wt % | 1.18 | 1.12 |
| Pyrolysis gasoline | wt % | 7.28 | 6.91 |
| Pyrolysis fuel oil | wt % | 16.30 | 7.95 |
| **Sum** | **wt %** | 100 | 100 |

*Propene to ethylene ratio, a measure of severity.

**Table 10.** Properties of AGO and HCR used for yield calculations in Table 5

| | AGO | HCR |
|---|---|---|
| Density at 20 °C, g/mL | 0.8174 | 0.8280 |
| C, wt % | 86.20 | 85.28 |
| H, wt % | 13.64 | 14.34 |
| S, wt % | 0.18 | 0.003 |
| BMCI | 24.8 | 9.37 |
| Paraffins + naphthalenes, wt % | 80.38 | 89.4 |
| Monoaromatics, wt % | 12.45 | 7.3 |
| Polyaromatics, wt % | 7.17 | 3.3 |
| Boiling point analysis, °C | | |
| ibp | 170 | 313 |
| 10 % | 203 | 351 |
| 30 % | 227 | 393 |
| 50 % | 248 | 405 |
| 70 % | 273 | 422 |
| 90 % | 316 | 451 |
| 95 % | 340 | 460 |
| fbp | 352 | 475 |

**Hydrocracker Residue (HVGO or HCR; Boiling Range 350–600 °C).** Hydrocracker residues are the unconverted product fraction from hydrocrackers. Due to the severe operating conditions of the hydrocrackers, HCR is a highly saturated product, with only a limited content of aromatics and low contents of polyaromatics. HCR or HVGO is a feedstock that can result in ethylene yields as high as in naphtha cracking. Typical yields for a HCR are shown in Table 9 for an AGO with properties as listed in Table 10.

A comparison of the feedstock requirements as a function of residence time for a 1000 000 t/a plant for ethane, propane, butane and naphtha is shown in Figure 9. It can be seen that a naphtha

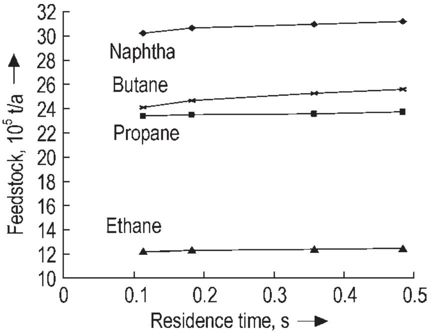


**Figure 9.** Feedstock requirements for a 1 000 000 t/a ethylene plant

cracker has about three times the feedstock throughput of an ethane cracker, and that naphtha cracking shows some sensitivity to short residence times, whereas ethane crackers are not very sensitive with respect to feedstock savings as short residence times are applied. A careful economic analysis is required to select the optimum residence time range for a given feedstock, since shorter residence times lead to reduced availability due to shorter run length, as shown for ethane cracking in Figure 8.

### 5.1.4. Commercial Cracking Furnaces

**Furnace Design.** Modern cracking furnaces typically have one or two rectangular fireboxes with vertical radiant coils located centrally between two radiant refractory walls. Firebox heights of up to 15 m and firebox widths of 2–3 m are standard design practice in the industry. Firing can be performed with wall- or floor-mounted radiant burners, or a combination of both, which use gaseous or combined gaseous and liquid fuels. Fireboxes are under slight negative pressures with upward flow of flue gas. Flue gas flow and draft are established by induced-draft fans. In some furnace designs, burners are mounted on terraced walls.

Firebox length is determined by the total ethylene production rate desired from each furnace and the residence time of the cracking operation. This also determines the number of individual radiant coils needed, with short residence times requiring many more individual coils than longer residence times for the same production capacity. This is due to the shorter lengths of the short-residence-time coils, which can be as short as 10–16 m per coil. Long-residence-time coils can have lengths of 60–100 m per coil. The number of coils required for a given ethylene capacity is determined by the radiant coil surface, which is in the range of 10–15 $m^2$ per tonne of feedstock for liquid feedstocks.

Production rate for each coil is determined by its length, diameter, and charge rate, which translates into a certain heat flux on the radiant coil. Values of 85 $kW/m^2$ for the average heat flux of a coil should be the maximum.

Radiant coils are usually hung in a single plane down the center of the firebox. They have also been nested in a single plane or placed parallel in a staggered, double-row tube arrangement. Staggered tubes have nonuniform heat-flux distributions because of the shadowing effect of one coil on its companion. If maximum capacity and full utilization of the firebox are desired, tube staggering can be adjusted so that the shadowing effect is only marginally greater than with a single-row arrangement.

Heat transfer to the radiant tubes occurs largely by radiation, with only a small contribution from convection. Firebox temperature is typically 1000–1200 °C.

The radiant coil of an ethylene furnace is a fired tubular chemical reactor. Inlet conditions must meet the required temperature, pressure, and flow rate. Hydrocarbon feed is heated from its convection-section entry temperature to the temperature needed for entry into the radiant coils. Dilution steam is introduced into the hydrocarbon stream in the convection section. The combined hydrocarbon and steam stream is then superheated to the target temperature at the radiant coil inlet (crossover temperature, XOT). Gaseous feeds require only the energy necessary to heat the feed and steam to the radiant coil inlet temperature. Liquid feeds require additional energy to heat the liquid to its vaporization temperature plus its latent heat of vaporization.

Energy is saved in the convection section by preheating the cracking charge; by using utility preheating, i.e., boiler-feedwater preheating, dilution-steam superheating, high-pressure steam superheating or by preheating the combustion air.

A typical arrangement of furnace elements is shown in Figure 10. In this case, the convection section contains six separate zones. As an example, the feed could be preheated in the upper zone, the boiler feedwater in the next, and mixed feed and dilution steam in the third zone. The process steam is superheated in the fourth zone, the HP (high-pressure) steam is superheated in the fifth zone and the final feed and dilution steam are preheated in the bottom zone. The number of zones and their functions can differ according to furnace design. For example, the upper zone could be used to recover heat for air preheating.

With the trend to higher capacities per individual furnace a new furnace set-up has been introduced to the industry with great commercial success. In this type two fireboxes are connected to one convection section. This design allows

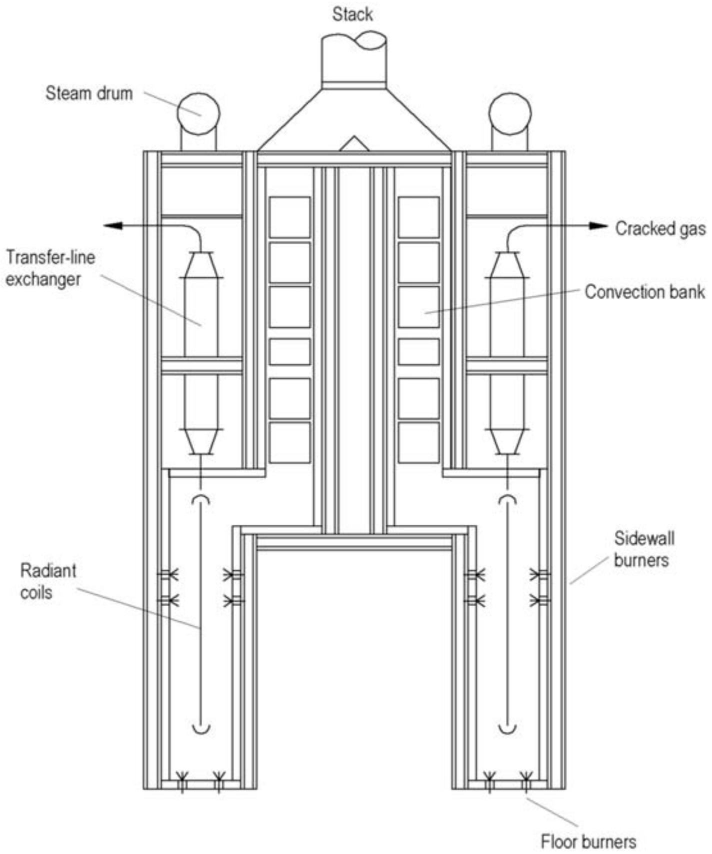


**Figure 10.** Typical arrangement of furnace elements

liquid feedstock cracking furnaces with capacities of 130 000 – 200 000 t/a to be installed. Capacities of gas furnaces are higher and can reach up to 250 000 to 300 000 t/a. This is a result of the general trend to built ethylene plant in much larger scale, which started with the number of gas-based projects erected in the Middle East in 2000.

The induced-draft fans allow complex convection sections to be designed with very high gas velocities to give optimum heat transfer in the convection section banks. Modern designs include integrated catalyst systems for $NO_x$ removal by SCR (selective catalytic reduction) technology, whereby the $NO_x$ present in the flue gas reacts with ammonia:

$$4\,NO_x + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

The temperature of the cracked gas leaving the radiant coils can range from 750 to 900 °C. Rapid reduction of gas temperature to 500–650 °C, depending on the feedstock, is necessary to avoid losses of valuable products by secondary reactions. This is accomplished by a transfer-line exchanger (see Fig. 10), which cools the cracked gases and recovers much of the heat contained in the cracked gas as high-pressure steam. The transfer-line exchanger can be a conventional or a linear exchanger as shown in Figure 11. Linear exchangers are preferred today for gas cracking, in order to avoid erosion problems with the very hard coke in gas cracking.

In all modern furnaces the radiant coils exit the firebox at the top; the TLEs are top-mounted. In older designs coils also leave the bottom of the firebox, with TLEs mounted vertically along the side of the furnace or horizontally underneath it. Radiant-coil designs are generally considered proprietary information. All modern designs strive for short residence time, high temperature, and low hydrocarbon partial pressure. Most coil configurations have two features in common:

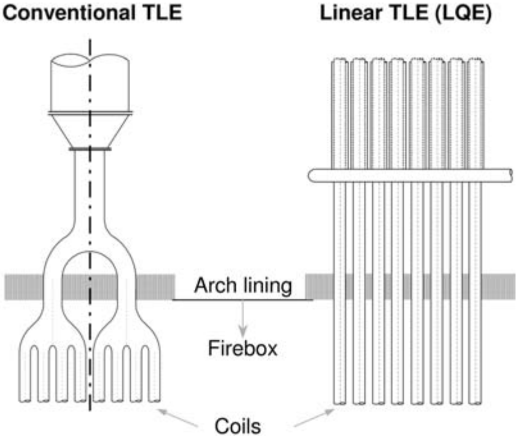


**Figure 11.** Conventional and linear transfer-line exchangers

coils are hung vertically, usually suspended on spring or constant hangers above the top of the radiant firebox, and they are fired from both sides of the radiant coil. Horizontal tubes are no longer used in ethylene furnaces.

Coils can range from a single, small-diameter tube with low feed rate and many coils per furnace, to long, large-diameter tubes, with high feed rate and few coils per furnace. Longer coils consist of lengths of tubing connected with return bends. Individual tubes can be the same diameter or swaged to larger diameters one or more times along the complete coil; two or more individual tubes may be combined in parallel.

An example of a so-called split radiant coil arrangement is shown in Figure 12; here parallel small-diameter coils are combined into a larger diameter outlet coil. This arrangement allows advantageous temperature profiles to be applied, with a rapid temperature increase in the inlet section, and offers slightly higher yields than a uniform diameter coil of the same residence time.

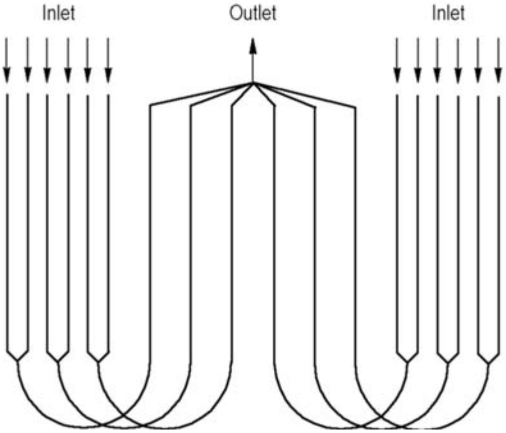


**Figure 12.** Short-residence-time coil arrangement

Coil lengths and diameters vary widely as can be seen from the following design characteristics:

| | |
|---|---|
| Ethylene capacity (per furnace) | (50–250) × $10^6$ t/a |
| Number of coils (per furnace) | 4–200 |
| Tube diameter | 25–180 mm |
| Coil length | 10–100 m |
| Coil outlet temperature | 750–890 °C |
| Tube wall temperature | |
| clean | 950–1040 °C |
| maximum | 1040–1120 °C |
| Average heat flux | 50–90 kW/m$^2$ |
| Residence time | 0.08–1.0 s |

Cracking coils with internal fins have been offered to the industry, to increase the inner surface of a coil. These coils should offer the advantage of processing more feedstock in a coil of identical external dimensions. However, the fins result in a higher pressure drop of the coil, with disadvantages in yields, and coke spalling problems occur when the furnace is cooled down rapidly. Several new designs of fins and new processes for production of finned coils have been developed by different companies (Fig. 13).

Different developments are offered to the industry to reduce the coke deposit, resulting from catalytic coking and pyrolytic or thermal coking occurring during cracking. One approach is coating of the coil surface with inert materials to minimize the amount of catalytic coking (Fig. 14). Solutions are offered by several companies, but these technologies are rarely used, especially not in the large-scale new plants. For retrofits these coatings have been applied mostly in the USA. Coating can occur by, e. g., chemical vapor deposition (CVD) or physical vapor deposition (PVD).

The coils can also be passivated by chemical treatment during operation or prior to start-up. Passivation technologies are offered by various companies, including Atofina, ChevronPhillips, SK Corporation, Ondea Nalco, and Nova. Until today (2005) these technologies have not

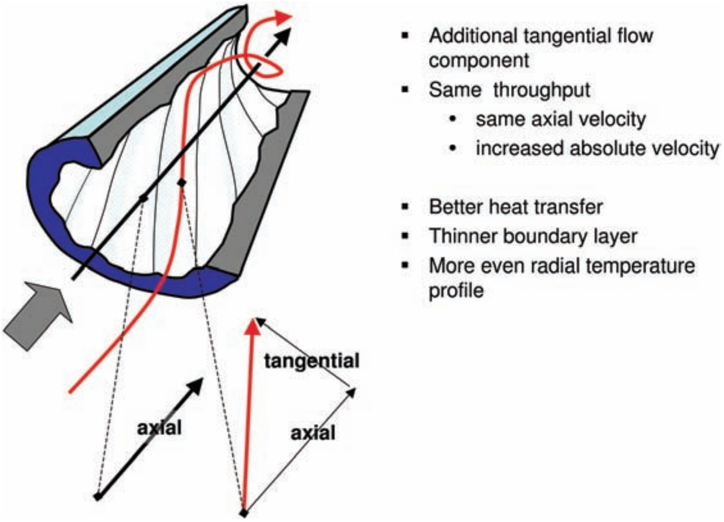


**Figure 13.** Coil with internal fins and improved heat transfer

achieved a major breakthrough in new cracker projects. The advantage of chemical treatment is that the costly process of deposition by CVD or PVD can be avoided and the dosing can be adjusted during operation. A disadvantage is that chemicals are introduced that end up in the cracker products and should not influence the quality of the products significantly.

Another novel development in furnace technology is the application of new coil materials, especially 45Ni35Cr steels, offered by many suppliers. These high-alloy steels are superior to other HP modified materials and offer advantages with respect to carburization at similar creep rates as other HP modified materials.

An interesting new material is offered by Schmidt and Clemens (Kaiserau, Germany) under the designation Centralloy 60 HT. The product has an increased content of aluminum (≈6 %) and can be operated up to 1200 °C. Despite the high aluminum content the material can be machined, bent, and welded.

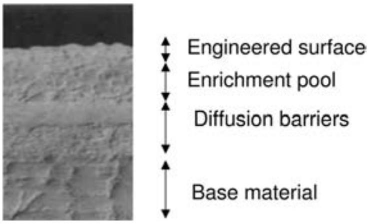


**Figure 14.** Coated radiant coil surface

A different approach is the application of ODS (oxide dispersion strengthening) leading to “superalloys”. ODS materials can be used up to 1300 °C with still good creep resistance but despite these ceramic-like properties are ductable and weldable like metallic materials. Due to the non-casting production process based on metal oxide powders, the costs for such materials are much higher than those for conventional HP modified or similar materials. The industrial breakthrough of ODS in ethylene plants has not been achieved until today [34].

**ABB Lummus Global Furnace.** The coil design of Lummus furnaces has been modified in the light of pilot-plant investigations. Several generations of coils SRT-I (short residence time-first model) through SRT-X, have been produced.

The SRT-I model radiant coil is uniform in diameter. Many SRT-I heaters are still operating, primarily for cracking ethane, propane, or butane. All other coils are so-called split coils, with smaller inlet coils combined into larger outlet coils. The latest designs – SRT-V SRT-VI and SRT X – are short residence time coils with residence times in the range of 0.15–0.20 s. In the SRT-V coil, 8–12 small coils of ca. 40 mm internal diameter are headered into a single outlet coil of large diameter (150–180 mm). In SRT-VI designs a smaller number of parallel coils is headered into a larger outlet tube, which is connected to a linear quench exchanger.

ABB Lummus Global furnaces can be paired, as shown in Figure 10, or can operate alone. Stacks may be shared, with a common induced-draft fan; the flue gas flows upward. Some convection sections contain boiler feedwater preheating coils and steam superheating coils, along with steam desuperheat stations and process-heating coils. In some designs, steam is superheated in separate heaters. Lummus heaters can be fired by wall-mounted burners or by combinations of wall- and floor-mounted burners. Oil-fired floor burners are available.

Overall fuel efficiencies of 92–95 % net heating value (NHV) can be obtained, depending on feedstock, fuel sulfur content, firing control, and convection section type. Lummus furnaces can use any available transfer-line exchanger. Radiant-coil outlets may be paired, leading to a common exchanger. Capacities per furnace for full-range naphtha or atmospheric gas oil vary from 25 000 to 200 000 t/a.

**Millisecond Furnace (KBR, Houston Texas).** The Millisecond Furnace is designed for shortest residence times and low hydrocarbon partial pressures. It is recommended for gas and liquid feedstocks, offering the greatest advantages for the latter. This heater, developed in the early 1970s from a prototype installed by Idemitsu Petrochemical in Japan, reduces residence time to ca. 0.10 s. Kellogg successfully marketed the Millisecond concept in the mid-1980s, but with the trend of the industry to robust furnaces rather than maximum selectivity, which started in the 1990s, Kellogg lost market shares.

KBR has enhanced its olefin technology portfolio through a licensing agreement with ExxonMobil Chemical. This agreement allows KBR to offer a combination of its own technology and that of a premier producer. Furnaces offered included the designs SC-1, SC-2, and SC-4 (Fig. 15).

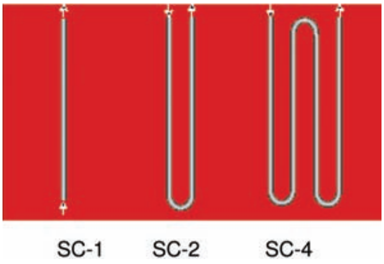


**Figure 15.** Radiant coils applied in KBR furnaces

Furnaces can be paired to use a common steel structure or they can stand alone. Paired furnaces can have a common stack and induced draft fan. Burners are located on opposite walls of the firebox at floor level; they use gas, oil, or combinations thereof with forced or induced draft. The design can be adapted easily for preheating combustion air. A Millisecond furnace is shown in Figure 16.

Flow is distributed to the many small-diameter radiant coils by pigtails connecting the individual radiant coils to their common feed header. Due to the short residence time and the resulting higher process temperatures, run lengths of Millisecond furnaces are shorter than those of competing furnaces and they thus require more decokes per year.

**Shaw Furnace (The Shaw Group, Baton Rouge, USA).** Shaw supplies an ultraselective cracking (USC) furnace coupled with a quench exchanger (see Section 5.2). Radiant coils have internal diameters of 50–90 mm. In contrast to many other contractors, Shaw is not offering split coils.

Their swaged USC-U (Super U Coil) coil configuration consists of two tubes connected with a return bend. The diameter of the outlet tube is larger than that of the inlet tube, allowing for thermal, molecular, and pressure expansion. Generally, outlet tubes from two USC-U coils are combined to feed a single linear exchanger.

The swaged USC-W coil configuration consists of four thin tubes, which differ in diameter. Individual diameters for each coil increase from inlet to outlet. A coil outlet can go directly to a LinEx (linear exchanger) quench system or two coils can share a quench system. The individual furnace capacity is obtained by installing 12–24 USC-W coils in the same firebox. Spring hangers support radiant coils from the top in the center plane of the firebox. Feed to the coils is equalized by critical-flow venturi nozzles.

The USC furnaces may be paired as shown in Figure 9, with a common stack and induced-draft fan, or they can stand alone. Burners are mounted on the wall, or on the wall and floor. Floor burners are gas- or oil-fired.

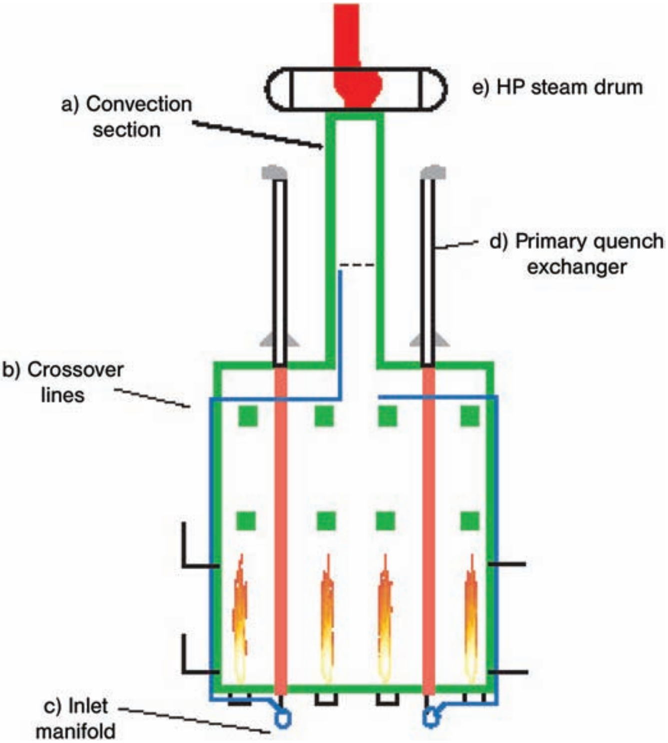


**Figure 16.** KBR SC furnace module

For furnaces using gas-turbine integration (GTI) or preheating of combustion air, a floor-fired, short-residence-time (FFS) design is available. This is completely floor fired, which reduces large-volume ductwork to a minimum. Coil geometry is similar to USC-U or USC-W designs, but to maintain a uniform firebox temperature, more and shorter coil legs are used. Overall fuel efficiencies of Shaw furnaces are competitive.

**Technip Furnace (Technip, Paris, France).** A number of radiant-coil designs (GK and SMK) are available, ranging from a simple serpentine coil of constant diameter to GK-1 (gradient kinetics, model 1) and GK-6 coils.

Gaseous feed, naphtha, and gas oil can be cracked with all coils. Residence times range from 0.15 to 0.5 s. Capacities range up to 250 000 t/a per furnace.

The GK radiant coil has two thin, parallel tubes from the coil inlet to ca. 66 % of the total coil length, where they combine to a single, larger tube. The thin tubes can be staggered or in-line; the larger diameter tubes must be in-line.

The Technip furnaces can be paired with a common stack and induced-draft fan, or they can stand alone. Top outlet coils are preferred. Burners are wall-mounted or wall- and floor-mounted.

**Linde-Pyrocrack Furnace (Linde AG, Munich, Germany).** Linde-Pyrocrack furnaces provide capacities of 20 000–300 000 t/a. Feedstocks can be all straight-run or pretreated hydrocarbons from ethane, propane, butane, natural gas liquids, naphthas, raffinates, gas oils, gas condensates and hydrocracked vacuum gas oils. Furnaces are designed for segregated cracking or co-cracking and for maximum feedstock flexibility. Linde and its U.S. subsidiary Selas Fluid Processing have installed furnaces with a total ethylene capacity $> 25 \times 10^6$ t/a.

Pyrocrack coils are all split coils with small inlet coils headered into a larger outlet coil, with residence times from 0.15 to 0.5 s. The three basic Pyrocrack coil types are shown in Figure 17. Coil diameters range from ca. 40/ 55 mm (inlet/outlet) for Pyrocrack 1–1 coils to 100/ 150 mm for Pyrocrack 4–2 coils. Critical

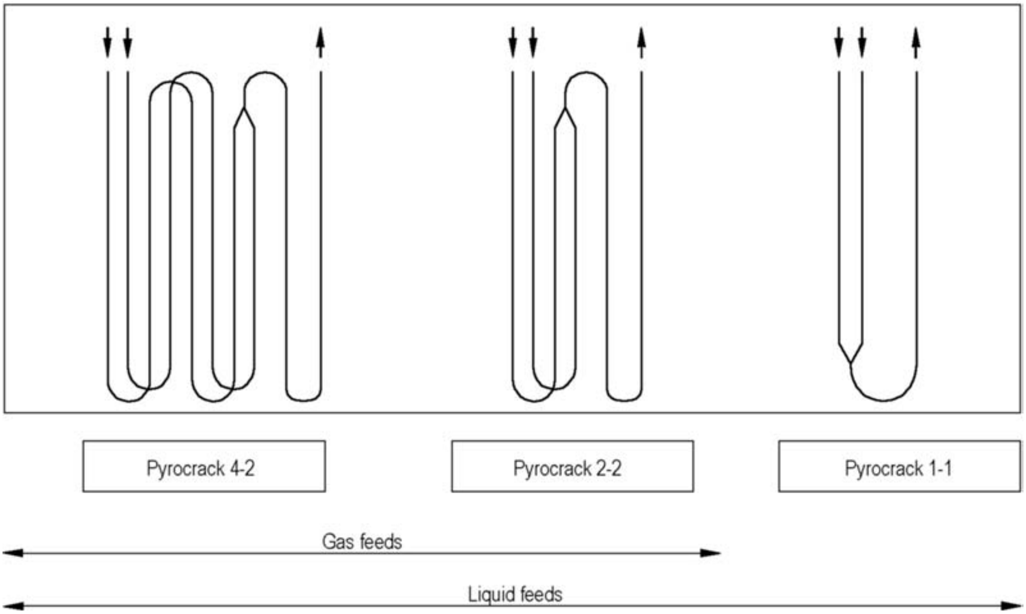


**Figure 17.** Linde-Pyrocrack coils

venturi nozzles are used to ensure equal distribution and residence times in all parallel coils of a furnace.

Today floor firing or a combination of sidewall and floor firing is used, the latter offering the best distribution of the released heat over the whole firebox and a excellent radiant efficiency. Especially for large-capacity furnaces with high fireboxes the combination of floor and sidewall firing offer the advantage of an even distribution of the heat release. Fuel for the radiant burners can be gas or oil or both. Oil firing offers the opportunity to use a fraction of the pyrolysis fuel oil (i.e., the liquid product of the pyrolysis boiling above 180 °C) as fuel and thus of increasing the amount of the pyrolysis methane fuel fraction available for export to other consumers. With today's requirements of low $NO_x$ emissions, the application of liquid fuel burners in ethylene plants is the exception, as the $NO_x$ emissions for liquid fuels are above the BAT levels (best available technique), forming the basis for local regulations in Europe. Present BAT levels in Europe are 80 to 100 mg/Nm$^3$ for furnaces in ethylene plants without catalytic DeNOx systems. Floor firing offers the advantage of somewhat lower $NO_x$ levels than sidewall burners.

The convection section of Linde Pyrocrack furnaces contains process heating bundles for feed, dilution steam, boiler feedwater, and high-pressure steam superheater bundles. Overall efficiencies of up to 94–95 % (on lower heating value, LHV) are typical for Linde furnaces. High-pressure steam systems for heat recovery have been developed by Linde for up to 14 MPa. Linde has built furnaces with SCR-based DeNOx technology integrated into the convection section. The design of the side and front walls of the convection section provides uniform heat distribution and prevents flue gas bypassing. Furnace draft is maintained by an induced-draft fan mounted over the convection section.

Linde has introduced with great commercial success the Twin Radiant Cell concept, in which a single high-capacity furnace has two radiant sections, which are connected to a common convection section (Fig. 18). The two radiant sections can be operated independently with different feedstocks or even with one firebox in cracking operation and the other in decoke operation. This offers the advantage of less capacity loss during decoke operation of a large capacity furnace. Other new features are a proprietary system for processing gas condensates,

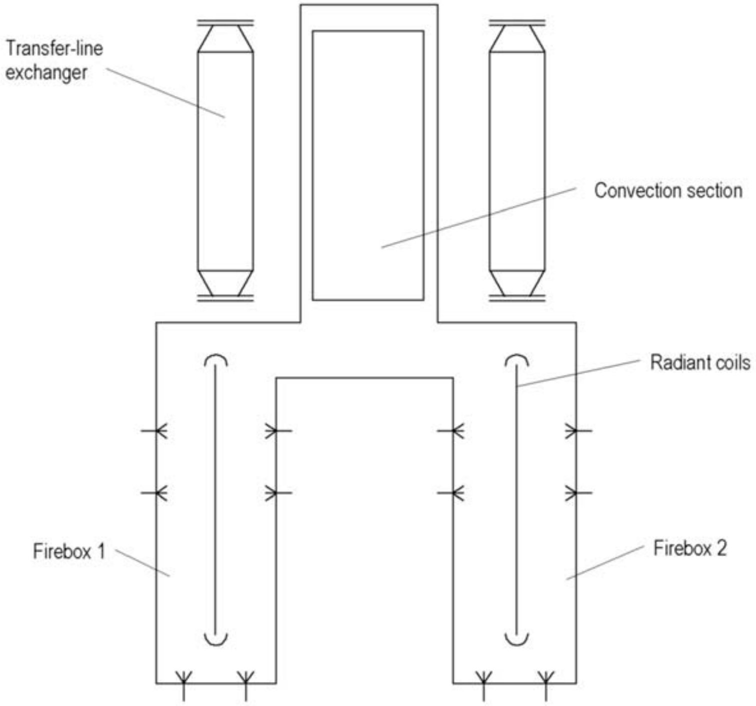


**Figure 18.** Twin radiant cell furnace

which have an extremely high and variable final boiling point. This system was developed from the well-established Linde technology for heavy hydrocracker bottoms and adapted to the requirements for gas condensates.

**Other Furnaces.** The furnaces listed below show some interesting features, but none is of commercial importance in today's worldwide olefin business. Only the furnace designs of the contractors listed above (ABB Lummus Global, KBR, Shaw, Technip, and Linde) are considered to be competitive.

The *terraced-wall furnace* (Foster & Wheeler Energy Corp., Livingston, N.J.) uses burners firing upward from shelves or ledges built into the walls of the firebox (Fig. 19). A similar firebox design is used for reformer heaters. This arrangement apparently gives uniform heating of the radiant coil. Furnaces are all-gas or all-liquid fuel fired.

The *Mitsui advanced cracker* (Mitsui Engineering & Shipbuilding Co., Tokyo, Japan) offers lower construction costs, smaller land area requirements, high thermal efficiency, and low $NO_x$ emissions. The mass of steel used in a 400 000 t/a ethylene plant is 30 % lower than that used in a 300 000 t/a plant with conventional furnaces. This is achieved by a patented installation of three radiant coils in the firebox space normally occupied by one or two coils [35].

The *Mitsubishi Furnace* jointly developed by Mitsubishi Petrochemical Co. and Mitsubishi

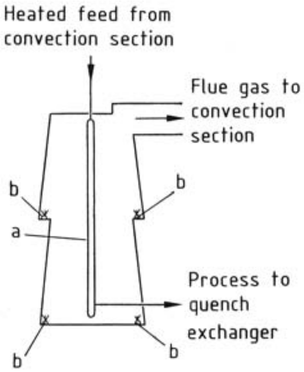


**Figure 19.** Foster–Wheeler terraced wall furnace
a) Radiant coil; b) Burners

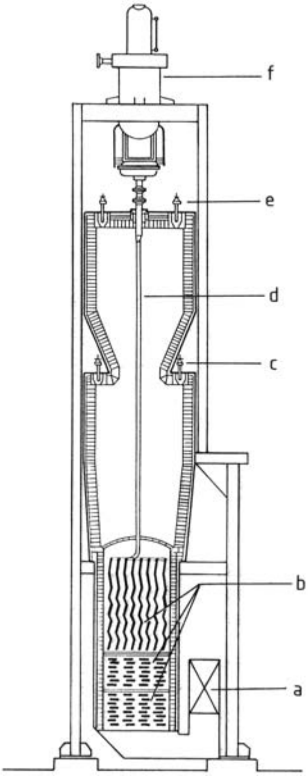


**Figure 20.** Section view of Mitsubishi M-TCF furnace*
a) Flue-gas duct; b) Convection tubes; c) Side burners; d) Cracking coil; e) Roof burner; f) TLE
* Reprinted with permission of Mitsubishi Heavy Industries.

Heavy Industries of Japan is quite different in design from other furnaces (Fig. 20). Known as the Mitsubishi thermal cracking furnace (M-TCF), it is a vertical, downdraft furnace with the convection section located below the radiant firebox. It is fired with gas or oil burners located in two rows mounted on the ceiling and two rows mounted on terraced walls. All burners are down-firing, with long flat flames. According to Mitsubishi, up to 70 % of the total heat can be supplied with any type of distillate fuel, including the cracked residue from an ethylene plant. Flue gas flows to a common stack by means of an induced-draft fan, which produces suction at the bottom of the convection section.

### 5.1.5. Tube Metallurgy

Ample evidence indicates that maximum yields of ethylene from tubular cracking of hydrocarbons require high temperature, short residence time, and low hydrocarbon pressure in the radiant coil. Modified coils can help achieve these conditions, but coil design is limited by metallurgy. Radiant coils must be selected in light of the following considerations:

- Operating temperature
- Tube service life
- Cost
- Carburization resistance
- Creep-rupture strength
- Ductility
- Weldability

An outside tube wall operating temperature up to and even exceeding 1100 °C is now possible. Coils are designed to operate at 975–1000 °C with an internally clean radiant coil. Tube wall temperature rises with time because of coke deposition inside the coil. Coke acts as a thermal insulator inside the coil, requiring increased tube wall temperature for a given furnace loading. Localized overheating must be avoided during removal of coke from the coil (when steam or a mixture of steam and air is used). With steam-air decoking, combustion occurs inside the coils.

Tube service life is economically important in plant operation. Furnace capital costs represent ca. 20 % of the total cost of an ethylene plant. About one-third of this is for radiant coils. With current metallurgy, a five-year service life in the hottest section and a seven-year service life of the inlet section of a furnace are typical. Service life is shortened by carburization of the inner tube surface, which is favored by the environment inside a cracking coil. Temperature is high, and feeds are usually highly carburizing; reaction occurs between the gaseous phase in the tube and its base metal.

Coil alloys are normally protected by an oxide layer on the inner surface. If this layer is destroyed and cannot be regenerated, carbon diffuses into the base metal, which itself diffuses toward the inside surface. Carburization may be more severe during decoking and can be reduced by lowering the percentage of air mixed with steam during this cycle. Aluminized coatings on the inner surface of the tube may reduce carburization [36–41]. The extent of carburization can be measured by magnetic tests [39].

The materials used for cracking coils are high-alloy steels, e.g. with 45 % Ni, 35 % Cr and several important trace metals (Si, Mn, Nb, Mo, W, Ti) [42]. The technical designation of this most common radiant coil material is HP 40 modified. The new materials offered by the leading vendors can be operated up to 1150 °C. Only a limited number of manufacturers worldwide are able to produce these materials according to very strict quality standards.

### 5.1.6. Thermal Efficiency of Ethylene Furnaces

Cracking furnaces represent the largest energy consumer in an ethylene plant; their thermal efficiency is a major factor in operating economics. New plants are designed for 93–95 % thermal efficiency, and revamping of older ones can increase efficiencies to 89–92 %. Only a limited number of heat sinks are available for heat released in the radiant firebox of a cracking furnace:

1. Process heat duty and duty for utility heating
2. Wall or radiation loss
3. Stack heat loss

Process heat duty is the energy required to heat the feedstock and dilution steam from the temperature at which they enter the furnace convection section to the temperature at which they leave the radiant coil. Process heat duty varies with feedstock composition, feed rate, and cracking severity. The duty for heating the utilities is the heat requirement to heat boiler feedwater in the convection section (from 110 °C to ca. 180 °C), before it is used for the HP steam production in the TLEs, and for superheating the saturated HP steam produced in the TLEs in the convection section.

Wall or radiation loss is that portion of the heat released in the radiant firebox which is lost to the atmosphere through the refractory and outer steel shells of the radiant and convection sections. Wall loss is initially determined by the type and thickness of thermal insulation in the furnace. Typical wall losses in modern furnaces are 1.2 % of the fired duty for the radiant section and 0.3 % of the fired duty for the convection section.

Stack heat loss is that portion of the heat released in the radiant firebox which is discharged to the atmosphere in the flue gas. Stack heat losses are around 5 % of the fired duty. This is the only heat loss that furnace operators can control, given a fixed furnace design, quality of maintenance, feed rate, and coil outlet temperature. Stack heat loss is sensitive to excess combustion air in the furnace and, thus, to draft, fuel composition, and air leakage.

**Radiative Heat Transfer and Furnace Thermal Efficiency.** The heat absorbed by the radiant coils and lost through the walls of a radiant-section firebox must equal the heat given up by the flue gas as it drops from the adiabatic flame temperature to the temperature at which it leaves the firebox [43]. The heat absorbed by the radiant coils of a furnace is a function of coil geometry, burner location, flame emissivity, temperature of the flue gas leaving the radiant firebox, and tube wall temperature of the radiant coil [44]. Typical radiant efficiencies are in the range of 38–42 % for side wall firing, 40–45 % for a combination of sidewall and floor firing and 42–47 % for 100 % floor firing. The differences result from the direct radiation loss to the convection section if the burners are mounted in the upper section of the radiant box.

The effects of excess combustion air and combustion air preheating on radiative heat transfer have been determined [45, 46]. Excess air rates in modern furnaces are ca.10 %, but some plants are operated at rates as low as 5 % excess air, resulting in reduced fuel consumption.

At 20 % excess combustion air (for a given furnace configuration and a radiant-section process duty), a 21 % reduction in fuel consumption is possible if combustion air is heated to 270 °C. Fuel usage increases rapidly as excess combustion air increases. At 49 % excess air, fuel consumption is the same as if combustion air were not preheated.

Combustion air preheating may be used in a new ethylene plant or in a modernized furnace to increase thermal efficiency. Various heat-exchange techniques can be used, including direct exchange between flue-gas discharge and inlet combustion air by use of rotating refractory vane elements, and indirect exchange by means of heat pipes, high-pressure water, or circulating high-temperature thermal fluids.

The most common technique for combustion air preheating is the use of hot exhaust gas from gas turbines (GTs). Such plants co-produce electricity (in the range of 30–60 $\mathrm{mW_{el.}}$), and this has a major impact on the plant economy. The GTs are exclusively used for electricity production. Direct driving of large compressors by the GTs is not feasible, due to the maintenance requirements for GTs, which require an annual shutdown. In modern plants the ethylene plant can run with and without the GT [47]. The economy of operation with an integrated GT is highly dependent on the credit for the electricity and the increased HP steam production. Scenarios that favor GT integration in Japan, Korea, and Brazil have existed in the eighties.

Radiant-coil inlet and outlet process temperatures in an ethylene furnace must be the same after application of preheated combustion air as they were before, to obtain the same cracking severity.

**Convective Heat Transfer and Furnace Thermal Efficiency.** Convective heat transfer is widely used in isolated green-fields ethylene plants to improve thermal efficiency by preheating boiler feedwater, generating steam, or superheating HP steam in the convection section of a furnace. Recovered energy must be considered in the overall energy balance for a plant of this type. Such techniques can be employed in older plants if boiler feedwater, generated steam, or superheated steam can be used. Otherwise, preheating the combustion air is an alternative.

### 5.1.7. Coking and Decoking of Furnaces and Quench Coolers

**Radiant-Coil Coking.** Hydrocarbon pyrolysis produces acetylenic, diolefinic, and aromatic compounds, which are known to deposit coke on the inside surface of the radiant coil [48, 49]. This coke layer inhibits heat transfer from the tube to the process gas, raises tube wall temperature, and reduces the cross-sectional flow area of the tube, thus increasing the pressure drop along the radiant coil. Cracking yield is thus lowered because of increasing hydrocarbon partial pressure. When tube temperature limits are reached, or pressure limitations of the sonic venturi nozzles used for flow distribution in short-residence-time furnaces, the furnace must be shut down to remove the coke. During the course of one on-stream cycle, deposited coke can reduce the heat-transfer efficiency of the firebox by 1–2 %, resulting in a 5 % increase in fuel consumption [50]. As radiant efficiency decreases, convection section heat transfer increases. This results in an unwanted increase in process crossover temperature and a lower demand for radiant-coil heat input. After furnace firing equilibration, actual fuel demand increases by 1–3 %.

Gaseous feedstocks such as ethane yield a harder, denser coke with higher thermal conductivity than naphthas or gas oils. Highly aromatic feeds produce the most coke.

The mechanism of coil coking is not fully understood [51]. Two types of coke can be distinguished, the catalytic coke and pyrolytic coke (Fig. 21).

The possibility that tube metals such as iron and nickel catalyze coke formation is supported by the observation that sulfur in the feed inhibits coking. A sulfur content above 400 ppm, however, may increase coking.

**Quench-Cooler Coking.** Coke deposited in TLEs reduces both heat transfer and the amount of steam generated to such an extent that the equipment must be cleaned. Different

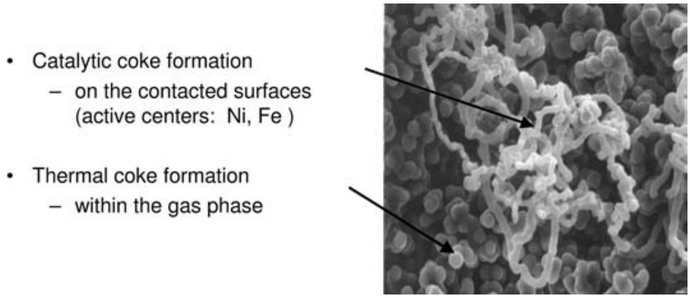


**Figure 21.** Catalytic and thermal coke

mechanisms have been proposed for TLE coking or fouling [52]:

1. Spalled coke produced in the radiant coil is carried into the TLE inlet cone where it blocks some of the tubes on the TLE entry tube sheet. Such fouling is most serious in ethane cracking.
2. Poor flow distribution in the entry cone and at the tube sheet causes eddies and backmixing. Gas so trapped experiences long residence time at high temperature, which increases tar and coke production.
3. Heavy polynuclear aromatics and other high-boiling components in the cracked gas condense on the cool TLE tube walls. This is particularly true for gas oil and heavy naphtha feedstocks. The condensed high-boiling substances are gradually converted to coke-like materials. This mechanism is supported by the fact that fouling is fastest at the start of the run (SOR). Typically, TLE outlet temperatures increase by 50–100 °C during the first day or two in gas oil cracking. Deposits during this period reduce the heat-transfer rate, and inner surface temperature at a given location in a tube becomes higher than the original clean wall temperature. The fouling rate drops as the surface temperature increases; with time process gas temperature slowly increases.

**Decoking.** At some time, furnace operation that is affected by coke deposits must be stopped so that the coke can be removed. Mechanical techniques are not feasible. Usually, the coke is burned out with a mixture of steam and air (Fig. 22).

The furnace is taken off-line, the residual hydrocarbons are purged downstream with steam, and the process flow is rerouted to a special decoking system. A steam–air mixture is then introduced into the radiant coils to burn out the coke at coil outlet temperatures of ca. 800 °C. The air concentration is increased carefully to avoid overheating the radiant coil. In modern furnaces the $CO_2$ content is measured continuously during decoking and the air flow rate is adjusted accordingly. After ca. 20 h the decoking of the radiant coils is complete and the decoking conditions are adjusted to decoke the TLE. Total decoking of radiant coil and TLE takes ca. 36 h. Mechanical cleaning of the TLE is not required in modern plant employing appropriate decoking procedures.

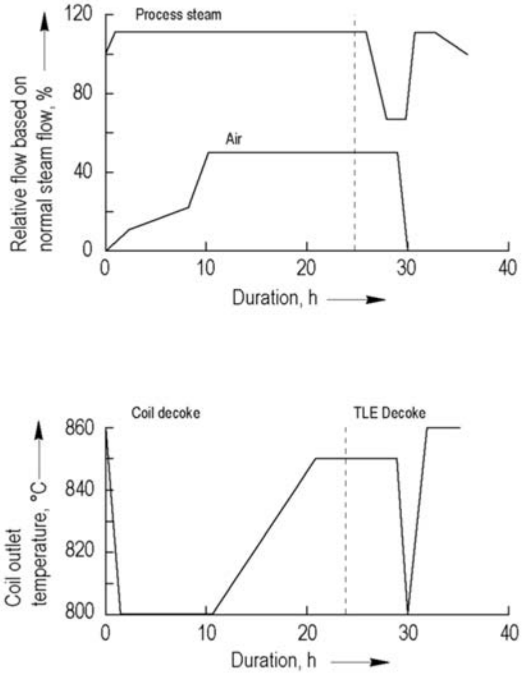


**Figure 22.** Steam–air decoking

Steam-only decoking makes use of the water–gas reaction, which is endothermic and less likely to burn out the radiant coils. This method does not require the furnace to be disconnected from downstream processing equipment, if that equipment is designed to accept the required amount of steam and handle the carbon monoxide produced. Temperatures as high as 950–1000 °C are required for steam-only decoking. The decoking gas from the radiant coils may be routed through the transfer-line exchangers, to partially decoke them.

Decoking time and radiant-tube wall temperature decrease as the amount of air mixed with steam increases [53]. The result of a steam-only decoking operation is poorer than that of a steam–air decoke.

Modern furnace quench systems are designed so that off-gas from radiant-coil decoking passes directly through the transfer-line exchangers, which are decoked as a result. About once a year a modern TLE must be opened for inspection and cleaned mechanically. This is carried out by shutting down the furnace, disconnecting the TLE, and removing the coke from the tubes mechanically or hydraulically.

The furnace should never be shut down and cooled without radiant-coil decoking. Differences between the coefficients of thermal expansion of the coke and of the metal tube wall are such that the radiant coils may rupture.

Off-gas from decoking is usually diverted to a decoking system containing a knockout pot equipped with a quench water inlet or a high-performance cyclone separator with dry or wet separation of the coke particles in the effluent. The cleaned, cooled gases are discharged to the atmosphere. Alternatively, the decoke off-gas can be rerouted to the firebox, where the coke particles are incinerated.

## 5.2. Quenching of Hot Cracked Gas

Cracked gases leave the radiant coil of an ethylene furnace at 750–875 °C. The gases should be cooled instantaneously to preserve their composition. However, this is not practical, so furnaces are designed to minimize residence time of the hot gas in the adiabatic section between furnace outlet and quench-system cooling zone. Typically, residence time in this adiabatic zone should not exceed 10 % of the residence time in the radiant coil.

The cracked gas is generally cooled by indirect quenching in the TLEs, which permits heat recovery at a temperature high enough to generate valuable high-pressure steam. Direct quenching by injection of oil has been displaced almost totally by indirect quenching.

Design objectives for transfer-line exchangers are as follows:

1. Minimum residence time in the adiabatic section between furnace outlet and TLE cooling surfaces, limiting secondary reactions that reduce the value of the cracked gas
2. Uniform flow to all tubes across the surface of the tube sheet, preventing eddies in the entry cone, which prolong residence time of the cracked gas and favor coke deposition.
3. Low pressure drop across the exchanger; pressure drop across the TLE is directly reflected by the outlet pressure of the radiant coil; increasing pressure at the outlet of the radiant coil degrades the value of the cracking pattern.
4. High heat recovery in the cracked gas, which directly affects operating economics. The pressure for steam generation is affected by the cracking feedstock. For light hydrocarbon cracking, in which little TLE fouling from condensation results, steam of much lower pressure (60 bar) can be generated. With such feeds, two TLEs can be used in series, one for generating high-pressure steam, the other for low-pressure steam or other heat recovery. The TLE outlet temperature must be higher for liquid feeds (360 °C) because of condensation of heavy components in the cracked gas; therefore, the pressure of the generated steam can be higher (8–12 MPa). In these cases, because of the high outlet temperature, TLEs are generally followed by a direct oil quench to lower the gas temperature for entry into the downstream portion of the plant.
5. Reasonable TLE run lengths. Fouling of TLE tubes by condensation and blockage by coke increase outlet temperature and pressure drop. Ultimately, the system may have to be shut down and cleaned. The TLE outlet temperature usually increases rapidly for several hours from the start-of-run (SOR) value; the increase then falls to a few °C per day.

Figure 23 shows the TLE outlet temperature over the run length for ethane, naphtha, and heavy feedstock (AGO, HVGO) cracking in a modern highly selective furnace.

The length of run for a TLE in gas cracking service is limited by coke blockage of the TLE inlet tubes [51]. For liquid feeds, TLE run length is governed by fouling at the outlet end of the

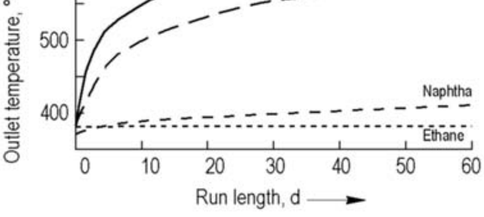


**Figure 23.** Transfer-line exchanger outlet temperatures

tubes resulting from condensation of heavy components in the cracked gas. Fouling rate increases as boiling range and relative density of the feed increases.

The transfer-line exchangers with commercial importance are the Borsig exchangers (shell-and-tube and a double pipe closed coupled linear exchanger), Alstom (multi double pipe and a double pipe linear exchanger), the Shaw USX exchanger and the KBR exchanger (similar to the USX).

**Borsig Transfer-Line Exchangers (Borsig, Berlin, Germany).** The Borsig TLE design has gained a large share of the world market (over $50 \times 10^6$ t/a ethylene capacity) for use with feedstocks ranging from ethane to atmospheric gas oils. Borsig offers two alternatives: a conventional shell-and-tube design and a linear exchanger. The latest series of the shell-and-tube exchanger, the tunnel-flow exchanger (Fig. 24 details of the TLE are shown in Fig. 25), which was introduced in 1989, is specially designed to operate with large temperature and pressure differences across the hot-end tube sheet. This sheet is thin (ca. 15 mm) but is supported by a studded stiffening system. The main feature of the tunnel-flow exchanger is the controlled water flow pattern in the inlet section to avoid particle deposition on the tube sheet causing hot spots.

Water flows from downcomers (a) into a circumferential water-jacket annulus (b). From here water enters several parallel tunnels (c), which distribute the water perfectly over the bottom tubesheet and via annular gaps in the stiffening plate (e) to the individual tubes (d) containing the hot cracked gas, which is cooled down by the water, producing high-pressure saturated steam.

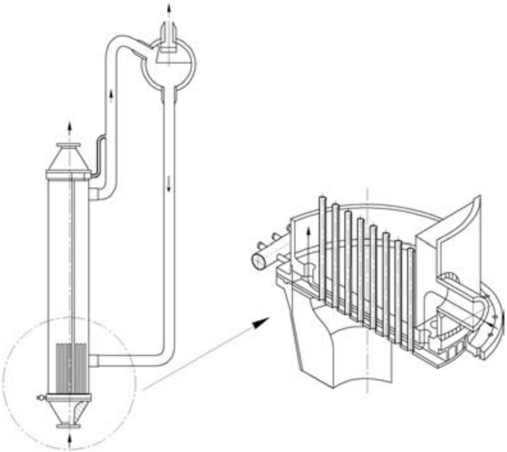


Figure 24. Borsig tunnel-flow exchanger

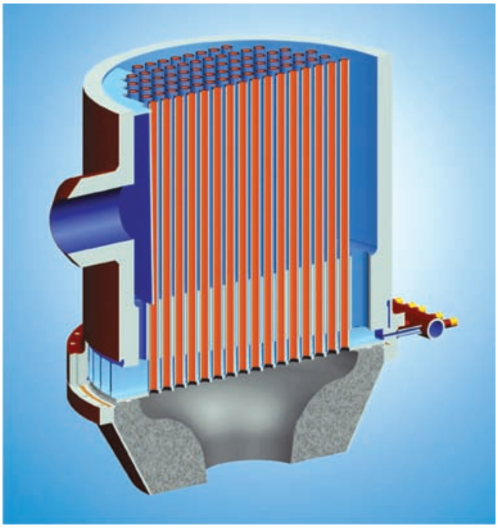


Figure 25. Details of Borsig TLE

Water flows through the tunnel system toward the opposite side at high velocity in intimate contact with the tube sheet, thereby preventing deposition of solids. On the opposite side, water flows upward through the circumferential annulus and enters the main shell volume (f). Debris may be deposited on the outer edges of the tube sheet as water flows from it to the main shell, where blowdown nozzles are present. Minor deposits here cause no problems because no heat load is present in this area.

Borsig exchangers can be mounted horizontally or vertically; the latter is the design for all modern furnaces with a top-out concept. Outlet tube sheets are generally thick and uncooled. Thin, studded tube sheets may be needed for TLEs with high outlet temperatures, e.g., in gas-oil cracking [54].

The is the Borsig Linear Quencher, is a double-pipe exchanger, connected directly to the coil outlet. This concept offers a minimum adiabatic volume of the cracking system. However, due to the larger tube diameter of this exchanger (up to 85 mm od), the heat transfer is not as efficient as in the conventional system with smaller tubes. This translates into tube lengths of ca. 20 m,

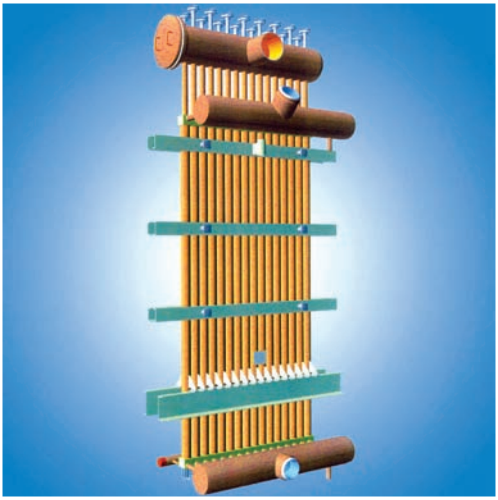


**Figure 26.** Details of the Borsig Linear Exchanger

which lead to the characteristic U shape of the linear exchangers, to keep the elevation of the steam drum within a reasonable range. Due to the length of 20 m, the pressure drop is higher than in a conventional system.

Figure 26 shows a Borsig Linear Quencher (BLQ); Figure 27. a Linear Exchanger Module. The main features of the BLQ are the turboflow inlet chamber, with high water velocities to avoid solids deposition and a stepped bend at the end of the primary leg to resist erosion in the U-shaped return bend.

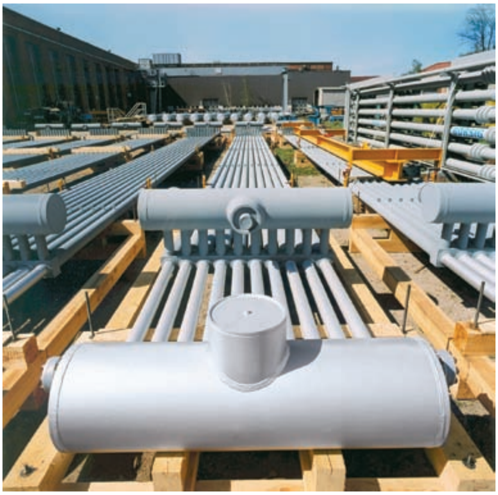


**Figure 27.** Borsig Linear Exchanger module

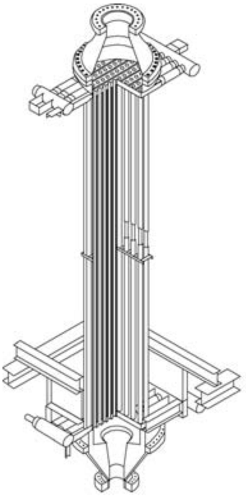


**Figure 28.** Alstom double-pipe transfer-line exchanger

**Alstom Exchangers.** Alstom Power and Energy GmbH, Kassel-Bettenhausen, Germany has been designing transfer-line exchangers for ethylene crackers since 1960 (formerly as SHG). The Alstom transfer-line exchanger shown in Figure 28 has separate exchangers, steam drums, risers, and downcomers. The basic heat-exchange element consists of concentric tubes (a, b) welded at each end to oval tubes (c). Process gas flows through the inner tube, and water circulates through the annulus between the tubes. Many double-tube elements are combined into a single exchanger by welding the oval headers to form a gastight tube sheet at each end. Process gas is delivered to the inner tubes of the basic tube element by a specially designed entry cone (h), which provides uniform process gas flow through all tubes and reduces the probability of eddy formation in the cone. Process gas leaving the exchanger is collected in a conical chamber and delivered to downstream equipment. Water flow to and from the oval tubes is provided by downcomers and risers (e) connected to the oval tubes by transition pieces (j).

The Alstom transfer-line exchangers can be mounted vertically with upward or downward flow of process gases. They may also be mounted horizontally with the gas-discharge end slightly elevated with respect to the gas-inlet end. They are normally cleaned by steam–air decoking and from time to time cleaned by hydrojetting.

Alstom offers also a closed coupled linear exchanger, with a reduced adiabatic reaction

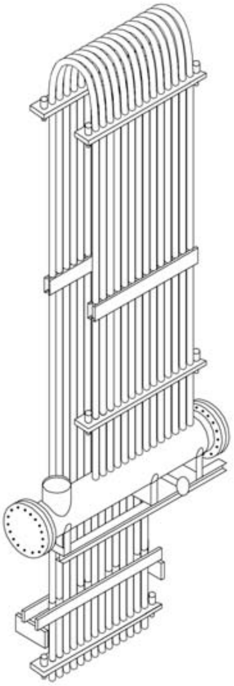


**Figure 29.** Alstom close coupled linear exchanger

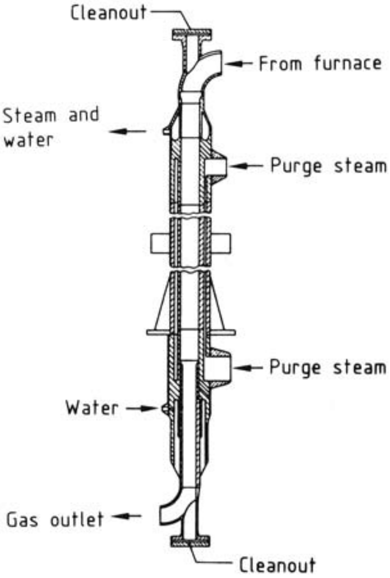


**Figure 30.** Ultraselective exchanger (USX) quench cooler*
* Reprinted with permission of Stone & Webster Engineering Corp.

zone, but due to the increased length has a higher pressure drop than the conventional exchanger. Figure 29 shows an Alstom close coupled linear exchanger in the typical U-shape. Feeds for all Alstom exchangers range from ethane to gas oils [55].

**Shaw Quench System (Shaw, Baton Rouge, USA).** The Shaw proprietary quench system does not rely on a tube sheet. The USX (ultraselective exchanger) quench cooler shown in Figure 30 is a double-pipe exchanger, with the inner pipe slightly larger than the radiant-coil connecting piping. This design can quench the effluent from one to four radiant coils. The USX outlet temperature (500–550 °C) is higher than in most other transfer-line exchanger designs; this helps to reduce coking in the exchanger. Normally, effluents from all USX exchangers on a given furnace are combined downstream and fed to a conventional multitube exchanger where the gases are quenched to a more normal TLE outlet temperature.

This design, by eliminating the tube sheet and entry cone, eliminates turbulent eddies and backmixing between the coil outlet and the cooling surfaces, thereby reducing fouling in the TLE entry zone. The large USX gas flow tube reduces pressure drop across the exchanger and, thus, the probability of plugging by coke from the radiant coil.

The USX exchangers can be steam–air decoked; cleaning, when required, is facilitated by openings at each end of the exchanger.

**KBR Millisecond Primary Quench Exchanger (KBR, Houston, Texas).** A special primary quench exchanger (PQE) was developed for use with KBR’s Millisecond furnace. The exchanger has a double-pipe arrangement (Fig. 31) capable of generating high-pressure steam.

A special high-alloy section of tubing is inserted to avoid excessive thermal stress at the high-pressure steam transition piece. This section has the Y-fitting at its base and extends up to the boiler feedwater inlet nozzle. A steam bleed helps to control thermal gradients and to prevent coke deposition in the annulus between the high-alloy insert and the exchanger inner surface.

The steam system is a thermosiphon type, with individual risers and downcomers tied together in common headers connecting to a single steam drum. KBR’s PQEs are normally

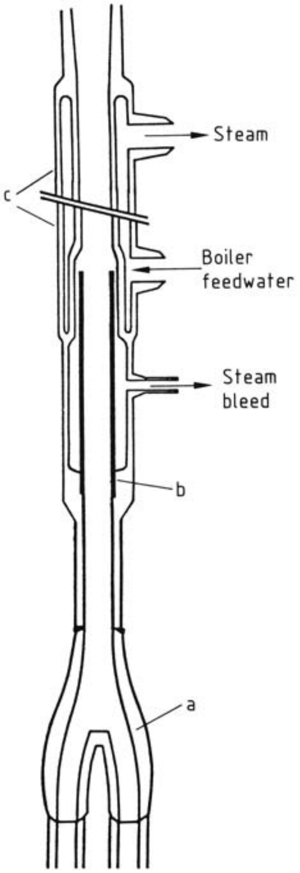


**Figure 31.** KBR millisecond primary quench exchanger *
a) Y-shaped fitting; b) High-alloy insert; c) Double pipe
* Reprinted with permission of KBR.

fabricated in bundles for ease of shipping and installation. Typically, one PQE serves two coils in a Millisecond Furnace.

**Other Quench-Cooler Designs.** Proprietary quench coolers have been developed by ABB Lummus Global,KBR, Foster-Wheeler, and others.

## 5.3. Recovery Section

The cracked gas leaving the cracking furnaces must be cooled to recover the heat it contains in the cracked gas and render it suitable for further processing. The temperature of the cracked gas leaving the primary TLE depends on the feedstock type; it varies from 300 °C for gaseous feedstock, to 420 °C for naphtha feedstock, and up to 600 °C for AGO and hydrocracker residues. In ethane and propane cracking, cooling to ca. 200 °C is performed in heat exchangers by preheating feedstock or BFW. However, this step can not be done in heat exchangers for feedstocks heavier than propane, due to the condensation of the liquid portion contained in the cracked gas. Cooling such cracked gases to 200 °C would lead to excessive fouling of the heat exchangers by carbon deposits. Thus, cooling is performed by injection of oil into the cracked gas (oil quench) by means of special tangential-injection mixing devices. Oil quenching is performed individually for each furnace or in the combined cracked gas line after collection of the cracked gas from all furnaces. In modern designs, the oil injection is located in the furnace area, integrated into the cracked gas line downstream from the TLEs.

The cracked gas leaving the furnace section has a temperature of ca. 200–250 °C and is routed to the separation section via a large cracked gas line. The collected gas stream contains the effluents of all cracking furnaces, including those processing recycle streams.

Table 3 to Table 5 shows the yields of the product fractions for all typical feedstocks and for varying cracking conditions. Apart from the type of feedstock, the gas composition and, therefore, the design of the downstream recovery process also depends on the cracking severity and the applied coil design.

Further processing, i.e., separation into the main products or fractions, can be performed in different sequences and depends on the feedstock type and the number and the specification of the plant products. The main downstream processing steps are the removal of the heat contained in the cracked gas, condensation of water and heavy hydrocarbons, compression, washing, drying, separation, and hydrogenation of certain multiply unsaturated components. The main task of these steps is to recover the desired products at given specifications and at the desired battery-limit conditions.

Ethane, propane, and butane can be recycled to the furnace section to increase the overall yield of ethylene per tonne of feedstock processed. Processing differs for cracked gas derived from gaseous and liquid feedstocks, since the portion of heavy components increases, especially when processing naphtha or even heavier feedstocks such as gas oil and hydrocracker bottoms. When pure ethane is the feedstock, the amount of $C_3$ and heavier byproducts is small, and only rarely is the recovery of heavier products economically feasible. As the concentration of heavier components increases, recovering them for direct sale becomes feasible. Addition of significant amounts of propane to ethane feedstock makes a depropanizer necessary and hydrotreating and fractionation of the $C_3$ cut may be required; butane feeds make oil and gasoline removal from the cracked-gas compressor necessary; pentane-range feeds require fractionation of light from tarry oils, and so on.

### 5.3.1. Products

Local market conditions and the degree of integration of the ethylene units into refining or petrochemical complexes influence the desired products and the feedstocks used. Many types of coproduct can be generated with different equipment [56–58]; only the major product options are discussed here.

The principal ethylene coproducts are as follows:

- Acetylenes ($C_2$ and $C_3$) are hydrogenated to ethane, ethylene, propane, and propene; or they may be recovered and sold as products.
- Aromatics (various fractions) can be recovered or they may remain in the hydrotreated pyrolysis gasoline.
- The $C_4$ fraction can be refined for butadiene, butene, isobutene, or mixtures thereof. If no $C_4$ products are desired, $C_4$ dienes and olefins are hydrogenated and recycled to cracking
- $C_5$ olefins can be either recovered and refined to give isoprene, piperylene, and cyclopentadiene, or hydrotreated in the pyrolysis gasoline fraction.
- Ethane is recycled as cracking feedstock or used as fuel.
- Fuel oil is used as such or to produce coke or carbon black.
- Hydrogen is purified and used for hydrogenation steps in the plant; excess hydrogen is sold or used as fuel in the plant.
- Methane is used as fuel or sold.
- Naphthalene is recovered for sale or left in the pyrolysis fuel oil fraction.
- Propane is recycled as a cracking feedstock, used as fuel, or sold.
- Propene is sold in various grades.
- Raw pyrolysis gasoline is sold as motor gasoline component after hydrotreatment, or it is used as feedstock for aromatics production.
- Tar is sold for fuel, used as coke feedstock, or diluted with hydrocarbon stocks to produce feedstocks for resins.
- Sulfur is recovered in some plants and sold.

### 5.3.2. Cracked Gas Processing

Many options are available for general process configuration [56, 59–65]. The sequence for isolation of hydrocarbon fractions can be varied, depending on plant size, amounts of ethylene and coproducts, impurities, product range, product purity desired, and other factors.

The following discussion of the recovery process is split into two sections:

1. Front-end section, including cracked gas compression and associated units
2. Hydrocarbon-fractionation section

Difference between the two sections is made for simplicity reasons. The basic process route for the front-end section is identical for all commercial processes, however major difference exists between gas- and liquid feedstock cracking. For the hydrocarbon fractionation section there are a large variety of process routes available, while the feedstock type results only in minor differences of the basic process route.

#### 5.3.2.1. Front-End Section

The front-end section (Figs. 32, 33) receives the effluent stream from the cracking furnaces. Its main task is to cool the cracked gas stream, recovering waste heat and providing it to other plant sections, to condense and to produce dilution steam, and to remove heavy hydrocarbon components such as tar, oil, and heavy gasoline. The resulting purified gas is compressed in the cracked gas compression section and dried to prepare it for further cryogenic separation in the fractionation section. An acid-gas removal step that eliminates all $CO_2$ and $H_2S$ from the cracked gas is incorporated between the final compressor stages.

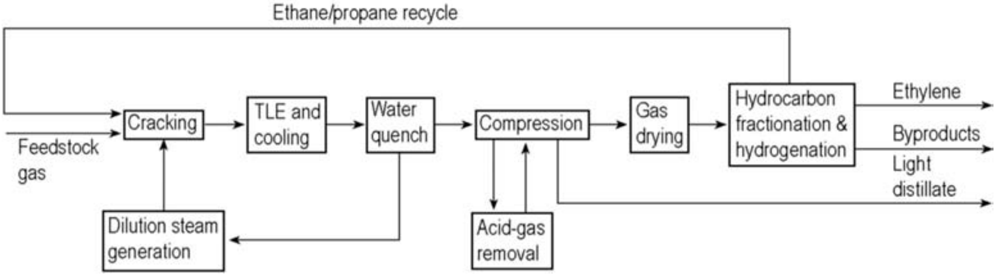


**Figure 32.** Simplified process flow diagram for the front-end process of an ethylene plant cracking gaseous feedstocks

The process configuration of this front-end section is fairly independent from licensors as they all follow the same process principals. However there are many variations in detailed design. Major differences are observed between plants processing gaseous feedstocks (ethane, propane, and butane) and those treating liquid feedstocks like naphtha and heavier fractions. Processing of cracked gas resulting from liquid feedstocks is more complex as higher amounts of heavy hydrocarbons are condensed and must be removed in this section.

**Process Description.** The main difference between the process for gaseous feedstock (Fig. 32) and liquid feedstock (Fig. 33) is the presence of a primary fractionator that by contacting with circulating oil removes tar and oily material (*bp* $> 200$ °C) from the cracked gas in the latter. In the case of cracking gaseous feedstock only, this step is not necessary, as the small amounts of heavy hydrocarbons present in the cracked gas can be removed in the water-quench column. Furthermore, additional installations are required in the water-quench system and in the compressor and drying units to treat the larger amount of pyrolysis gasoline that condenses in these units. The point when oil quench must be applied is reached, when substantial amounts of $C_4$ hydrocarbons are contained in the feedstock mixture.

**Primary Fractionation.** With liquid pyrolysis feedstocks, the primary fractionation column is the first step in the cracked gas processing route. Cracked gas enters the column typically at 230 °C. In the column it is contacted with circulating oil and, at the top of the column, with a heavy pyrolysis gasoline fraction obtained from the subsequent water-quench tower. Cracked gas leaves the top of the primary fractionator at ca. 100 °C, free of oil but still containing all the

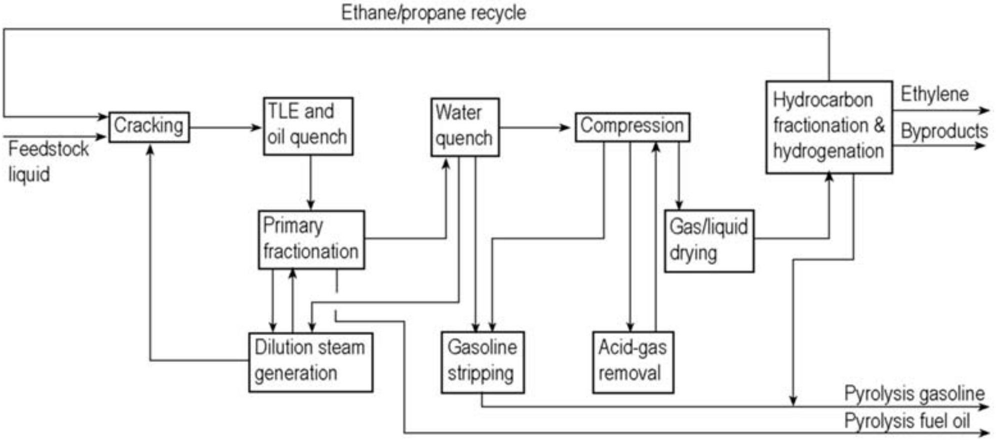


**Figure 33.** Simplified process flow diagram for the front-end process of an ethylene plant cracking liquid feedstocks

dilution steam. Hot oil, which functions as a heat carrier, is collected at the bottom of the column and, after cooling, recirculated as reflux to the middle section of the primary fractionator and to the quench nozzles downstream of the TLEs. Most of the heat contained in the cracked gas leaving the TLEs is removed by the circulating quench oil. Heat is reused for generation of process steam as well as for other purposes such as preheating of feedstock, preheating of process water, or for other energy consumers at an appropriate temperature level. Excess oil is removed from the primary fractionation system and sent out as product. Pyrolysis oil is generally produced as one fraction, containing all hydrocarbons boiling above 200 °C. However some plants produce two qualities of pyrolysis oil, one called PGO (pyrolysis gas oil) boiling in the range 200–400 °C and PFO (pyrolysis fuel oil) containing the heavier components.

**Water-Quench Column.** The overhead of the primary fractionator is routed to the water-quench column, in which the cracked gas is cooled to near ambient temperature by contacting it with a large stream of circulating quench water. In this cooling step most of the dilution steam and a heavy gasoline fraction are condensed and collected at the bottom. After gravity separation, heat is extracted in a circulating loop and most of the excess water stream is used to produce dilution steam. Large amounts of low-temperature heat (60–80 °C) are recovered and used for various heating purposes in the recovery section. The largest consumer of this low temperature heat is typically the reboiler of the propene–propane fractionation tower. Most of the condensed gasoline is recycled as reflux to the top of the primary fractionator. The excess gasoline fraction is sent to a gasoline hydrotreater or fractionated further into higher quality gasoline and heavier oil streams. Both water and gasoline fractions, except when fractionated further, are stripped of dissolved light gases [56, 59, 66, 67].

In the case of processing cracked gas from gaseous feedstock, the furnace effluent stream is directly fed to the water-quench tower after cooling in a secondary TLE to ca. 200 °C. In this case the system is simpler as no or only small amounts of tar and oil condense and must be removed. A general problem in all quench towers is the separation of hydrocarbons and water. Tarry material with a density similar to water, which is present in small quantities, tends to accumulate in the system and to stick to the surface of the column internals. On-line or off-line washing with high-boiling, aromatic-rich solvents is applied to extend the on-stream time of the system up to five years. There is furthermore a strong tendency for formation of emulsions, leading to fouling problems in the generation of dilution steam and in the processing of the wastewater from the system. Emulsification is avoided by careful control of the pH value in the quench-water system.

Numerous options exist in the design and operation of the quench column and primary fractionator units for removing pyrolysis tars, recovering various heavy hydrocarbon streams, and isolating quench oil for recycle [56, 66, 67].

**Dilution-Steam System.** The dilution steam required in the cracking process forms a closed loop over the cracking furnaces and the quench-water column. Excess water from the bottom of the quench column is stripped in a process water stripper to remove volatile hydrocarbons. Some 5–10 % of the process water is purged to avoid concentrating dissolved solids. The generation of the process steam is typically performed at 800 kPa. In liquid feedstock processes, 50–80 % of the dilution steam is generated by recovering heat from the hot quench oil cycle from the bottom of the primary fractionator. The balance heat duty is provided by condensing steam. Dilution steam is typically generated in dedicated heat exchangers and routed to the cracking furnaces where it is mixed to the feedstock at appropriated position in the convection section.

Some licensors use a different approach for the generation of dilution steam in gaseous feedstock processes. Ethane - propane feedstock is saturated in a dedicated column by direct contact with circulating water. Heat input is performed by heating the circulating water and the water - hydrocarbon ratio is adjusted by controlling pressure and temperature in this column [68].

*Compression.* After cooling and purification of the cracked gas in the primary fractionator and/or in the quench tower, further processing requires compression to ca. 3200–3800 kPa. Some condensation of water and hydrocarbons occurs during compression, and in the later stages, acidic gases are removed. Compression is typically performed by a turbine-driven centrifugal compressor in four to five stages with intermediate cooling. The number of stages depends primarily on the cracked-gas composition the temperature level of the cooling medium, and the highest temperature allowed for interstage discharge. Interstage cooling and temperature control keep the cracked gas below 100 °C to prevent diolefin polymerization and subsequent equipment fouling. Various injection systems, using aromatic rich oil or water, are applied to reduce fouling of compressor internals and intercooling equipment. Interstage cooling usually employs water coolers to minimize inlet temperature in the subsequent stages. First-stage compressor suction is normally maintained somewhat above atmospheric pressure to prevent oxygen intrusion. The operating pressure is set to economically balance yield in the cracking coils against higher energy consumption for compression [56]. The compressor discharge pressure is set by the choice of process design and by the choice of refrigerant. With a high-pressure demethanization methane condenses in the demethanizer overhead condenser. Condensation temperature varies with hydrogen/methane ratio. The discharge pressure, with the coldest ethylene refrigerant level typically at ca. $-100$ °C, is normally 3200–3800 kPa. Processes involving low-pressure or medium-pressure demethanizers can use discharge pressures of 2000 kPa only, however, in such cases the total compression power is fairly constant, because the power is just shifted from cracked-gas compression to refrigerant compressors. The criteria used to determine suction pressure and discharge pressure are selectivity and energy consumption, and equipment costs. [56, 67]

Interstage cooler pressure drops must be kept low, especially in the initial stages, to reduce compressor and energy costs. The water and hydrocarbon condensates may be routed to another compressor stage, to the quench column preceding the compressor, or to a fractionation tower. In liquid cracking most of the gasoline fraction containing the $C_6$ to $C_8$ aromatics is condensed in the interstage coolers of the compressor. After gravity separation from process water this gasoline stream is fractionated in a stripper to remove $C_4$ and lighter components before routing it to a hydrotreating step. Drying is required for all liquid and gas streams subjected to temperatures below 15 °C [56, 59, 65, 66].

*Acid-Gas Removal.* Before further processing, carbon dioxide and hydrogen sulfide are removed from the cracked gas by once-through (caustic wash) and regenerative solvent (MEA) scrubbing. Sulfur may also be removed from the cracker feedstock. [56].

The acid-gas removal system is typically located between the 3rd and 4th, or between the 4th and 5th stages. In all process configurations acid-gas removal must be located upstream of the drying unit in order to avoid formation of ice and hydrates in the following fractionation steps.

Carbon dioxide is removed because it can freeze at low temperature in heat-exchange and fractionation equipment. Carbon dioxide can also be absorbed into ethylene, affecting product quality and further processing. Hydrogen sulfide is corrosive and a catalyst poison as well as a potential product contaminant [58, 59]. $CO_2$ and $H_2S$ concentrations in the overhead stream of the caustic wash are typically below 0.2 ppm.

These acid gases are scrubbed with sodium hydroxide on a once-through basis or in combination with a regenerative chemical. Regenerative pre-scrubbing before final sodium hydroxide treatment is applied at high-sulfur feedstocks. This reduces sodium hydroxide consumption, which is desirable for economic and environmental reasons, however, it requires the handling of a sulfur-rich off-gas stream.

Regenerative scrubbing can employ alkanolamines, but it is not possible with this treatment alone to lower the concentration of $CO_2$ to that required to meet standard ethylene specifications (e.g., to 0.2 ppm). In any case a polishing scrubber consisting of a caustic wash unit is applied to achieve the required $CO_2$ specification in the effluent stream. Acid-gas removal systems are frequently subject to fouling, especially at high concentrations of $C_4$ and $C_5$ diolefins. Insiders talk about "yellow oil" or "red oil", an unpleasantly smelling polymeric material. The fouling process can be controlled by applying special inhibitors.

Acid gases liberated from the regenerative solvent can be incinerated or recovered [56, 59, 66, 67, 69]. Waste caustic, containing sulfides and carbonate in the range of a few % is usually oxidized and neutralized in a wet caustic oxidation unit or neutralized and stripped, before feeding it to the sewer system. Spent caustic is the most contaminated liquid effluent in the ethylene plant, because it is the outlet for various trace components accumulating in the process. In addition to the sulfur and carbonate load the stream further carries traces of dissolved hydrocarbons, organic acids, ketones, alcohols, and aldehydes.

*Drying.* The cracked gas is saturated with water before compression and after each intercooler stage. Moisture must be removed before fractionation to prevent formation of hydrates and ice. Typically, this is accomplished by chilling and by adsorption on molecular sieves. Older plants also used absorption by a glycol scrubbing system or adsorption on alumina [58]. Drying is arranged before the first fractionation step, typically after the last compression stage. Before feeding the compressor effluent to the molecular sieve dryer it is cooled in a water cooler and subsequently by propene refrigerant. A temperature of 15 °C upstream of the dryer is desirable for removing as much water as possible to reduce load on the dryers. However, the temperature must remain above the hydrate-formation point, which lies in the range 10–15 °C [56, 66]. Water is adsorbed on molecular sieves, preferably after the highest compression pressure is reached to minimize adsorption costs. Higher pressure allows smaller dryer volume with lower adsorbent cost and less water removal because the water content in the gas stream decreases with increasing pressure. Multiple adsorption beds make continuous water removal possible. One or more adsorption beds are in operation while at least one unit is being regenerated. Regeneration requires the use of heated gas that is free of polymerizable components. Byproduct methane and hydrogen used as fuel are typically good choices for this gas [56–59, 66, 67]. In liquid-feedstock cracking processes large amounts of hydrocarbons are condensed at 15 °C. If these liquid hydrocarbons are to be fed to the fractionation column they are also dried over molecular sieve adsorbers.

#### 5.3.2.2. Hydrocarbon Fractionation Section

The fractionation section receives the compressed cracked gas at a pressure of 3200–3800 kPa for further fractionation into different products and fractions at specified qualities and battery limit conditions. Over the history of design and construction of ethylene plants many different process schemes have been developed and implemented for this task.

Cryogenic separation is the predominant method for cracked-gas separation. Although gas separation processes via adsorption, absorption, or membrane technology has made remarkable progress in the recent past, it has not found major application in the ethylene industry. Rare applications of these methods can be found in very special cases like revamps or pretreatment of off-gases from polymerization plants or from refineries, containing valuable components, before being sent to the ethylene plant.

Today, three processing routes have gained commercial importance, with the main characteristics being the first separation step and the position of the hydrogenation of the acetylene contained in the cracked gas. These three process sequences are:

1. Demethanizer first with tail-end hydrogenation
2. Deethanizer first with front-end hydrogenation
3. Depropanizer first with front-end hydrogenation

These basic processes differ in the configuration of process steps for any given feedstock, but provide similar overall capabilities for fractionation and hydrogenation. The differences are primarily in the sequence of fractionation and hydrotreating steps downstream of cracked-gas compression [56].

**Process Description.** Compressed cracked gas can be:

1. Condensed and fed to a demethanizer column (front-end demethanizer), as shown in Figure 34
2. Condensed and fed to a deethanizer (front-end deethanizer), as shown in Figure 35

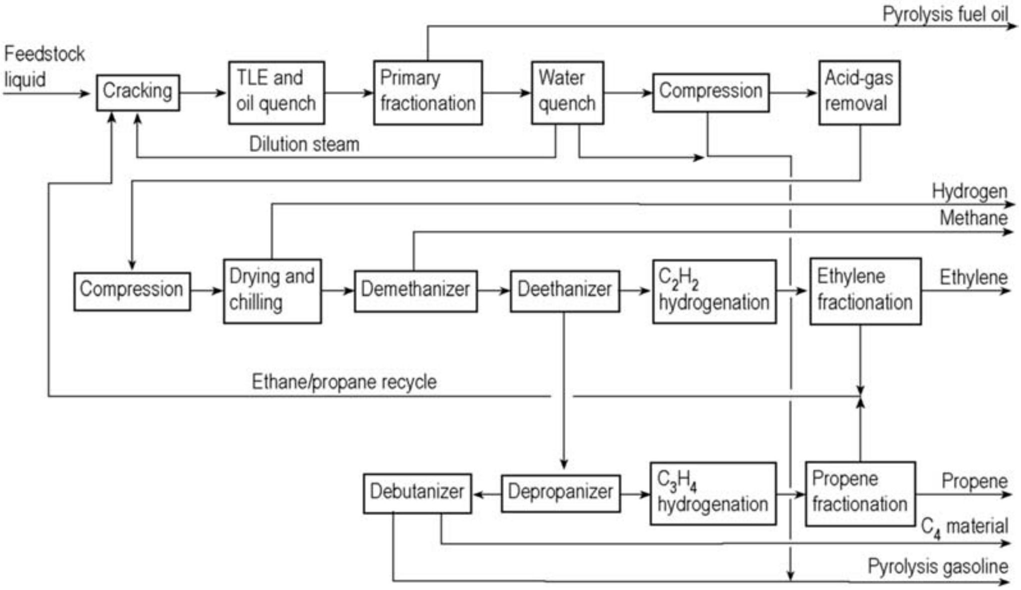


**Figure 34.** Simplified process flow diagram for the production of ethylene by liquid cracking with a front-end demethanizer

3. Removed from an intermediate compressor stage, condensed, and depropanized in a column, whereby the light gas is returned to the last compressor stage (front-end depropanizer), as shown in Figure 36

Combinations are possible; for example, intermediate compressor stage condensate and vapor are sent to different parts of the plant [66, 62].

Traditionally the demethanizer first/tail-end hydrogenation process sequence was used by American contractors. With the need for reduction of energy consumption in the separation section and process simplification for cost reasons, the deethanizer first/front-end hydrogena-

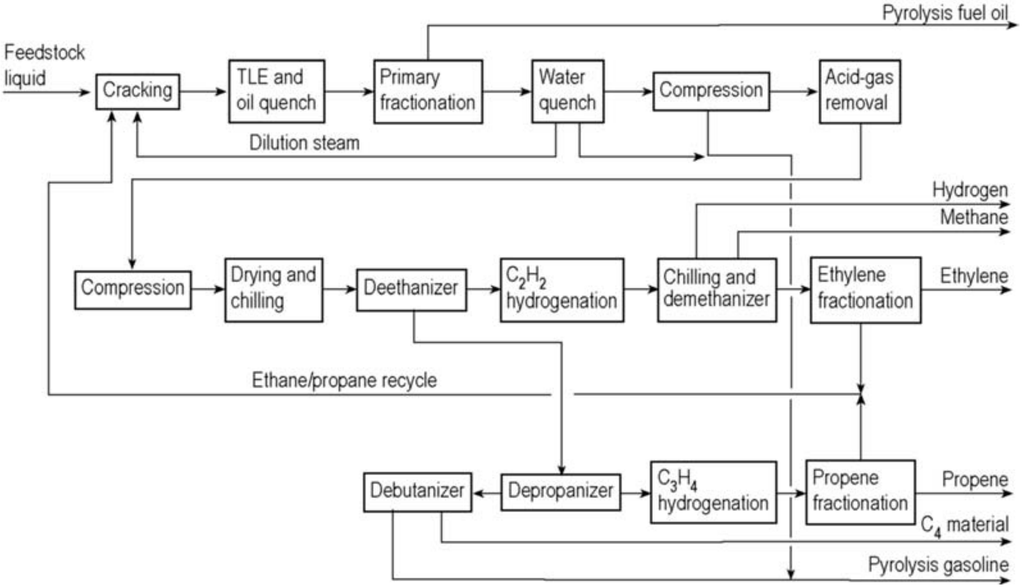


**Figure 35.** Simplified process flow diagram for the production of ethylene by liquid cracking with a front-end deethanizer

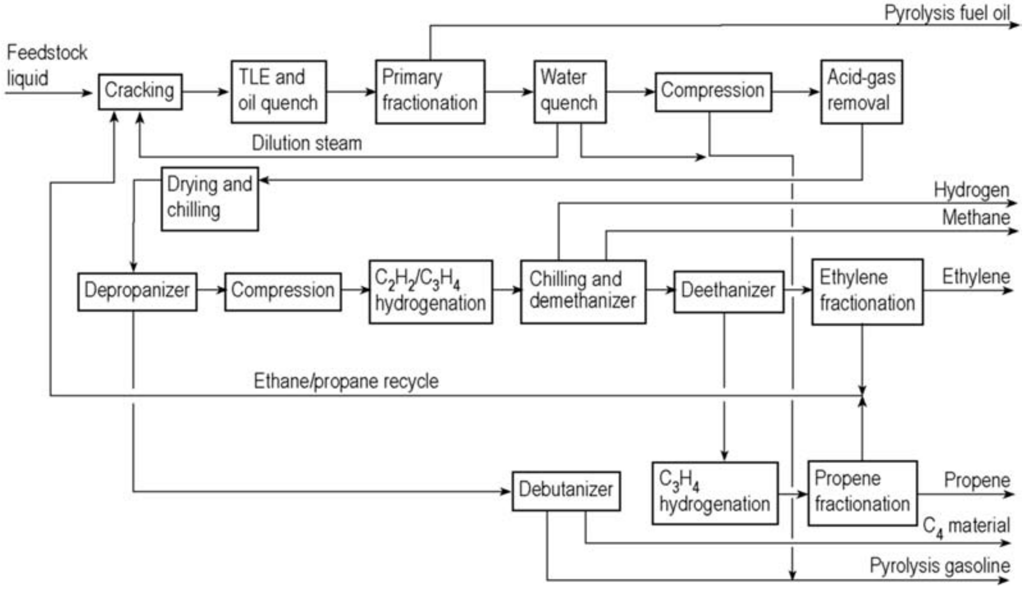


**Figure 36.** Simplified process flow diagram for the production of ethylene by liquid cracking with a front-end depropanizer

tion process, which had long been used by Linde, was also applied by some American contractors. A comparison of all routes has shown that this sequence seems to have the best energy efficiency [70]. New developments in this area are the combination of the advantageous sequence with special equipment (dephlegmators) [71] and the application of washing steps for demethanization [72].

*Front-End Demethanizer* (Fig. 34). The hydrocarbon-separation sequence begins with removal of methane and lighter components, primarily hydrogen, from higher molecular mass components. Hydrogen may be removed before or after methane. The bottom product is routed to a deethanizer column where acetylene, ethane, and ethylene are removed as overhead product, and $C_3$ and heavier components as bottom product.

Typically, the overhead product from the deethanizer is first hydrotreated to convert acetylene to ethylene and ethane. This treated overhead mixture is then fractionated to ethylene product and ethane recycle.

The bottom product from the deethanizer is depropanized to separate $C_4$ and heavier components as a bottom stream; methylacetylene, propadiene, propane, and propene are taken as an overhead stream. This overhead fraction is hydrogenated to remove methylacetylene and propadiene, which can also be recovered by distillation or absorption and stripping. In the propene fractionation step, propene is recovered for sale and propane for recycle. The propene product can be of chemical grade or polymer grade with additional purification. Depropanizer bottoms are sent to a debutanizer for separation into other product streams ($C_4$ materials, raw pyrolysis gasoline, $C_5$ materials, aromatics, etc.) [56, 58–60, 65, 66].

*Front-End Deethanizer* (Fig. 35). Deethanization of dried cracked gas is used as the first fractionation step to produce an overhead stream of ethane and lighter components, and a bottom stream of $C_3$ and heavier materials; subsequently, the lighter components are hydrogenated to remove acetylene and fractionated cryogenically. Because this overhead stream is hydrogen rich, no supplementation is necessary for hydrogenation. During the chilling and demethanizer operation, the overhead is separated into hydrogen and methane; the bottom stream is fractionated to yield ethylene product and ethane; and the ethane is recycled to the cracking furnaces.

The bottom stream from the deethanizer is treated in the same way as in the front-end demethanizer system described above.

*Front-End Depropanizer* (Fig. 36). Depropanization of dried cracked gas is used as the first fractionation step to produce a propane and lighter component overhead stream and a $C_4$ and heavier bottom stream. The depropanizer overhead stream is compressed and hydrogenated to remove acetylene, and to partially hydrogenate methylacetylene and propadiene. It is then chilled and demethanized, and the bottom fraction of demethanization is deethanized. The deethanizer overhead components are fractionated to ethylene product and ethane, which is recycled as cracking feedstock. Deethanizer bottom product is hydrotreated to remove methylacetylene and propadiene, and fractionated to propene product and propane, which is recycled to the cracking furnaces. The depropanizer bottom components are fractionated to produce $C_4$ materials and raw pyrolysis gasoline [59, 60, 65, 66].

For all three of the above-mentioned basic processes numerous process variants exist. For liquid cracking acetylene hydrogenation is always performed in the $C_2$ stream, in the $C_{2-}$ or in the $C_{3-}$ stream. In the case of cracking gaseous feedstock with little coproduction of $C_4$ hydrocarbons the hydrogenation step can also be arranged in the total cracked gas stream during or just after cracked-gas compression (after or before drying). This is not feasible for cracked gas streams resulting from liquid cracking because 1,3-butadiene, typically a valuable byproduct, would be cohydrogenated almost completely to butene and butane.

Acetylene may also be recovered for sale by an absorption process. This absorption process step is located in the gas phase upstream of the ethylene fractionation column. N-methyl-2-pyrrolidone, acetone, and N,N-dimethylformamide are typical solvents used for acetylene recovery. The acetylene absorption tower yields a very pure ethylene product, because acetylene is removed practically down to the detection limit.

Acetylene recovery, however, is becoming more and more a niche application due to the disappearing importance of the acetylene chemistry and due to the limited acetylene production rate that can be obtained from a large-scale plant (ca 10 000 t/a) This quantity, however, on the other hand is too large to be totally used by the welding industry.

*Pre-fractionation Feed Chilling.* Before being fed to any of the fractionation towers, dried cracked gas must be cooled and partially condensed. Dried cracked gas is cooled by the refrigerant systems and by the low-temperature product and recycle streams leaving the cold fractionation equipment down to a temperature of typically −140 to −160 °C. At this temperature $C_2$ components are entirely removed by partial condensation, and the noncondensed gas stream has a hydrogen concentration of 80–95 vol %. The type of refrigerant, number of refrigeration levels, and the design of the refrigeration and heat-exchange systems depend on the temperature and pressure required in the downstream fractionation equipment. Fractionation and purification consume much energy. Cryogenic purification of methane, ethane, and ethylene requires costly refrigeration. Design optimization is complex because:

1. The most efficient routing must be considered for the condensates and vapor streams from each stage of the cool-down sequence in the individual refrigeration loops (e.g., 2–6 stages each)
2. The energy requirements for fractionation must be determined
3. The freezing of components, such as acetylene, butadiene, and benzene, must be avoided

When acetylene content is high, prevention of freezing and safe hydrogenation are important. Also of importance from a safety standpoint for the chilling section and downstream equipment is the choice of appropriate construction materials for cryogenic conditions [56, 58]. Process equipment that may accidentally be exposed to cryogenic conditions should also be carefully studied. National standards are available in most countries to assist in making appropriate selections [56, 58].

**Demethanization.** Demethanization of cracked gas separates methane as an overhead component from $C_2$ and heavier bottom components; concurrently, hydrogen is removed from the cracked-gas stream and may be obtained as a product by purification before or after demethanization. In case of naphtha cracking hydrogen is recovered at high purity because it is needed in the plant itself for various hydrogenation steps and because any excess can typically be sent out when the plant is embedded in a refinery environment. In gas-cracking plants hydrogen is only required at low quantities. The bulk of hydrogen is recovered together with methane, forming the tail-gas stream, that is sent to the fuel system after expansion.

Methane is typically used as plant fuel or sold; $C_2$ and heavier components are sent to the recovery system. This overall fractionation is important from a design and operational standpoint because of its high share of the capital, energy, and fuel consumption of the ethylene plant. Demethanization typically consumes the greatest proportion of net energy from the refrigeration system (see Fig. 37 and discussion of refrigeration, Section Refrigeration) [61, 69].

In the demethanizer system and the associated process for the isolation of high-purity hydrogen the lowest temperatures in the plant (down to $-165$ °C) prevail.

The industry offers a large variety of combinations of process steps to achieve the desired separation result. All processes consist of a combination of cooling steps, partial condensation, and a demethanizer tower system. Liquids, knocked out during cooling are fed to the demethanizer at an appropriate position. Some licensors apply special equipment like dephlegmators or recontactors in this process configuration to perform a preseparation of the material before sending it to the column. Both dephlegmators and recontactors incorporate an additional number of theoretical equilibrium stages in the cooling train contributing to the demethanization.

Demethanizer systems operate in a wide pressure range between 1000 and 3500 kPa (LP, MP, and HP demethanizers), each of these having their specific characteristics.

A special challenge in this process is the provision of the respective chilling duty for individual cooling steps. The classical method for generating chilling duty down to a temperature of $-100$ °C is the refrigerant cascade of ethylene and propene. Temperatures below

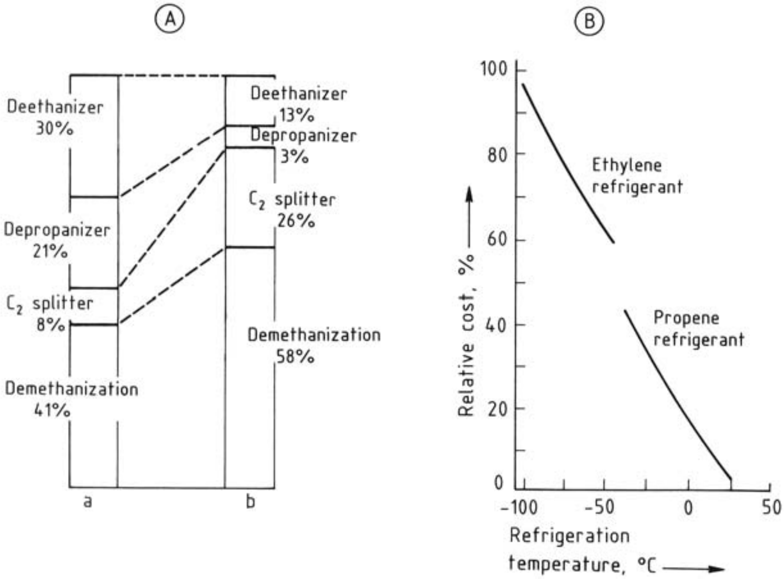


**Figure 37.** Distribution of heat load and work requirement of the refrigeration system in a typical front-end demethanizer ethylene plant*

A) Distribution of heat load and work requirement

a) Net heat absorbed by the refrigeration system; b) Net work done by the refrigeration system

B) Relative cost of heat absorbed by the refrigeration system at different temperatures

*Reprinted with permission [69].

−100 °C are achieved by one of the following methods:

- Adding another element in the refrigerant cascade, namely a methane refrigerant cycle
- Generation of a light recycle stream, i.e., vaporizing condensed cracked gas fractions and recycling the vapors to the cracked gas compressor
- In the case of gas cracking, hydrogen is not recovered at high pressure and can be depressurized to fuel gas pressure in a turbo-expander, generating chilling duty at very low temperature
- Applying a mixed refrigerant cycle that covers the full temperature range

[63, 67].

The demethanizer bottom stream contains $C_2$ and heavier components. With the front-end demethanizer, components from $C_2$ through pyrolysis gasoline may be present. However, with front-end deethanization, $C_{3+}$ components are removed, and with front-end depropanization, $C_{4+}$ components are removed. The demethanizer design changes significantly as heavier components are eliminated, especially with regard to the refrigeration needed to condense the incoming cracked-gas feed stream and to reboil the bottom stream.

**Deethanization.** Deethanization of cracked gas separates acetylene, ethylene, and ethane as overhead components from $C_{3+}$ bottom components. In newer plants, low-pressure fractionation may be used, or feed streams from the cracked-gas chilling section can be supplied as multiple feeds to the deethanization tower. The deethanizer is usually the third largest user of refrigeration energy in a front-end demethanizer ethylene plant (Fig. 37) [56, 66, 67, 69].

With front-end demethanization and front-end depropanization, the feed stream to the deethanizer comes primarily from the demethanizer. With front-end deethanization, the deethanizer feed comes from the chillers that follow the gas dryers. In the simplest cases, single feed streams from these units are separated into overhead and bottom fractions for further processing. [56]. Dual-pressure deethanizer systems improve energy consumption and reduce the bottom temperature, thus reducing fouling in reboilers. As with the demethanizer, these designs conserve refrigeration energy but increase capital costs and operating complexity. The overhead product condensation temperature is typically ca. 0 to −50 °C, based on a column operating pressure of 1500–2700 kPa [59, 60, 65].

**Depropanization** of cracked gas separates propane and lighter fractions as overhead components from $C_{4+}$ fractions as bottom components. Feed streams from compression, and sometimes streams from the gas-chilling section, can be routed to the depropanizer, which, compared to other fractionation units, requires less refrigeration because of its higher operating temperature (Fig. 37) [69].

The feed stream to the depropanizer comes primarily from the deethanizer when front-end demethanization and deethanization are employed. With front-end depropanization, the feedstock is taken from the gas dryers. In the simplest case, the dried cracked-gas feed stream is separated into a propene–propane overhead stream, which contains small amounts of methylacetylene and propadiene, and a bottom stream which contains components from $C_4$ materials to raw pyrolysis gasoline. Energy requirement is reduced by mixing smaller feed streams removed from intermediate compression or gas-chilling stages with the main feed stream, or by having them enter separately at a point in the depropanizer consistent with the composition of column components. Condensate is usually stripped before entry into the depropanizer [56, 67].

Operating pressure and temperature of the depropanization step in ethylene plants, even downstream of the deethanizer, are kept low to reduce fouling of the fractionator by acetylenic and diolefinic contaminants. Hydrogenation of cracked gas in the compressor zone lowers the amount of these polymerizing contaminants substantially, but also destroys most of the butadiene [56, 60, 65].

**Debutanization.** Debutanization of cracked gas separates $C_4$ materials as overhead components from $C_5$ and heavier fractions as bottom components. The feed stream comes typically from the depropanizer column or is a depropanized condensate stream from the compressor.

The mixed $C_4$ overhead fraction may be sent to an extraction unit for removal of 1,3-butadiene and further processing. The bottom stream and the debutanized fraction from the compression section can be used as pyrolysis gasoline feedstock or processed to produce aromatics and specialty chemicals feedstocks [56].

**Acetylene Hydrogenation.** Cracked gas is selectively hydrogenated to remove acetylene from ethylene, except when acetylene is recovered for sale. Hydrogenation is performed with palladium-based catalysts. Ethylene specification requires less than 1 ppm of acetylene, thus acetylene content at the outlet of the hydrogenation must be $< 0.5$ ppm. Pressure ranges typically from 20 to 35 bar and the temperature from 25 to 100 °C. There are two basic processes for the hydrogenation of acetylene.

*Tail-End Hydrogenation.* Acetylene hydrogenation takes place in the gas phase of a pure $C_2$ fraction, consisting of ethylene, ethane, and acetylene only. The unit is typically incorporated after demethanization, upstream of the $C_2$ fractionation tower. Hydrogenation reactors consist of one or two adiabatic beds. Hydrogen is added upstream of the reactor at a molar $H_2/C_2H_2$ ratio of ca. 1.5–2, resulting in an ethylene gain of up to 50 % of the acetylene present. Hydrogen and small amounts of methane and CO introduced after demethanization must be removed by additional fractionation. Sometimes purging the light ends from the overhead ethylene fractionator condensate is possible, but additional multistage fractionation is usually required in the ethylene fractionator or in a small separate demethanizer. A useful design provides five to ten overhead stages above the product drawoff point in the ethylene fractionator column for further separation of the light ends. The overhead condensate is returned to the top of the tower, and the light ends are removed from the overhead partial condenser for reprocessing [56, 61, 66, 69].

*Front-End Hydrogenation.* Acetylene is hydrogenated:

1. In the total cracked gas stream after or before drying
2. In the $C_{3-}$ stream with front-end depropanizer
3. In the $C_{2-}$ stream with front-end deethanizer

In the case of (1) and (2) any methylacetylene, propadiene and butadiene, present in the gas stream is cohydrogenated. (methylacetylene ca. 80 %, propadiene 30 %, butadiene $> 90$ %).

Although hydrogenation in the cracked gas (1) may offer advantages for the lighter feedstocks, disadvantages exist with heavier feedstocks. In particular, the volume of gas treated at this stage is high; butadiene is hydrogenated and lost; and a single hydrogenation to concurrently remove acetylene, methylacetylene, and propadiene to the required levels without significant olefin loss is not possible. Hydrogenation of individual mixed $C_2$ and $C_3$ streams after deethanization and depropanization, respectively, appears to permit more efficient use of catalyst and result in higher product yields. However, proponents of the front-end deethanization and depropanization process with front-end acetylene hydrogenation report that bed sizes are equivalent for that reaction. Higher hydrogen concentration and improved catalysts allow higher gas space velocities than can be achieved downstream [66].

General advantages of the front-end hydrogenation versus the tail-end hydrogenation unit are: (1) no hydrogen make up is required as hydrogen is already present in the feed stream; (2) longer run length between catalyst regenerations; (3) No removal of light ends, as required in tail-end hydrogenation, is necessary.

Front-end hydrogenation is typically conducted in multistage adiabatic beds with intercooling, or less frequently in a single tubular reactor that allows an isothermal reaction.Due to the high concentration of hydrogen and ethylene in the process gas front-end hydrogenation requires a very selective catalyst, that promotes the hydrogenation of acetylene only.

Acetylene hydrogenation requires heat-exchange systems for incoming low-temperature process streams (2) and (3). Hydrogenation in the compressor section (1) does not require the heat-exchange system necessary for cryogenic streams. Most of the troublesome polymerizable components are removed before fractionation, although rapid fouling of the hydrogenation bed must be avoided. Hydrogenation may be necessary before chilling if a high acetylene concentration in the cracked gas would result in plugging or in unsafe downstream operation [56, 58, 66].

Although tail-end hydrogenation is the most common process in currently operating plants, it seems there is a strong tendency to increasingly apply the front-end hydrogenation system in new projects. This tendency is supported by a continuous improvement of front-end hydrogenation catalysts. New catalysts show an increased operating temperature window in which only acetylene or dienes are selectively hydrogenated. Furthermore, new catalysts are less sensitive toward CO. These improvements result in higher operational stability decreasing the danger of reaction runaway, where in addition to acetylene also ethylene participates in the reaction. The shapes of catalyst particle were typically little spheres, tablets, or extruded particles of a size of a few millimeters. New catalysts are available with different geometrical structures such as rings or other shapes that result in lower pressure drop. This contributes in overall energy saving, because the front-end hydrogenation is located in the main cracked gas stream where this pressure drop directly affects the cracked gas compressor outlet pressure.

**Ethylene Fractionation.** Ethylene fractionation separates ethylene as a high-purity overhead product ($>$ 99.9 wt %) from ethane, which is combined with propane and recycled for cracking. For this difficult fractionation, the net work done by the refrigeration system is high because of the high reflux and low temperature required (Fig. 37) [56, 69]. Fractionation requires a high reflux ratio (ca. 4) and as many as 90–125 separation stages [59, 60, 65, 66, 69]. The ethylene purity desired is typically $>$ 99.9 wt %. The feed stream comes from the acetylene-removal step that follows chilling, or from the demethanizer or deethanizer.

There are basically two processes in commercial use: high-pressure fractionation and heat-pumped $C_2$ fractionation.

*High-Pressure Fractionation.* High-pressure fractionation, operating in the pressure range of 1700–2800 kPa, is typically used in tail-end hydrogenation systems. Heating and cooling of the column is integrated into the propene refrigeration cycle. Low-pressure propene refrigerant is vaporized in the top condenser, providing chilling duty. Vaporized propene is typically compressed in two stages of the refrigerant compressor. After compression, propene vapors are condensed in the reboiler, providing heat duty. By means of this system the propene refrigerant compressor acts as an indirect heat pump, shifting heat from the condenser of the column to the reboiler. The top of the column is equipped with some pasteurization trays to remove light ends introduced when acetylene is hydrogenated in the feed stream to this column. Ethylene product is withdrawn as a liquid side stream some trays below the top, pumped to the required product pressure, and delivered to battery limits after vaporization and heating.

*Heat-Pumped $C_2$ Fractionation.* In heat-pumped $C_2$ fractionation, the column operates at a pressure of ca. 800 kPa. Overhead gases of the column, consisting of on-spec ethylene, are routed to a compressor after heating to ambient temperature in a feed–effluent exchanger and are compressed to ca. 2000 kPa. Part of the compressed ethylene vapor is cooled and routed to the reboiler where it is condensed, providing heat duty for reboiling. The condensed ethylene is recycled as reflux to the top of the column. Ethylene product is discharged to battery limits from the discharge side of the compressor. Heat-pumped ethylene fractionation can use a dedicated compressor. More common is the integration of the heat-pumped ethylene splitter in the ethylene compressor, using the 3rd stage of this compressor as a heat pump.

This process has some advantages over the high-pressure fractionation process with respect to investment and energy consumption. Less equipment is involved, and because of the better relative volatility of ethylene and ethane at lower pressure, a lower reflux ratio and less column trays are required,altogether resulting in lower power consumption, smaller column size, and generally less equipment. However it is not feasible to use the heat-pumped process in combination with tail-end hydrogenation because of the light ends present in the feed stream.

Ethylene is generally discharged to battery limits as a gas. However, production of up to 50 % of production as the liquid phase and the use of storage facilities is also practiced.The ethylene plant is typically equipped with ethylene product storage capacity in order to balance production and consumption of downstream plants. Two storage types are commercial practice:

Semirefrigerated storage at about 1500 kPa and −40 °C, using spherical containers of a size of up to 3000 m$^3$ (for smaller storage inventories).

Atmospheric storage tanks, operated at atmospheric pressure and −103 °C. The size of these tanks is not limited, typically in the range of 10 000–20 000 m$^3$. Tank systems are usually equipped with liquefaction facilities in order to handle boil-off gases and incoming flash gases. Product vaporization facilities for the full capacity of the plant are provided in order to continue ethylene supply to downstream users in the case of a plant upset.

### Hydrogenation of Methylacetylene and Propadiene (MAPD); $C_4$ Fraction; and Pyrolysis Gasoline.

*$C_3$ Hydrogenation.* The $C_3$ fraction coming from the top of the depropanizer typically contains 2–6 % of methylacetylene (MA) and propadiene (PD). For removal of these components from the propene product and for economic reasons MAPD is hydrogenated to propene and propane. Hydrogenation is performed in gaseous phase in multistage adiabatic bed reactors with intercooling steps or, more frequently, in liquid phase in a single trickle-bed reactor. Tubular reactors are applied in rare cases. The heat of reaction is removed in the trickle-bed reactor by partial vaporization of the processed liquid, this being condensed later by cooling water. Tubular reactors use a branch stream of the propane refrigerant compressor as coolant. Modern hydrogenation processes typically yield a net propene gain of 60 % of the MAPD present in the feed stream. The balance is converted to propane, which is recycled to the cracking furnaces as cracker feedstock.

MAPD concentration at the reactor outlet is typically 500–1000 ppm, when the propene product has polymer-grade quality. This figure results in high selectivity of the reaction. Residual MAPD is removed in the propene splitter along with propane by distillation. If only chemical-grade propene is required, the MAPD concentration after hydrogenation must be below 20 ppm as the propane–propene splitter will not be able to reduce MAPD down to the required level due to reduced reflex rate Recovery of MAPD is theoretically possible, applying a similar system as that one for acetylene recovery; however it is practically not used because of lacking demand for this product.

*$C_4$ Hydrogenation.* The $C_4$ cut from the top of the debutanizer typically contains small amounts of vinylacetylene and ethylacetylene, ca. 50 % 1,3-butadiene, and a few percent of butanes; the balance consists of various types of butenes, of which isobutene is the most important. Depending on the nature of the downstream processes it may be necessary to hydrogenate some of the unsaturated components. The following hydrogenation steps are in commercial use:

1. Selective hydrogenation of ethylacetylene and vinylacetylene to butadiene
2. Selective hydrogenation of butadiene to butenes
3. Full hydrogenation of all unsaturated to butane
4. Hydroisomerization to maximize 2-butene yield

Process (1) is applied to increase the 1,3 butadiene yield; process (2) is used if no use can be made of butadiene and to increase the butene yield; process (3) is employed if the $C_4$ cut is to be recycled as cracker feedstock to improve olefin yields or used as LPG product. Hydrogenation is performed in tubular reactor systems or, in more modern processes, in trickle-bed reactor systems. By selecting catalyst type and process parameters, the hydrogenation result with respect to yields of different components, mainly the various types of butenes, can be controlled in a certain range.

$C_3$ and $C_4$ hydrogenation units consist typically of adiabatic beds or tubular reactors, integrated in a system of coolers, recycle pumps and separation drums. New developments try to integrate the reaction step into the separation column, e.g., the depropanizer or debutanizer, applying the so called “Catalytic Distillation Process”. In this application the catalyst is installed in the separation column and is acting not only as catalyst but also as separation element, providing some theoretical equilibrium stages. Process owners report a number of advantages for this process step. However, industry is still reluctant to apply this new process in large-scale plants [74, 75].

*Pyrolysis Gasoline Hydrogenation.* Pyrolysis gasoline — the $C_5$ to $C_{10}$ hydrocarbon product fraction — consists mainly of aromatics. The nonaromatics are mainly unsaturated hydrocarbons with a high portion of acetylenes and dienes. This stream is unstable and cannot be stored, as the unsaturated components react further, forming polymers and gum. Depending on the downstream processes pyrolysis gasoline is hydrogenated and fractionated in different steps. The most common process route is as follows:

1. Selective hydrogenation of the total gasoline to hydrogenate acetylenes, dienes, and styrene to olefinic compounds. After stabilization and removal of oil this stream is suitable for use as motor fuel. The reaction is typically controlled in a way that the residual styrene value is ca 0.5 %.
2. Fractionation of the effluent of the 1st stage hydrogenation into a $C_5$ cut, a $C_6$–$C_8$ heart cut, and a $C_{9+}$ cut.
3. The $C_6$–$C_8$ cut is further processed in a 2nd stage hydrogenation step to convert olefins to paraffins and naphthenes and to convert all sulfur to $H_2S$, which is removed from the product in a downstream stripper. this process is necessary to prepare the heart cut for aromatics recovery. The specification is controlled via the bromine number, which is typically 0.5.

$C_2$, $C_3$, and $C_4$ hydrogenation as well as 1st stage, selective gasoline hydrogenation use palladium-based catalyst. Palladium catalyst, however, are sensitive with respect to metallic poisons such arsenic or mercury, that may be present in the cracked gas in small traces, originating from feedstock contaminants. If such contaminants are to be expected, the Pd catalyst must be protected by guard beds, consisting of various metallic oxides like CuO, ZnO, PbO, impregnated activated carbon, and other materials. The 1st stage gasoline hydrogenation catalyst, however, should preferably be based on nickel metal if these contaminants are present, because nickel catalysts are much less sensitive to them.

**Propene fractionation** separates propene as a chemical-grade overhead product (typically 93–95 wt % min.) or more frequently as polymer-grade propene ($>$ 99.5 wt %) from propane. This separation to polymer grade propene requires typically 150–230 stages and a reflux ratio of 20 because of the close boiling points of propene and propane. Two basic processes are applied for this difficult separation task: polymer-grade fractionators operate at ca 1800 kPa, with cooling water in the overhead condenser and hot quench water in the reboiler. In the case of naphtha cracking and where sufficient waste heat is available from the hot quench water cycle this is the most economic process. If no waste heat for reboiling is available, or where upstream cooling water temperature is higher than 35 °C a heat-pumped propene fractionator is applied. In this case the fractionator operates at ca. 800–1100 kPa, and the overhead gases are compressed and condensed in the reboiler. By means of this process the condenser heat is raised to a higher temperature level, and further use is made of it in the reboiler. The advantage of this system is that no external heat for reboiling and only small quantities of cooling water are required. The fractionation design depends on the concentration of propene in the feed, which varies from 70 % for propane cracking to 95 % for naphtha cracking [66, 67, 69].

The heat pump is typically driven by a dedicated compressor, in particular cases the heat pump is integrated into the propene refrigeration cycle combining heat pump and 3rd stage of this machine.

The feed stream to the propene fractionator usually comes from the methylacetylene and propadiene hydrogenation step. Excess hydrogen and methane are purged in an upstream stripper or as light ends in the column overhead or from the overhead condensate [59, 60, 65–67, 69].

**Hydrogen Purification.** Hydrogen is produced in the cryogenic section of the plant at a purity of typically 80–95 vol%. However, the product stream contains some 1000 ppm of carbon monoxide. Hydrogen product is required in the ethylene plant as make-up stream for the hydrogenation units. Excess hydrogen is typically a desired product. However, hydrogen must be free of carbon monoxide as CO is a poison for all hydrogenation processes. Today two processes are in commercial use in ethylene plants to purify hydrogen: (1) methanation of CO in a catalytic process, converting CO to methane and water, after which the effluent must be dried in adsorber beds; (2) hydrogen purification by adsorption in a pressure-swing adsorption unit, producing CO-free high-purity hydrogen.

### 5.3.3. Utilities

**Refrigeration.** Refrigeration in ethylene plants is important and costly. Refrigeration optimization is vital in plant design. Typically, two different refrigeration systems are employed, namely, ethylene and propene (or propene–propane), each of which generates chilling duty at two to five different temperature levels. Propene refrigeration is designed as a closed-loop system in which the heat removed by cooling water or by air cooling by condensing the refrigerant after the final compression stage. Ethylene refrigeration systems are designed as closed- and open-loop systems. Open-loop cycles integrate the ethylene-fractionation tower in the refrigeration system. Propene and ethylene refrigerant systems act as a chilling cascade. Heat removed from the process by the ethylene cycle at temperatures below −50 °C is shifted to the propene cycle by condensing high-pressure ethylene refrigerant by means of vaporizing low-pressure ethylene refrigerant. Refrigerant temperatures are chosen to accommodate diverse plant needs most efficiently. Methane refrigeration by simple expansion (not employed as a refrigeration loop) generates additional cooling and especially the lower temperatures needed to purify hydrogen for special purposes.

Some processes add a third refrigeration cycle to the cascade, using methane as refrigerant for the generation of low-temperature chilling duty below −100 °C.

Ethylene, propene, propane and methane are used because of their physical properties and availability in the ethylene plant [67].

One licensor recommends the application of a mixed refrigerant system, covering the full temperature range from −150 °C to +10 °C by one compressor only. Advantage of this system is the saving of one or even two compressor-turbine sets. This process applies a mixture of ethylene and propene or even ethylene, propene, and methane as refrigerant. Consequently the QT curve of the vaporizing coolant is not isothermal but follows on increasing line. [76].

Figure 37 shows the net heat and work required in a typical front-end demethanization plant with liquid feedstock. The less expensive refrigerant, propene, is used from + 25 to − 40 °C and the more expensive ethylene, from ca. −40 to −100 °C. The latter requires higher work input per unit of refrigeration;for example, Figure 37 shows that 41 % of the heat absorbed by the ethylene refrigeration system requires 58 % of the net work [69]. Refrigerants are usually generated by compression to 1600–2000 kPa in multistage units, followed by expansion to generate the lowest refrigeration temperature. Superheated ethylene is cooled and condensed with propene refrigerant. Propene, after compression, is cooled with process cooling water [59, 66, 69]. With open-loop systems, which are used less frequently, products are circulated in the refrigeration loops rather than isolated. Careful operation and reliable design of compressors (gas seals) reduces contamination [66].

**Energy.** Utility consumption, expressed in joules per kilogram, is the energy required to produce 1 kg of ethylene product. Feedstock, coproducts, and process design should be described fully for comparative purposes. Process optimization has to consider the cost of energy relative to capital costs, ease of process operation, product and byproduct quality control requirements, safety, and many other issues. The specific solution is always a compromise between the above mentioned parameters. Since the early 1970s until today, increased energy costs led to a reduction of energy consumption by nearly 50 %. This was accomplished by applying sophisticated process steps and designing the plants with a high degree of heat integration. Waste heat from cracked-gas cooling is utilized wherever possible, heat pumps, side reboilers, low-pressure distillation are applied. Modern design tools such as advanced process simulators or pinch analysis programs help the designer to find the optimum solution for an individual case. Efficiencies of major energy consuming equipment such as cracking furnaces and compressor-turbines have continuously been improved.

Approximate energy consumption to produce 1 kg of ethylene from various feedstocks is in the range of 15 000 kJ/kg to 27 000 kJ/kg (see below)

A reduction of ca. 2000 J/ per kilogram ethylene product is possible by using hot exhaust from gas turbines in the pyrolysis area as combustion air to preheat combustion fuel, or in a heat-recovery boiler. The turbines may also optimize energy use to produce electricity or can drive fractionation compressors and heat pumps [56, 58, 63, 64, 66, 67, 69]. The application of such a combined-cycle system, however, is costly and pays off only under special circumstances. Such installations are installed mainly in Japan and Korea, few of them in the rest of the world. In none of the new large-scale crackers built in the early 2000s such installations are applied.

Most of the energy consumed is introduced into the ethylene process via firing the cracking furnaces. The recovery process is driven by waste heat, recovered from the cracking furnaces via steam production in the TLEs or by recovering heat from the furnace effluent stream. The main energy consumers in the recovery section are the cracked-gas compressor and the refrigerant compressors, in which a total power of ca.0.6–0.7 kWh per kilogram ethylene is typically consumed. This power is usually provided by steam turbines, driven by steam generated and superheated in the cracking furnaces.Steam produced in the cracking furnaces and steam consumed in the ISBL ethylene plant is typically balanced. Depending on feed and byproducts some steam export or import is experienced.

**Cooling.** Ethylene production is a very energy-intensive process. Only some 20 % of the heat input is absorbed by the chemical reactions of the olefin production. The balance drives the process by driving turbines and pumps, heating columns, and process streams. At the end of the process the heat must be discharged to the ambient. Cooling is most commonly performed via a cooling-water cycle, discharging heat to the ambient via a cooling tower. In areas where cooling water is not available (e.g., new large petrochemical complexes in the Persian gulf area) heat is discharged to the sea via the primary/secondary cooling-water cycle, or to the air via air-fin coolers. Both options require higher process temperatures leading to a slight reduction in energy efficiency and higher installation costs.

The ethylene process requires a number of utilities, some of them like fuel gas and steam being produced in the plant itself. Depending on feedstock and plant specifics fuel and steam must be supported by import or may be in excess. Typical consumption figures for various feedstocks for a standard-size 1000 t/a ethylene plant are summarized in Table 11.

Because feedstock composition, flow schemes, and product distribution are undefined, these values are approximate but they are representative.

### 5.3.4. Process Advances

Major advances have been made in feedstock availability and process design [56, 69],:

- Feedstock cost and availability, new cracking technology, and concerns for the environment and health have influenced changes in process technology.
- Rapid development has occurred in process control, data management, and optimization systems. Control of individual units, as well as of the overall process, has had a significant

**Table 11.** Typical consumption figures of a standard-size ethylene plant

| Feedstock | Ethane | Propane | FR Naphtha | Gasoil |
|---|---|---|---|---|
| ethylene/propene product rate, t/h | 125/0 | 125/50 | 125/55 | 125/75 |
| Fired duty of cracking furnaces, MW | 613 | 621 | 772 | 848 |
| Fuel gas import (+) export (−), MW | 28 | − 540 | − 142 | 40 |
| SHP[a] steam production of the furnaces, t/h | 450 at 6.5 MPa | 454 at 7.5 MPa | 458 at 11.5 MPa | 463 at 11.5 MPa |
| HP Steam import (+) / export (−), t/h at 4.6 MPa | − 72 | 83 | balanced | 98 |
| Electric power, $kW_{el}$ | 3.5 | 4.8 | 7.5 | 9 |
| Circulating cooling water temperature rise 10 °C, $m^3$/h | 28 000 | 42 000 | 47 000 | 60 000 |
| Total compressor power, MW | 72 | 90 | 85 | 93 |
| Specific energy consumption, kJ/kg ethylene | 16 000 | 20 000 | 23 000 | 27 000 |

[a] SHP: super high pressure

impact on operations. Improved analysis and cracking-simulation models are required to more fully apply state-of-the-art process control.

- Major improvements have been made in the selectivity and efficiency of cracking by operating at higher temperature. Coils with shorter residence time and faster quenching systems have been developed. Energy requirements have been reduced by heat recovery from furnace flue gas, economizer gas, and cracked gas; refrigeration energy requirements have been lowered by increased application and improved design of heat-exchange and distillation systems. Use of gas turbines has increased, with the sale of electricity generated. At the same time, control, reliability, and efficiency of operation have improved [66, 67].
- The reliability,plant availability service life, have considerably improved.Plants are designed today for uninterrupted operation between turnarounds of five years.
- Improved fractionation process designs provide additional flexibility and further reduce process energy consumption while meeting plant-reliability and product-quality demands [67].
- Improved hydrogenation catalysts allow more selective and more stable removal of impurities and better quality control.

### 5.3.5. Plant Size

At the beginning of industrial ethylene production, in the 1950s, first commercial ethylene plants had a standard size of some $20 \times 10^3$ t/a. In the next generation of plants, built in the 1960s, plant capacity was already expanded to $60 - 80 \times 10^3$ t/a. The era of large-scale plants started in the 1970s when the standard size reached some $300 - 400–10^3$ t/a. Since then until today typical plant capacity has continuously been increased to more than $10^6$ t/a. Most of the large crackers, contracted during the boom period 2004–2006, most of them in the Middle East, have an ethylene capacity of $1 - 1.5 \times 10^6$ t/a.

The maximum plant capacity of a single-train ethylene plant is limited by the size of the cracked-gas compressor. Machinery manufacturers report that this capacity limit is most likely close to $2 \times 10^6$ t/a for a gas cracker considering current technology. However, it seems that technical constraints may not be the ultimate limiting factor. The industry will face the challenge of building larger plants if demanded by the market. Nontechnical issues such as logistic, feed availability, product offtake, and risk analysis will dominate this decision.

## 5.4. Ethanol based Production of Ethylene

Ethanol (→ Ethanol, Section 5.1.1.) (space-filling model in Fig. 38) can be produced commercially by hydration of ethylene, a reaction known for more than 100 years, or by fermentation of starches, sugar crops, or lignocellulose [77].

The synthetic production of ethanol from ethylene is currently not economical because of high raw-material costs and accounts only for less than 5 % of world's ethanol production. More than 95 % of world's ethanol production stems from agricultural crops with increasing share. A proportion of 35 % of the ethanol is used in beverages or food applications whereas 65 % is utilized as fuel.

As can be seen from Table 12, the biomass used for production of ethanol can vary in a wide range in composition.

Independent of the biomass utilized for fermentation, four main steps are always involved in the production of bioethanol:

1. Feedstock treatment to get a sugar solution
2. Addition of yeasts or bacteria to convert sugar into ethanol and $CO_2$
3. Distillation to separate ethanol from fermentation broth
4. If required dehydrating (water removal)

**Figure 38.** Space-filling model of ethanol

**Table 12.** Typical composition of the main feedstocks used for ethanol production [78]

| | Sugars, wt% | Fiber, % | Protein, wt% | Oil/fat, wt% | Ash, wt% | Water, wt% |
|---|---|---|---|---|---|---|
| Sugar cane | 16.5 | 3.1 | 0.6 | 0.1 | 0.3 | 82.5 |
| Sugar beet | 20.4 | 1.1 | 1.1 | 0.1 | 0.7 | 76.6 |
| Corn | 68.3 | 2.9 | 7.4 | 2.8 | 0.9 | 17.7 |
| Wheat | 69.1 – 75.4 | 1.8 – 2.3 | 9.4 – 14.0 | 1.8 – 2.5 | 1.7 | 11.6 – 14.0 |
| Oat | 67.4 | 5.8 | 13.1 | 6.1 | 2.4 | 11.0 |

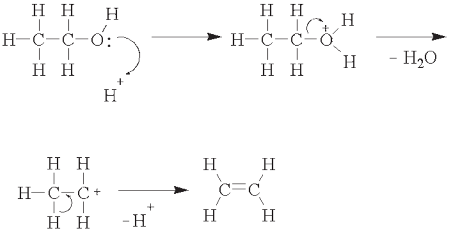
Leading producers today are Brazil and the United States with a production of $17 \times 10^9$ L/a and $18 \times 10^9$ L/a, respectively (Figure 39, Table 13). The strong growth of world ethanol production is a result of the increasing demand as motor fuel.

With the recent boom in the fuel ethanol market, particularly in Brazil and the United States, the production of chemicals from ethanol has attracted renewed interest. Environmental concerns over the use of fossil-based resources and the concept of sustainability have also broadened worldwide interest in renewable sources for both chemical feedstocks and for energy. In the case of bio-derived ethanol, production costs declined significantly over the years as a result of productivity improvements and economies of scale. These, combined with the promise of new technologies from cheap cellulosic biomass, could make ethanol a competitive feedstock for chemicals in the future.

## 5.4.1. Chemistry of Dehydration

The hydration reaction of ethylene is catalyzed by acidic catalysts at temperatures above 200 °C:

For the reverse dehydration reaction, also acidic catalysts are applied at approximately 300 °C. The reaction is an elimination reaction:



Due to the temperature range and the tailored catalysts for the dehydration of ethanol, selectivities of over 99 % can be achieved.

This elimination reaction has been known for a long time and typically sulfuric acid or phosphoric acid has been used in homogeneous catalysis. Modern systems utilize solid acid catalysts such as alumina, silica, manganese and ferric oxides, special zeolites, and various solid acid catalysts as described in scientific publications and the patent literature [80, 81].

**Figure 39.** Bioethanol production in Brazil, the EU, and the United States (1975 – 2006) [79]

**Table 13.** Ethanol production in $10^9$ L/a (2004 – 2006) [79]

| Country | 2004 | 2005 | 2006 |
|---|---|---|---|
| Brazil | 15.098 | 15.999 | 16.998 |
| U.S. | 13.380 | 16.139 | 18.376 |
| China | 3.649 | 3.800 | 3.849 |
| India | 1.749 | 1.699 | 1.900 |
| France | 829 | 908 | 950 |
| Russia | 749 | 749 | 647 |
| South Africa | 416 | 390 | 386 |
| U.K. | 401 | 348 | 280 |
| Saudi Arabia | 299 | 121 | 197 |
| Spain | 299 | 352 | 462 |
| Thailand | 280 | 299 | 352 |
| Germany | 269 | 431 | 765 |
| Ukraine | 250 | 246 | 269 |
| Canada | 231 | 231 | 579 |
| Poland | 201 | 220 | 250 |
| Indonesia | 167 | 170 | 170 |
| Argentina | 159 | 167 | 170 |
| Italy | 151 | 151 | 163 |
| Australia | 125 | 125 | 148 |
| Japan | 117 | 114 | 114 |
| Pakistan | 98 | 91 | 91 |
| Sweden | 98 | 110 | 114 |
| Philippines | 83 | 83 | 83 |
| South Korea | 83 | 64 | 61 |
| Guatemala | 64 | 64 | 79 |
| Cuba | 61 | 45 | 45 |
| Ecuador | 45 | 53 | 45 |
| Mexico | 34 | 45 | 49 |
| Nicaragua | 30 | 26 | 30 |
| Mauritius | 23 | 11 | 8 |
| Zimbabwe | 23 | 19 | 26 |
| Kenya | 11 | 15 | 19 |
| Swaziland | 11 | 11 | 19 |
| Others | 1.279 | 2.687 | 1.022 |
| Total | 40.764 | 45.988 | 51.056 |

### 5.4.2. Bioethanol as Intermediate to Ethylene

The production of bioethanol is driven by the fuel ethanol market, which was developed first in Brazil and has been adapted recently by other countries, where ethanol is added to the gasoline in various ratios.

Compared to the hydrocarbon feedstock, ethanol contains oxygen, which in the dehydration reaction is eliminated as water. This translates into a utilization of only 63.6 wt % of ethanol for ethylene production.

#### 5.4.2.1. First- and Second-Generation Bioethanol

The typical production capacity of first-generation bioethanol plants is in the range of 100 000 – 200 000 t/a, limited in most cases by the biomaterial (sugar cane, corn, wheat) logistics.

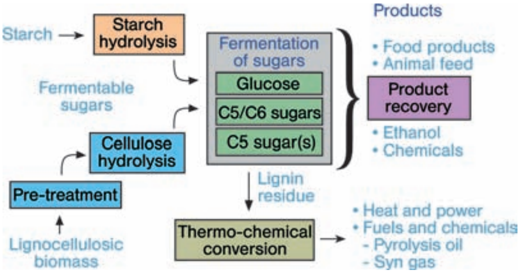


**Figure 40.** Schematic of biomass and starch processing in a biorefinery

In first-generation (1G) bioethanol plants, the contained sugar is transferred during the fermentation step into ethanol, or in the case of starch a hydrolysis step is carried out prior to the fermentation of sugars.

Second-generation (2G) bioethanol production is targeted for cellulosic biomaterial that has to be disintegrated and depolymerized in a first step of pretreatment and hydrolysis, followed by the fermentation process as shown in Figure 40 [82].

The starting material could be starch and/or lignocellulosic biomass that is treated in a hydrolysis step to result in glucose and C5/C6 sugars that can be used for the fermentation. As this approach requires a complete biorefinery with a scale that fits more to modern ethylene applications, typical ethylene downstream units such as polymer units can be integrated into this scheme.

The limitation of the capacities for today's first-generation bioethanol plants is a consequence of the land requirement for biomass production and the logistics for the crop transportation.

In Brazil with an ethanol production of approximately 17 × $10^9$ L/a in approximately 350 ethanol refineries, the average size per refinery is 40 000 t/a. For a typical ethylene application, several of the small local refineries need to collect the ethanol product to have sufficient raw material for feeding an olefin plant cracker of economic size.

A typical polyethylene unit today has a scale of 450 000 t/a to produce the polymers competitively and requires ethanol input from several

**Table 14.** Productivity of first-generation biomass for ethanol production [83, 84]

| | Sugar cane | Sugar beet | Corn |
|---|---|---|---|
| Ethanol, L/ha | 5500 | 5000 | 3000 |
| Nitrogen fertilizer, kg/ha | 64 | 101 | 164 |

average-size ethanol refineries, if based on bioethanol.

The productivity of the current first-generation materials is shown in Table 14. Sugar cane is the material with the best productivity and if combined with sugar and energy production the most economic raw material [83, 84]. The major concern in expanding ethanol production based on sugar cane in Brazil today is the logistics of raw-material transportation.

With an ethanol productivity of 5500 L/ha, the theoretical ethylene equivalent of approximately 2.7 t/ha can be produced. For a typical ethylene plant, which feeds a polyethylene unit of 450 000 t/a, roughly 165 000 ha of agricultural land (approx. 40 × 40 km) are required. However, for a PVC production typical ethylene requirements are only in the range of 100 000 t/a, which requires 37 000 ha (19 × 19 km) and fits better to the sizes of today's bioethanol plants. Second-generation processes based on sugar cane, bagasse, and other cellulose material would double the ethanol productivity to 12 000 L/ha. These technologies are under development with large scale industrial application to be expected within a period of 5 to 10 years.

### 5.4.2.2. Raw-Material Costs

Based on the productivities of first-generation processes, local small refineries to produce ethanol and partly electricity or heat as coproducts can be rather cost-effective.

With the ethanol production costs of 0.21 US$/L based on Brazil sugar cane (Tab. 15), raw material costs per ethylene unit are in the range of 420 US$/t, and in the case of US and Canada corn 860 US$/t. European cereals and sugar beet result in raw material costs of 600 – 1000 US$/t.

A typical process scheme of the typical plants for ethanol from sugar cane in Brazil with integrated sugar and energy (electricity) production is shown in Figure 41.

**Comparison with Naphtha Cracking.** Comparing the raw material costs of ethylene production from ethanol with the costs for ethylene production by naphtha cracking from 2001 until today (Figure 42), it can be seen that ethylene production using schemes as applied in Brazil is competitive since 2005, as a consequence of the increasing crude-oil costs. In 2005, costs have been in the range of 60 US$/bbl, which marks the borderline for competitiveness of ethylene from bioethanol.

### 5.4.3. Production of Ethylene by Dehydration

Due to the feasibility of ethylene production, several plants for ethylene production from low-cost ethanol have been announced or are studied in detail.

The process for production of ethylene from ethanol by catalytic dehydration is rather simple because of the high selectivity of the catalyst systems. The technology has been used in Brazil and India in the 1950s and the 1960s, but thereafter has been replaced by steam cracking because of the availability of low-cost feedstocks.

There is only limited information available on the different processes that are applied but the scheme for all processes follows the scheme as in Figure 43.

Ethanol is routed through a heat exchanger and preheater to the reactor where the dehydration reaction takes place on an acidic catalyst. The reactor effluent then leaves through a heat exchange to a gas liquid separation unit, where

**Table 15.** Costs for bioethanol production from different feedstocks

| Reference | | Cereals | Sugar beets | Sugar cane | Lignocellulose |
|---|---|---|---|---|---|
| [85] | US$/L | 0.6 – 0.8 | 0.6 | 0.3 – 0.5 | 1 |
| [86, 87] | US$/L | 0.43 | 0.21 | 0.21 | |

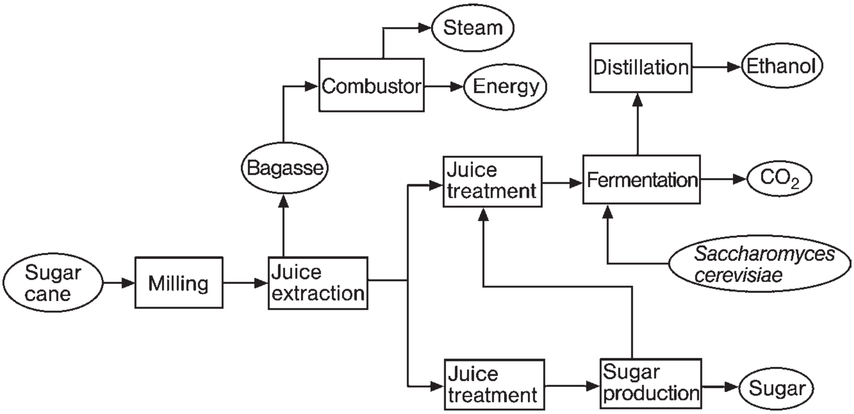


**Figure 41.** Scheme of a sugar-cane-based bioethanol refinery with integrated electricity and sugar production

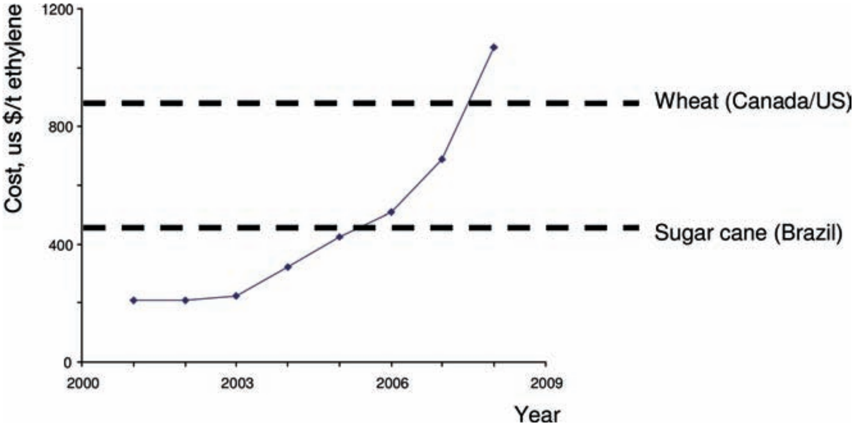


**Figure 42.** Net naphtha costs (naphtha minus byproduct revenue) per ton ethylene and costs of wheat (Canada, US) and sugar cane (Brazil) [10, 85, 86] (average wheat and sugar cane costs 2000–2007)

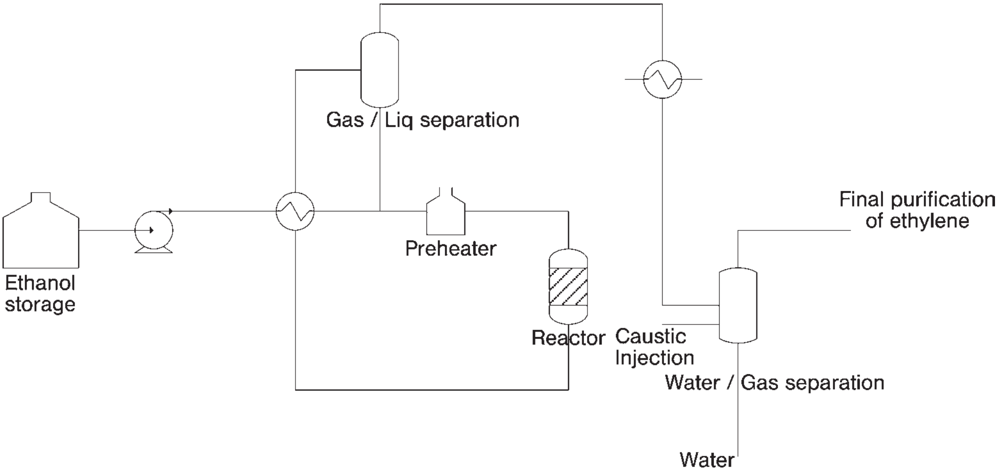


**Figure 43.** General scheme of ethylene production by dehydration of ethanol

nonreacted ethanol is separated from gaseous products. In the caustic wash system, oxygenate byproducts are removed and a crude ethylene stream leaves to a final purification unit in order to obtain the purity required in the downstream application.

In the patent literature, several schemes with fixed- or fluidized-bed reactors are described [81].

For polymerization to polyethylene, the final purification has to bring the coproducts, such as oxygenates, hydrocarbons, etc to the typical polymer specification by distillation, adsorption, etc.

Other applications such as ethylene for EDC requires less stringent specification and will have a simpler purification unit.

Due to the economics and the availability of low-cost ethanol in sufficient quantities in Brazil, several projects have been announced recently. Solvay announced a 60 000 t/a bioethylene plant based on sugar-cane-derived ethanol for production of 360 000 t/a of PVC in Santo Andre (Brazil). Braskem plans a 450 000 t/a biopolyethylene plant in Brazil based on sugar-cane ethanol, to be started up in 2009. DOW has a joint venture with Crystalserv in Brazil and plans a 350 000 t/a Dowlex plant for linear low-density polyethylene to start up in 2011 [88–90].

These three projects together represent 860 000 t/a of ethylene, equivalent to $1.365 \times 10^6$ t/a or $1.72 \times 10^9$ L of ethanol.

### 5.4.4. Environmental Issues

An important factor of bio-based ethylene production is the reduction in $NO_x$ and $CO_2$ emissions and the fact that renewable raw materials are utilized.

In the conventional steam-cracking process, only 30 % of the fired heat is required chemical energy, 50 % of the fired duty is recovered from the process fluids and utilized in the separation. Typically 6 to 7 % of the fired heat are losses to the atmosphere. Energy consumption per ton of ethylene of a modern ethylene plant is in the range of 16 to $22 \times 10^9$ J/t depending on the type of feedstock.

In an ethanol dehydration scheme for ethylene production, the temperatures are much lower at approximately 300 °C and thus the losses are much smaller. Due to the high selectivity (99 %), the amount of unwanted byproducts is small. The energy consumption for the dehydration varies according to the required purification grade. In total, the ethanol-based ethylene production requires less than half of the energy consumption of a modern steam cracker.

$CO_2$ emission per ton of ethylene is lower as a consequence of the selectivity (99% vs. 40 % in a naphtha cracker) by almost 60 %.

As an energy source, bioethanol in principle is carbon-neutral. The amount of $CO_2$ released during ethanol production and combustion has already been absorbed from atmosphere during the growth of the crops due to photosynthesis. However, application of fertilizers during growth of crops has a negative impact on the greenhouse gas balance.

An overall $CO_2$ balance for ethanol as biofuel (including transportation and the process itself) shows 70 % lower $CO_2$ emissions compared to the balance for fossil fuel [91, 84, 87, 92]. For ethylene production, $CO_2$ emissions must be even less because this is a more selective process. Data for $CO_2$ balances are not published, but a significant reduction of more than 80 % of $CO_2$ emissions and significantly less $NO_x$ production, due to lower temperatures, can be assumed.

In summary, from environmental point of view a bioethanol-based ethylene production is much better than the conventional steam cracking process because less $CO_2$, CO, $NO_x$, and particulates are produced due to the use of renewable raw materials and because of lower temperatures and a more selective process.

### 5.4.5. Future Outlook

In the future, we will see more complex petrochemical projects based on bioethanol, because at the current price level for crude oil this route is economical and environmental friendly.

Projects are more likely in areas with favorable climatic conditions like Brazil, USA, Indonesia, and Australia. In the next years, projects based on first-generation bioethanol production will be seen, whereas in longer term second-generation processes will be the basis. Due to the availability of biomass, applications like PVC and medium-sized PE plants will be the typical application for green-ethylene downstream processing in the near future. Second-generation processes based on lignocellulose biomass will be fully integrated into petrochemical complexes and are the future of biorefining.

## 5.5. Other Processes and Feedstocks

Ethylene has also been produced by other processes and from other feedstocks [93]. Options for long-range feedstock availability and price, as well as in-place refining and chemical processes, influence process design and feedstock selection because of their high economic impact on manufacturing cost. Other drivers for new developments are the utilization of associated gas and natural gas as petrochemical feedstock, as the value of these fractions offers advantages with respect to costs compared to crude oil based feedstock. In addition as flaring of associated gas is no option anymore, other utlization is required for those streams.

**Recovery from FCC Offgas.** Recovery of ethylene and propene from FCC off-gas has gained importance, but due to the $NO_x$ content, some steps have to be integrated to reduce the risk of formation of explosive resins from butadiene and $N_2O_3$.

**Crude Oil or Residual Oil.** A number of nontubular reactors, developed to crack unprocessed hydrocarbon feedstocks, exist in various stages of development and commercial operation [93].

A process offered by Shaw (Deep Catalytic Cracking, DCC) employs catalysts particles, for cracking and heat transfer functions. The DCC process is suitable for cracking VGO and similar heavy feedstocks. Main target light product of the DCC process is propene, similar to FCC processes in which propene output can be increased significantly by catalyst modification.

**Methanol** can be catalytically dehydrated and partially converted to ethylene over alumina and zeolite catalysts. The process based on novel zeolite catalysts (ZSM-5) was developed by Mobil (MTO, Methanol to Olefins). A new development introduced by UOP/Norsk Hydro, converts methane to methanol in a first stage and then converts the methanol to olefins. Economics of this new process seem to be competitive with conventional processes [94]. The process is based on a fluidized-bed reactor for conversion of methanol. 80 % of the carbon content of methanol is converted into ethylene and propene. The process has been tested in a 0.5 t/d unit in Norway. Methanol obtained from syngas can be converted in high selectivity (but at a low rate) to ethanol with the help of catalysts and promoters.

In order to be competitive to the mega-scale ethane crackers in the Middle East with lowest feedstock costs worldwide, methanol has to be produced in huge quantities of approximately $5 \times 10^6$ t/a leading to an olefins output of approximately $2 \times 10^6$ t/a of ethylene and propene. The ratio of propene to ethylene can be adjusted over a wide range and propene - ethylene ratios as required by the market (0.8 to 0.9) can be produced via this route.

Another development by Lurgi is the MTP process, similar to MTO, however, with a maximized propene output.

**Syngas.** Fischer–Tropsch and modified Fischer–Tropsch processes are used to produce (1) olefins directly as a byproduct of gasoline and diesel fuel production; (2) LPG and paraffin intermediates, which are cracked to produce olefins; and (3) intermediate oxygenated liquids, which are dehydrated and separated to produce olefins (→ Coal Liquefaction). Syngas is produced by gasification of coal and other materials (→ Gas Production, Section 8.2.2.3.).

**Oxidative Coupling of Methane to Ethylene.** Many researchers worldwide have been active in this field, using metal oxide catalysts at 700–900 °C for the oxidative coupling of methane. However, the yields obtained so far (20–25 %) are not competitive with conventional routes, since the ethylene concentration in the product gas is only ca. 10 vol % [95, 96]. Application of special separative reactors has led to improved yields up to 50–60 % [97, 98].

**Dehydrogenation.** Dehydrogenation of ethane over Cr or Pt catalyst is limited by equilibrium and allows only very poor yield of ethylene. This route is not competitive with conventional routes.

**Metathesis.** Metathesis of propene leads to ethylene and 1-butene:

$2\,C_3H_6 \rightleftarrows C_2H_4 + C_4H_8$

Since this reaction is reversible the ethylene/ propene production of a plant can be adjusted to market conditions. So far this technology has been applied in a plant in Canada and at the U.S. Gulf Coast.

As the demand for propene is increasing faster than the ethylene demand and due to the lack of propene production in new ethane crackers in the Middle East, metathesis has gained importance for the production of propene based on ethylene and 2-butene feedstock. Several commercial units applying metathesis for propene production via this route are in operation. Contents of isobutene and butadiene in the feed create problems, as coking rates of the applied catalysts are increasing.

## 6. Environmental Protection

Ethylene plants with a production of up to $1.5 \times 10^6$ t/a ethylene and a fired duty of up to 1000 mW require special measures for protection of the environment. Though national standards vary widely, the following general measures are required for every new plant:

**Flue-Gas Emissions.** $NO_x$ emissions are limited by use of UltraLowNox burners or integrated SCR technology for catalytic reduction of $NO_x$. In some regions limits for $NO_x$ emissions are already $< 50$ ppm. Particulate emissions during decoking can be reduced by incineration or separation in cyclones. Incinerators can achieve a reduction of 90 %, and high-performance separators, up to 96 %.

**Fugitive Emissions and VOC.** The equipment used in a modern olefin plant has to meet the standards for emission of critical components such as benzene. All components with a potential to emit critical components must have a certain tightness classification and have to be monitored (pump seals, valves, etc.). Storage tanks and piping are other sources of fugitive emissions.

**Flaring.** Flaring during start up should be avoided as much as possible, especially in highly populated areas. New procedures have been developed that allow for flareless start up of plant [99].

**Noise Protection.** Ethylene plants contain equipment that produces noise emission in the range above 85 dBA. These are the burners at the furnaces and the large compressors. Noise abatement measures are essential (silencers for burners, hoods for compressors) to bring the overall emissions into the range below 85 dBA. Other sources of noise emission can be high velocities in piping or vibrations. The detection of the source in this case is sometimes very difficult and requires much expertise.

**Water Protection.** The water emissions of the plant result from quench water, dilution steam, decoking water, and flare water discharges. These streams have to be treated properly before being fed to the wastewater plant. Streams from the caustic-scrubbing section require chemical treatment (oxidation) before discharge to the wastewater unit.

**Solid and Hazardous Wastes.** Examples of process wastes are cleaning acids; filter cartridges; catalysts; tars; polymers; waste oils; coke; sodium nitrite used in column passivation; *N,N*-dimethylformamide, acetone, or *N*-methyl-2-pyrrolidone used in acetylene removal; sulfuric acid from cooling towers; amine tars; and antifoaming agents. These wastes have to be treated according to the relevant regulations for disposal.

## 7. Quality Specifications

Ethylene quality worldwide is matched to customer requirements; no single chemical-grade ethylene exists. However, ethylene content normally exceeds 99.9 wt %. The reason for variation in ethylene specifications is due to the use of ethylene in downstream processes that differ in sensitivity to impurities in ethylene, due to different catalyst systems being used. In general, the trend is towards lower impurity contents as more active catalyst systems are developed. The largest application for ethylene is polymerization to HDPE, LDPE, and LLDPE. For these processes

**Table 16.** Typical ethylene specifications (in ppm vol unless otherwise noted) [100]

| | Polymer Process | | | | |
|---|---|---|---|---|---|
| Component | Gas phase | Slurry | Solution | Metallocene[a] | Polymer grade (today) |
| Ethylene | 99.9 % min. | 99.95 % min. | 99.9 % min. | 99.9 % | 99.9 % min. |
| Methane | 500 | [b] | 500[b] | [e] | 300 |
| Ethane | 500 | [b] | 500[b] | [e] | 500 |
| Propene | 20 | 20 | 50 | 20 | 10–15 |
| Acetylene | 0.1 | 2 | 55 | 0.1 | 2 |
| Hydrogen | 5 | 5 | 10 | 5 | 10 |
| Carbon monoxide | 0.1 | 1[c] | 2[d] | 0.1 | 2 |
| Carbon dioxide | 0.1 | 1[c] | 5[d] | 0.1 | 2 |
| Oxygen | 0.1 | 1 | 5 | 0.1 | 5 |
| Water | 0.1 | 5[c] | 5[d] | 0.1 | 2 |
| MeOH | | 1[c] | 5[d] | 0.1 | 5 |
| Sulfur as $H_2S$ | | 1 (wt)[c] | 2 (wt)[d] | 0.1 | 2 (wt) |
| Other polar compounds | | 1 | 2 | 0.1 | |
| DMF | | | | | 2 (wt) |

[a] Values for metallocene catalyst are expected values.
[b] Total combined not to exceed 0.125 %.
[c] Total not to exceed 1 ppm wt.
[d] Total must be less than 6 ppm.
[e] Total combined not to exceed 300 ppm wt.

new catalyst systems have been developed, including the metallocene catalysts, which are more sensitive than other catalysts. Table 16 lists typical ethylene specifications for various polymerization processes.

Sulfur, oxygen, acetylene, hydrogen, carbon monoxide and carbon dioxide are the most troublesome and carefully controlled impurities, especially when ethylene from multiple sources is mixed in transportation.

## 8. Chemical Analysis

Laboratory analysis of ethylene is primarily by ASTM or modified ASTM gas chromatographic techniques.

Process control may use over 100 analyzers to monitor plant safety, operation, and optimization [101]. Measurements include personnel exposure, corrosion, furnace flue gas, steam systems, water systems, condensate systems, stack emissions, water emissions, feedstock quality, cracked gas analysis, distillation train product quality and moisture control, and, in some cases, heavy liquids product evaluation and control [102].

Process control instruments include gas chromatographs, combustible-gas detectors, conductivity analyzers, pH meters, densitometers, corrosion analyzers, oxygen and water analyzers, vapor pressure analyzers, and photoionization analyzers. Various automated wet methods are also used [101].

Process optimization is critical for ethylene production because cracking reactions change as the run proceeds. Operating costs for plants of this size are high [57, 103, 104]. Advances in computer control, data acquisition, and information analysis have given impetus to studies of process control, modeling, and optimization, especially in heavier liquid cracking operations.

Models for all kinds of feedstocks are applied, simulating all sections of the plant in detail, based on detailed chemical analysis of the various streams in the plant. With these tools operating strategies can be followed, e.g., production of a certain amount of ethylene, propene and other products at maximum profit, even if the feedstock quality or the type of feed change within short time. Such a computer controlled operation includes the individual control of cracking furnaces, columns, pumps, compressors, etc.

## 9. Storage and Transportation

Much of world ethylene production is consumed locally, requiring little storage and transportation. Interconnected pipelines and pressurized underground caverns in the United States and

Europe have been developed because of the complex petrochemical infrastructure. They provide flexibility and prevent interruption of supply. The following pipeline systems have been developed (Fig. 44):

| | |
|---|---|
| United States: | Texas–Louisiana [106] |
| Canada: | Fort Saskatchewan–Sarnia [105] |
| Great Britain: | Grangemouth–Carrington<br>Sevenside–Fawley [59] |
| Europe: | Northwest Europe (Frankfurt–Gelsenkirchen and Brussels–Rotterdam areas) and Spain [59, 107, 108] |
| Former Soviet Union: | Nizhnekamsk–Salavat and Angarsk–Zima [109, 110] |

In the U.S. Gulf Coast area the pipeline grid is composed of common carriers and privately owned pipelines. Storage caverns are naturally occurring or artificially excavated salt domes; limestone caverns are less usual. In contrast to U.S. pipelines, which normally transport only ethylene, the 3000 km pipeline between Fort Saskatchewan and Sarnia transports ethane, propane, and condensate in batches [57, 105].

In pipelines, ethylene is normally under a pressure of 4–100 MPa. The upper end of the pressure range is significantly above the critical pressure. Below critical conditions, the temperature must be > 4 °C to prevent liquid ethylene from forming. If water is present, hydrates can form below 15 °C at normal operating pressure and can plug equipment. Special procedures and precautions are used during commissioning of pipelines to pressure test and dry the line and to provide appropriate draining and venting during operation [108].

Ethylene decomposition and spontaneous ignition can occur under certain conditions and can result in pressure and temperature increases capable of producing explosions. Such decomposition is a function of pressure, temperature, impurities (e.g., acetylene and oxygen), and catalysts (e.g., rust and carbon). Appropriate compression procedures, especially when nitrogen, oxygen, or other diatomic gases are present, help to prevent decomposition [111].

Ethylene is also transported by ship, barge, railcar, and tank truck. In the United States, these methods are normally limited to consumers not served by pipeline. In Europe, pipelines move a lower proportion of ethylene than in the United States.

Ethylene is also stored in underground high-pressure pipelines and tanks (e.g., at 10 MPa) and in surface refrigerated tanks. In the latter, compression and liquefaction of vapor from the refrigerated tank, followed by reinjection of the liquid, allow operation of the tank at pressures of only 7–70 kPa [57, 112].

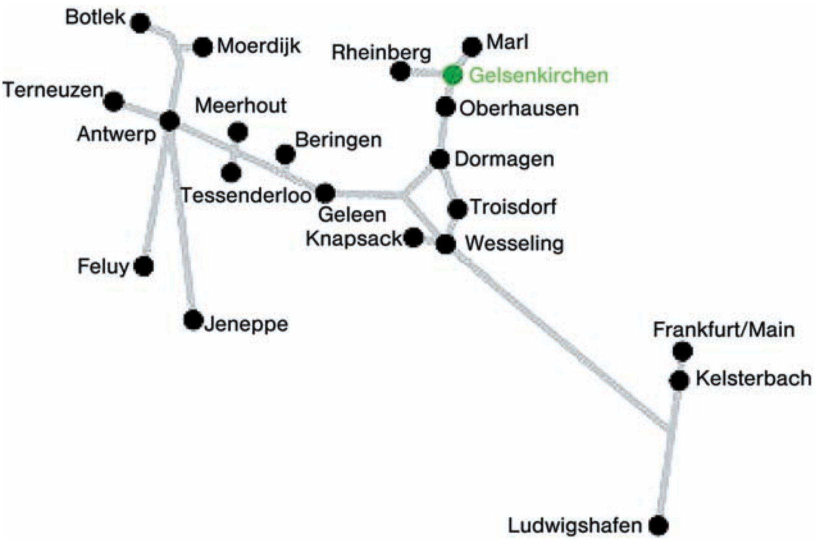


**Figure 44.** ARG pipeline grid in Europe

**Table 17.** World consumption of ethylene in 2000 (in %)

| Use | World |
|---|---|
| LDPE | 18 |
| LLDPE | 14 |
| HDPE | 26 |
| EO/EG | 12 |
| EDC | 14 |
| EB/SM | 7 |
| Others | 9 |

## 10. Uses and Economic Aspects

More than 80 % of the ethylene consumed in 1993 was used to produce ethylene oxide; ethylene dichloride; and low-density, linear low-density, and high-density polyethylene. Significant amounts are also used to make ethylbenzene, oligomer products (e.g., alcohols and olefins), acetaldehyde, and vinyl acetate. LDPE and LLDPE are the fastest growing outlets for ethylene.

Table 17 shows the uses of ethylene in 2000 [113].

Worldwide ethylene growth rate is projected at 4 to 5 % for the period of 2004 to 2009 [114] with the Asian market growing at 6 to 7 % per year.

The estimated 2005 world nameplate production capacity was over $112.9 \times 10^6$ t/a (Table 18).

The principal influences on ethylene product value from the manufacturer's viewpoint are primarily the price of feedstock raw materials, chemical and byproduct credits, and expected return on capital costs associated with the facilities. The fixed cost component for ethylene production is relatively modest because of the high-volume commodity operation that has become the industry standard (e.g., up to $1500 \times 10^3$ single-train plants). The cost breakdown per tonne of ethylene produced is listed below for a new plant based on naphtha feedstock in the Asia/Pacific region:

**Table 18.** Ethylene nameplate capacities by region in 2005 [115]

| Region | Capacity, $10^3$ t/a | % of World capacity |
|---|---|---|
| Europe (incl. Russia) | 31 494 | 27.9 |
| North America | 33 830 | 30.0 |
| South America | 5669 | 5.0 |
| Asia | 39 880 | 35.3 |
| Africa | 1528 | 1.4 |
| Australia | 504 | 0.4 |

| | |
|---|---|
| *Basis of economic analysis* | |
| Capacity | $1000 \times 10^3$ t/a |
| Location | Asia/Pacific |
| Feedstock | naphtha |
| Capital | 10 years linear depreciation for ISBL plant<br>15 years linear depreciation for storage |
| Investment cost estimate | \$ $720 \times 10^6$for ISBL plant<br>\$ $144 \times 10^6$ for OSBL plant |
| *Cost breakdown, %/t ethylene produced* | |
| Feedstock costs | 47.4 |
| Catalysts and chemicals | 0.5 |
| Utilities | 0.3 |
| Cash cost | 48.6 |
| Operating costs | 1.9 |
| Overheads | 1.9 |

## 11. Toxicology and Occupational Health [116]

Ethylene is not markedly toxic, but high concentrations may cause drowsiness, unconsciousness, or asphyxia because of oxygen displacement [117, 118]. The gas possesses useful anesthetic properties, with rapid onset, quick recovery, and minimal effects on the heart or lungs [119].

In animal studies, ethylene was not irritating to the skin or eyes [120]. It did not cause cardiac sensitization in a dog [121]. Mice and rats exposed repeatedly to ethylene showed minimal effects [122, 123]. In a chronic inhalation study with rats, no toxic effects were found by histopathology, hematology, clinical chemistry, urinalysis, eye examination, or mortality rate [123]. Ethylene improved wound healing following muscle injury to mice [124].

Studies with rodents have shown that ethylene caused increased serum pyruvate and liver weights [125], hypotension [126], decreased cholinesterase activity [123], hypoglycemia [127], and decreased inorganic phosphates [120]. No mutagenic activity was observed in *Escheria coli* B and *E. coli* Sd-4 exposed to ethylene [128].

Ethylene is a plant hormone and is useful for ripening fruits and vegetables [129, 130]. At high concentrations, it is phytotoxic [131]. Human exposure to ethylene is reported to cause anorexia, weight loss, insomnia, irritability, polycythemia, nephritis, slowed reaction time, and memory disturbances [132–134]. In the workplace, ethylene is treated as a simple asphyxiant [135]; the odor threshold is ca. 20 ppm [136]. NIOSH has published a procedure for evaluating ethylene exposure [137].

As with any compressed gas, skin and eye contact should be avoided. Appropriate precautions are required because the gas is highly flammable and explosive over a wide range of mixtures with air. Ethylene is also spontaneously explosive in sunlight in the presence of ozone or chlorine, and reacts vigorously with aluminum chloride and carbon tetrachloride [116].

# References

## Specific References

1 *Icis Business News* 2007, www.icis.com.

2 *Oil Gas J.* **104** (2006) March 27th special report.

3 *Oil Gas J.* **106** (2008) July 28, p. 53 – 59

4 R. Becker, *Chem.-Tech. (Heidelberg)* **8** (1979) 6.

5 *Oil Gas J.* **103** (2005) March 28th.

6 *SRI Consulting, Presentation at APIC*, May 19 (2005) .

7 *ICRA Report* "Petrochemicals", June 2005.

8 *WTRG Economics*; http://www.wtrg.com/prices.htm, May 2008.

9 *The Financial Forecast Center*; http://www.forecasts.org/oil.htm.

10 *Linde Engineering*, in-house data, June 2008.

11 M. Eramo: "Emerging Trends in Global Light Olefins, " *CMAI Paper presented at APTC 2002*, Seoul.

12 K. Weissermel, H.-J. Arpe: *Industrielle Organische Chemie*, 4th ed., VCH Verlagsgesellschaft, Weinheim, Germany 1994.

13 D. Lambert *et al.*, *Analysis Magazine* **23** (1995) no. 4, M9–M14.

14 K. M. Watson, E. F. Nelson, *Ind. Eng. Chem.* **25** (1933) 880–887.

15 H. M. Smith: "Correlation Index to Aid in Interpreting Crude-Oil Analyses," U.S. Bureau of Mines Technical Paper no. 610, 1940.

16 J. M. Collins, G. H. Unzelman, *Oil Gas J.* **80** (1982) June, 148.

17 Y. C. Hu, *Hydrocarbon Process* **61** (1982, Nov.) 109, Part 1.

18 R. N. Bell: "Review of Impact of Mercury on Aluminum Heat Exchangers, " Paper presented at *EEPC conference* Oct. 6, 2005, Prague.

19 M. E. Denti, E. M. Ranzi in L. F. Albright, B. L. Crynes, W. H. Corcoran (eds.): *Pyrolysis: Theory and Industrial Practice*, Academic Press, New York 1983, pp. 133–137.

20 D. Edelson, *J. Phys. Chem.* **81** (1977) 2309.

21 K. Ebert, H. Ederer, G. Isbarn, *Int. J. Chem. Kinet.* **15** (1983) 475.

22 M. Schärfe, H. J. Ederer, U. Stabel, K. Ebert, *Chem.-Ing.-Tech.* **56** (1984) no. 6, 488–489.

23 G. F. Froment, *Chem. Eng. Sci.* **47** (1992) 2163.

24 Q. Chen, *Chemtech* **26** (1996) Sept., 33.

25 M. Dente *et al. Chem. Eng. Sci.* **47** (1992) 2629.

26 F. O. Rice, *J. Am. Chem. Soc.* **53** (1931) 1959–1972.

27 S. B. Zdonik, E. J. Green, L. F. Hallee, *Oil Gas J.* **65** (1967) no. 26, 96–101; **66** (1968) no. 22, 103–108.

28 C. W. Gear: *Numerical Initial Value Problems in Ordinary differential Equations*, Prentice Hall, Englewood Cliffs, N.J. 1971.

29 M. Boudart: *Kinetics of Chemical Processes*, Prentice Hall, Englewood Cliffs, N.J. 1968.

30 N. N. Semenov (transl. by M. Boudart): *Some Problems in Chemical Kinetics and Reactivity*, Princeton University Press, N.J. 1959.

31 F. Rossini, K. Pitzer, R. Arnett, R. Braun *et al.*: *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, API Research Project 44 Report, Carnegie Press, Pittsburg, Pa. 1955, p. 706.

32 Kinetics Technology International, US 4 367 645, 1983 (G. F. Froment).

33 S. Barendregt, J. L. Monfils: "Steamcracking for Butane Upgrading," AlChE meeting, Houston, TX, 1991

34 D. Kaufmann: "New Developments for Radiant Coil Materials, " Paper presented at *EEPC HSE conference*, Vienna. 2004

35 Mitsui Advanced Cracker, Technical Bulletin, Mitsui Engineering & Shipbuilding Co., Tokyo, Japan, pp. 1–5.

36 S. Ibarra, in [19], pp. 427–436.

37 G. E. Moller, C. W. Warren, *Mater. Perform.* **20** (1981) no. 10, 27–37.

38 J. A. Thuillier, *Mater. Perform.* **15** (1976) no. 11, 9–14.

39 R. H. Krikke, J. Hoving, K. Smit: "Monitoring the Carburization of Furnace Tubes in Ethylene Plants," International Corrosion Forum Paper no. 10, National Assoc. of Corrosion Engineers, Houston, Tex., Mar. 22–26, 1976.

40 D. E. Hendrix, M. Clark: "Contributing Factors to the Unusual Creep Growth of Furnace Tubing in Ethylene Pyrolysis Service," International Corrosion Forum Paper no. 21, National Assoc. of Corrosion Engineers, Boston, Mass., Mar. 25–29, 1985.

41 J. J. Jones, J. L. D. Steiner: "A New Generation of Heat Resisting Alloys, Paralloys SH24T and SH39T," International Corrosion Forum Paper no. 22, National Assoc. of Corrosion Engineers, Boston, Mass., Mar. 25–29, 1985.

42 S. B. Parks, C. M. Schimoller, *Hydrocarbon Process.* **75** (1996) 53.

43 L. A. Mekler, R. S. Fairall, *Pet. Refiner* **31** (1952) no. 6, 100–107, Part 1.

44 W. E. Lobo, J. E. Evans, *Trans. Am. Inst. Chem. Eng.* **35** (1939) 743–778

45 R. L. Grantom: "Combustion Air Should Be More Than Simply Recycling Energy, " *Proc. 1980 Conference on Industrial Energy Conservation*, vol. **2**, Texas Industrial Commission, Austin, Tex. 1980, pp. 559–564.

46 R. L. Grantom: "Combustion Air Preheat and Radiant Heat Transfer in Fired Heaters–A Graphical Method for Design and Operating Analysis, " *Proc. 1981 Industrial Energy Conservation Technology Conference and Exhibition*, vol. **1**, Texas Industrial Commission, Austin, Tex. 1981, pp. 151–159.

47 J. V. Albano, E. F. Olszewski, T. Fukushima, *Oil Gas J.* **90** 1992, Feb., 55.

48 M. J. Graff, L. F. Albright, *Carbon* **20** (1982) no. 4, 319–330.

49 J. C. Marek, L. F. Albright: "Coke Formation on Catalysts or in Pyrolysis Furnaces, " *Am. Chem. Soc. Symposium, 182nd Am. Chem. Soc. Meeting*, New York 1981.

50 A. G. Goosens, M. Denti, E. Ranzi, *Hydrocarbon Process.* **57** (1978) no. 9, 227–236.

51 L. L. Ross, in [19], pp. 327–364.

52 B. Lohr, H. Dittmann, *Oil Gas J.* **70** (1978) no. 20, 63–68.

53 J. Chen, M. J. Maddock, *Hydrocarbon Process.* **52** (1973) no. 5, 147–151.

54 A. Mol, in [19], pp. 451–471.

55 "Transfer Line Exchangers in Ethylene Plants," Technical Bulletin, Schmidt'sche Heissdampf-Gesellschaft mbH, Kassel-Bettenhausen, Federal Republic of Germany, 1985.

56 E. S. Kranz, S. B. Zdonik, Personal Communication, Stone & Webster Engineering Corp., Boston, Mass., May 1985.

57 S. B. Zdonik, in [19], Chapter 15.

58 R. C. Updegrove, Personal Communication, E. I. du Pont de Nemours & Co., Chocolate Bayou, Tex., Jul. 1985.

59 *Ullmann*, 4th ed., **8**, p. 192.

60 H. E. Boyd, Y. H. Chen, O. J. Quartulli, *Oil Gas J.* **74** (1976, Sept. 27) 51–59.

61 C. W. Albers, T. A. Wells, *Oil Gas J.* **76** (1978) Sept. 4, 72–78.

62 K. W. Brooks, *Oil Gas J.* **62** (1964) Dec. 21, 70–75.

63 T. A. Wells, *Oil Gas J.* **80** (1982) Jun. 14, 63–68.

64 W. C. Petterson, T. A. Wells, *Chem. Eng.* **84** (1977) Sept. 26, 76–86.

65 L. K. Ng, C. N. Eng, R. S. Zach, *Hydrocarbon Process.* **62** (1983, Dec.) 99–103.

66 A. J. Weisenfelder, C. N. Eng., Personal Communication, C. F. Braun & Co., Alhambra, Calif., Aug. 1985.

67 C. Sumner, T. S. Williams, Personal Communication, Combustion Engineering, Bloomfield, N. J., Aug. 1985.

68 Greg Dunnels paper no 97C, *presented at the Ethylene Producer Conference 2002*, New Orleans, USA.

69 R. Orriss, Personal Communication, M. W. Kellogg Co., Houston, Tex., Jun. 1985.

70 R. Zeppenfeld, E. Haidegger, W. Borgmann, *Hydrocarbon Technology International* (1993) 129.

71 C. Bowen, R. McCue, C. Carradine, *Hydrocarbon Process.* **72** (1993) 129.

72 W. K. Lam, Y. R. Mehra, D. W. Mullins, AlChE Spring International Meeting, Houston 1993, session 18.

73 H. Zachariades, J. A. Reid, Article 19C, *presented at the Ethylene Producer Conference 1996*, New Orleans, USA.

74 ABB Lummus Global, US 5925799A 1999 (S. Stephen, C. Sumner).

75 G. Gildert, W. Groten, K. Rock, D. Weidert, Article 20B, *presented at the Ethylene Producer Conference* 1995, Houston, USA.

76 ABB Lummus Global, WO 03087022, 2003 (W. V. Tuan, M. Qi, WU J. Tzong-Chaur).

77 *PERP Report* "Ethanol", 04/05-8 January 2006, Nexant Inc., NY

78 F. Zimbardi *et al.*, *Overview of Bioethanol Production*, ENEA, (2000) .

79 F. O. Licht, *World Ethanol and Biofuels Report* **4** (2006) no. 16, 365; F. O. Licht, *World Ethanol and Biofuels Report* **4** (2006) no. 17, 391

80 *Int. J. Appl. Sci. Eng.* **4** (2006) 1.

81 Basic Ind Bureau Miti, JP2000281604, 2000 (Morikawa, Shigeru); BP Chem. Int. Ltd., WO2007063279, 2008 (Bayley, Bolton); BP Chem. Int. Ltd., EP1792885, 2007; US2006149109, 2006 (Ruziska, Jenkins); US2005107481, 2005 (Janssen, van Egmont)

82 K. A. Gray, L. Zhao, M. Emptage, *Curr. Opin. Chem. Biol.* **10** (2006) 141 – 146

83 http://www.greenergy.com/perspectives/Bioethanol.pdf

84 Brazil Institute Special Report, April 2007, Vol 3, http://www.wilsoncenter.org/topics/pubs/Brazil_SR_e3.pdf

85 IEA Energy Techonlogy Essentials, January 2007, http://www.iea.org/Textbase/techno/essentials2.pdf

86 M. S. Jank, L. F. do Amaral, "Potential Supply and Demand for Biofuels in the Coming Decade: Towards a US - Brazil Partnership", Presentation at the Woodrow Wilson International Center for Scholars, February 2007

87 Nordzucker, February 2008, http://www.nordzucker.de/index.php?id=395&L=1

88 Braskem pressroom, June 26 2007, http://www.braskem.com.br/site/portal_braskem/en/sala_de_imprensa/sala_de_imprensa_detalhes_6062.aspx

89 DOW press release, July 2007, http://news.dow.com/prodbus/2007/20070719a.htm?filepath=&fromPage=BasicSearch

90 Solvay press release, December 2007, http://www.solvinpvc.com/solvinservices/news/0,,62076-2-0,00.htm

91 GEA Wiegand, "Bioethanol Technology", p. 6, http://www.gea-wiegand.de/geawiegandde/cmsdoc.nsf/WebDoc/ndkw743dj4, 2008.

92 Aktuell-24.de, July 2 2008, http://www.aktuell-24.de/2008/07/02/ots-agrana-official-opening-of-bioethanol-plant-in-pischelsdorf/

93 Y. C. Hu, *Hydrocarbon Process.* **51** (1972) Nov., 109–116, Part 1; **62** (1983) Apr., 113–116, Part 2; **62** (1983) May, 88–95, Part 3.

94 M. Heathcote, *Asian Chemical News* **3** (1996) June 24, 19.

95 N. A. Baronskaya, L. S. Woldman, A. A. Davydiv, O. V. Buyevskaya, *Gas Sep. Purif.* **10** (1996) no. 1, 86.

96 L. Guczi, R. A. van Santen, K. W. Sarma, *Catal. Rev. Sci. Eng.* **38** (1996) no.2, 249.

97 A. L. Tonkovich, R. W. Carr, R. Aris, *Science (Washington D.C.)* **262** (1993) 221.

98 T. Nozaki, O. Yamzaki, K. Omata, K. Fujimoto, *Chem. Eng. Sci.* **47** (1992) no.9, 2945.

99 A. Shaikh, C. J. Lee, *Hydrocarbon Process.* **74** (1995) 89.

100 J. A. Reid, D. R. McPhaul: "Contaminant Rejection Technology Update," presented at AIChE Spring National Meeting, 8th Annual Ethylene Producers Conference, New Orleans, LA, Feb. 28, 1996.

101 W. H. Delphin, J. C. Franks, Personal Communication, E. I. du Pont de Nemours & Co., Chocolate Bayou, Tex., Mar. 1985.

102 CFR, vol. 40, 1985, Part 61.

103 M. Nasi, M. Sourander, M. Tuomala, D. C. White *et al.*, *Hydrocarbon Process.* **62** (1983) Jun., 74–82.

104 M. Sourander, M. Kolari, J. C. Cugini, J. B. Poje *et al.*, *Hydrocarbon Process.* **63** (1984) Jun., 63–69.

105 *Pipeline Gas J.* **210** (1983) Jun., no. 7, 34–37.

106 S. D. Govrau, MAP Search Services, Houston, TX, personal communication, May 1985.

107 *Eur. Chem. News* **27** (1975) Feb. 28, 19.

108 L. Kniel, O. Winter, K. Stork: *Ethylene, Keystone to the Petrochemical Industry*, Marcel Dekker, New York 1975, Chapter 5.

109 *Oil Gas J.* **75** (1977) no. 39, Sep. 19, 108.

110 *Eur. Chem. News* **31** (1977) no. 813, Nov. 25, 56.

111 F. F. McKay, G. R. Worrell, B. C. Thornton, H. L. Lewis, *Pipe Line Ind.* **49** (1978, Aug.) no. 2, 77–78, 80, 82, 84.

112 E. L. Pawlikowski, Storing and Handling Liquefied Olefins and Diolefins, Exxon Chemical Co. USA, 1974.

113 M. Eramo: CMAI, APTC, May 7, 2002, Seoul, Korea.

114 M. Yoneyama: SRI Consulting, *Asia Petrochemical Conference*, May 19, 2005, Yokohama, Japan.

115 *Oil Gas J.* **103** (2005) March 28, 54.

116 W. D. Broddle, Personal Communication, Conoco, Ponca City, Okla., May 1985.

117 G. D. Clayton, F. E. Clayton (eds.): *Patty's Industrial Hygiene and Toxicology*, 3rd rev. ed., vol. **28**, Wiley-Interscience, New York 1981, pp. 3198–3199.

118 W. B. Deichman, H. W. Gerarde: *Toxicology of Drugs and Chemicals*, Academic Press, New York 1969, p. 316.

119 A. L. Cowles, H. H. Borgstedt, A. J. Gillies, *Anesthesiology* **36** (1972) no. 6, 558.

120 W. R. von Oettingen, Toxicity and Potential Dangers of Aliphatic and Aromatic Hydrocarbons, Public Health Bulletin no. 225, Washington, D.C., 1940.

121 J. C. Krantz, Jr., C. J. Carr, J. F. Vitcha, *J. Pharmacol. Exp. Ther.* **94** (1948) 315.

122 C. Reynolds, *Anesth. Analg. (New York)* **6** (1927) 121.

123 T. E. Hamm, D. Guest, J. G. Dent, *Fund.Appl. Toxicol.* **4** (1984) 473–478.

124 P. Pietsch, M. Chenoweth, *Proc. Soc. Exp. Biol. Med.* **130** (1968) 714.

125 R. B. Conolly, R. J. Jaeger, S. Szabo, *Exp. Mol. Pathol.* **28** (1978) 25.

126 M. L. Krasovitskaya, L. Malyarova, *Gig. Sanit.* **33** (1968) no. 5, 7.

127 P. Cazzamali, *Clin. Chirurg.* **34** (1931) 477.

128 M. M. Landry, R. Fuerst, *Dev. Ind. Microbiol.* **9** (1968) 370.

129 H. K. Pratt, J. D. Goeschl, *Am. Rev. Plant Physiol.* **20** (1969) 542.

130 R. E. Holm, J. L. Rey, *Plant Physiol.* **44** (1969) 1295.

131 G. D. Clayton, T. S. Platt, *Am. Ind. Hyg. Assoc. J.* **28** (1967) 151.

132 J. M. Arena (ed.): *Poisoning*, 4th ed., C. C. Thomas, Springfield, Ill. 1979, p. 426.

133 L. R. Riggs, *Proc. Soc. Exp. Biol. Med.* **22** (1924–1925) 269.

134 Chemical Safety Data Sheets, Chemical Manufacturers' Assoc. (formerly the Manufacturing Chemists' Assoc. Inc.,) Washington, D.C., 1979.

135 ACGIH (ed.): *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment*, ACGIH, Cincinnati, Ohio 1986–1987.

136 M. L. Krasovitskaya, L. K. Malyarova, *Biol. Deistvie Gig Znach. Atmos. Zagryaz.* 1966, 74.

137 National Institute for Occupational Safety and Health Manual of Sampling Data Sheets, U.S. Dept. Health Education Welfare, U.S. Printing Office, Washington, D.C., 1977.

## Further Reading

B. Anantharaman: *Catalytic Partial Oxidation Mechanisms: Commercial Application to Industrial Ethylene Epoxidation*, VDM Verlag, Saarbrücken 2009.

G. P. Chiusoli, P. M. Maitlis (eds.): *Metal-Catalysis in Industrial Organic Processes*, Royal Society of Chemistry, Cambridge, UK 2006.

A. E. Comyns: *Encyclopedic Dictionary of Named Processes in Chemical Technology*, 3rd ed., CRC Press, Boca Raton, FL 2007.

F. H. Falqi: *Miracle of Petrochemicals*, Universal-Publishers, Boca Raton, FL 2009.

A. J. Kidnay, W. R. Parrish: *Fundamentals of Natural Gas Processing*, CRC/Taylor & Francis, Boca Raton, FL 2006.

M. Kjellin, I. Johansson (eds.): *Surfactants from Renewable Resources*, Wiley, Chichester 2010.

S. Liu: *Oxidative Dehydrogenation of Ethane to Ethylene with H2S and Sulfur*, VDM Verlag, Saarbrücken 2009.

D. Malpass: *Introduction to Industrial Polyethylene*, Wiley-Scrivener, Hoboken, NJ 2010.

G. A. Olah, A. Goeppert, G. K. S. Prakash: *Beyond Oil and Gas: The Methanol Economy*, 2nd ed., Wiley-VCH, Weinheim 2009.

K. M. Sundaram, M. M. Shreehan, E. F. Olszewski: *Ethylene*, "Kirk Othmer Encyclopedia of Chemical Technology", 5th edition, vol. 10, p. 593–632, John Wiley & Sons, Hoboken, 2005, online: DOI: 10.1002/0471238961.0520082519211404.a01.pub2 (April 2001).