Manufacture

Ethylene oxide has been produced commercially by two basic routes: the ethylene chlorohydrin and direct oxidation processes. The chlorohydrin process was first introduced during World War I in Germany by Badische Anilin-und Soda-Fabrik (BASF) and others (95). The process involves the reaction of ethylene with hypochlorous acid followed by dehydrochlorination of the resulting chlorohydryn with lime to produce ethylene oxide and calcium chloride. Union Carbide Corp. was the first to commercialize this process in the United States in 1925. The chlorohydryn process is not economically competitive, and was quickly replaced by the direct oxidation process as the dominant technology. At the present time, all the ethylene oxide production in the world is achieved by the direct oxidation process.

The direct oxidation technology, as the name implies, utilizes the catalytic oxidation of ethylene with oxygen over a silver-based catalyst to yield ethylene oxide. The process can be divided into two categories depending on the source of the oxidizing agent: the air-based process and the oxygen-based process. In the first, air or air enriched with oxygen is fed directly to the system. In the second, a high purity oxygen stream (>95 %) from an air separation unit is employed as the source of the oxidizing agent. Union Carbide Corp. was the first to commercialize an air-based direct oxidation process in 1937. The first oxygen-based system was commercialized by Shell Oil Co. in 1958 (96).

Several companies have developed technologies for direct oxidation plants. Union Carbide Corp. and Dow Chemical use their own technologies. Shell Development, Scientific Design (96), and more recently, Nippon Shokubai, license ethylene oxide technology, and over 70% of present world capacity is based on their processes. Shell and Nippon Shokubai technologies are solely oxygen-based, and Scientific Design offers both air- and oxygen-based processes. All the ethylene oxide plants that have been built during the last 15 years were oxygen-based processes, and a number of existing ethylene oxide plants were converted from the air to the oxygen-based process during the same period (97). Extensive information on the early developments of the chlorohydryn and direct oxidation processes are reported in Reference 98. The total world production capacity of ethylene oxide in 1992 was about 9.6 x 10^6 metric tons. Most ethylene oxide is consumed by its producers in making derivatives (99).

There are 12 producers of ethylene oxide in the United States. Table 9 shows the plant locations, estimated capacities, and types of processes employed. The total U.S. production capacity for 1992 was ca 3.4 x 10^6 metric tons. The percentages of total domestic production made by the air- and oxygen-based processes are ca 20 and 80%, respectively. The largest producer is Union Carbide Corp. with approximately one-third of the United States' ethylene oxide capacity. About 94% of domestic ethylene oxide capacity is located on the Gulf Coast near secure and plentiful ethylene supplies. Plans for additional U.S. production in the 1990s have been announced by Union Carbide (incremental expansions), Formosa Plastics (at Pt. Comfort, Texas), and Shell (at Geismar, Louisiana) (101).

### Table 9. Domestic Producers, Capacities, Process Types and Technology Used for Ethylene Oxide

<table>
<thead>
<tr>
<th>Producer</th>
<th>Location</th>
<th>Capacity, 10^3 t/yr</th>
<th>Process oxidant</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>Geismar, La.</td>
<td>218</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Dow</td>
<td>Plaquemine, La.</td>
<td>227</td>
<td>oxygen</td>
<td>Dow</td>
</tr>
<tr>
<td>Eastman</td>
<td>Longview, Tex.</td>
<td>91</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Hoechst-Celanese</td>
<td>Clear Lake, Tex.</td>
<td>209</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Olin</td>
<td>Brandenburg, Ky.</td>
<td>50</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Oxy Petrochemicals</td>
<td>Bayport, Tex.</td>
<td>250</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>PD Glycols</td>
<td>Beaumont, Tex.</td>
<td>202</td>
<td>oxygen</td>
<td>Scientific Design</td>
</tr>
<tr>
<td>Quantum</td>
<td>Morris, Ill.</td>
<td>113</td>
<td>oxygen</td>
<td>Scientific Design</td>
</tr>
<tr>
<td>Shell</td>
<td>Geismar, La.</td>
<td>364</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Sun Refining</td>
<td>Claymont, Del.</td>
<td>45</td>
<td>oxygen</td>
<td>Shell</td>
</tr>
<tr>
<td>Texaco</td>
<td>Port Neches, Tex.</td>
<td>332</td>
<td>oxygen</td>
<td>Scientific Design</td>
</tr>
<tr>
<td>Union Carbide</td>
<td>Seadrift, Tex.</td>
<td>340</td>
<td>air</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>Union Carbide</td>
<td>Tait, La.</td>
<td>668</td>
<td>air, oxygen</td>
<td>Union Carbide</td>
</tr>
</tbody>
</table>

* Total 3118

Ref. 100 and miscellaneous sources.

Joint venture: Oxychem and Du Pont.

**Direct Oxidation Processes.** The phenomenal growth in United States and world ethylene oxide production capacity since 1940 and the marked trend toward larger single-train plants is chiefly due to the great commercial success of the direct oxidation process. Compared to the chlorohydryn process, direct oxidation eliminates the need for large volumes of chlorine. Also, there are no chlorinated hydrocarbon by-products to be sold, processing facilities can be made simpler, and operating costs are lower (102). The main disadvantage of the direct oxidation process is the lower yield or selectivity of ethylene oxide per unit of feed ethylene consumed. The main inefficiency in the process results from the loss of ca 20% 25% of the ethylene to carbon dioxide and water. Consequently, operating conditions must be carefully controlled to maximize selectivity.

All ethylene oxide direct-oxidation plants are based on the original process chemistry discovered by Lefort in 1931 (7,8). The main reaction is as follows:

\[ \text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O} \]

The only significant by-products are carbon dioxide and water, which are formed either by complete combustion of ethylene:

\[ \text{C}_2\text{H}_4 + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} \]
or by further oxidation of ethylene oxide:

\[ \text{C}_2\text{H}_4\text{O} + 2\frac{3}{2} \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} \]

To prevent further oxidation of ethylene oxide, the ethylene conversion of the commercial processes is typically between 10 and 20%.

Although these reactions have been researched extensively and are the subjects of numerous patents, the precise reaction mechanism is not fully understood. The controversy has mostly centered on the nature of the oxygen species responsible for ethylene oxide formation (103). The results of various surface characterization studies indicate that there are at least three types of adsorbed oxygen species on silver: monoatomic chemisorbed oxygen, diatomic (molecular) oxygen, and subsurface oxygen. The first results from a dissociative adsorption of oxygen on a silver surface:

\[ \text{O}_2 + 4 \text{Ag} \rightarrow 2 \text{O}^{2-}_{\text{ads}} + 4 \text{Ag}^+ \]

The second is nondissociative, and is more weakly bonded:

\[ \text{O}_2 + \text{Ag} \rightarrow \text{O}^{2-}_{\text{ads}} + \text{Ag}^+ \]

The third case arises when the temperature is higher than 420 K, at which point diffusion of atomic adsorbed oxygen from surface to subsurface region becomes appreciable (103).

During the 1970s and early 1980s, the prevailing theory was that ethylene reacts with diatomic oxygen to form ethylene oxide, leaving one oxygen atom on the surface (103). Monoatomic chemisorbed oxygen reacts with ethylene to form carbon dioxide and water. Since \( \text{O}^{2-}_{\text{ads}} \) must be removed from the silver surface before more \( \text{O}^{2-}_{\text{ads}} \) can form, the two reactions must be combined. The stoichiometry for the complete reaction is:

\[ 7 \text{C}_2\text{H}_4 + 6 \text{O}_2 \rightarrow 6 \text{C}_2\text{H}_4\text{O} + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \]

This leads to a limiting ethylene selectivity of 6/7 or 85.7%, which has been exceeded, as reported in several patents (104–106).

More recent studies provided the evidence for a different theory (107). The results of these studies indicate that monoatomic chemisorbed oxygen leads both to ethylene oxide formation, and to carbon dioxide and water formation. The controlling factor is the charge state of adsorbed monoatomic oxygen. Strongly negative-charged monoatomic oxygen acts as a base, leading to the abstraction of hydrogen from ethylene and complete combustion. When subsurface oxygen is present, it competes with adsorbed atomic oxygen for silver electrons, reducing the negative charge on the adsorbed oxygen. This increases its affinity toward the electron-rich double bond of ethylene. The molecular framework of ethylene is preserved, and the reaction path to ethylene oxide becomes predominant. This theory has gradually gained support and now guides the thinking in ethylene oxide catalyst research.

In addition to ethylene oxide, carbon dioxide, and water, small quantities of acetaldehyde and traces of formaldehyde are also produced in the process. They generally total less than 0.2% of the ethylene oxide formed. Acetaldehyde is most likely formed by isomerization of ethylene oxide, whereas formaldehyde is most likely formed by direct oxidation of ethylene (108).

A large amount of heat is released by the ethylene oxidation reactions. At 600 K, each kg of ethylene converted to ethylene oxide releases 3.756 MJ (3564 Btu); each kg of ethylene converted to carbon dioxide and water releases 50.68 MJ (48,083 Btu). Energy recovery and integration is a prime concern in process design (108).

Commercial processes operate under recycle conditions in a packed-bed, multitubular reactor. Reaction temperatures of 200–300 °C are typical, and operating pressures of 1–3 MPa (10–30 atm) have been reported (96,102,109). The reactor is of the shell and tube type comprised of several thousand mild steel or stainless steel tubes, 20–50 mm inside diameter (96). The reactor can be either oil or boiling water cooled. Figure 1 is a schematic diagram of an oil-cooled reactor. Based on published information regarding catalyst productivities and space velocities, the reactor tube lengths are 6–12 m (96,102,109). These tubes are filled with a silver-based catalyst ca 3–10 mm dia supported on a carrier material with a surface area usually <1 m²/g (96,102,106,107). The yield (moles of product produced per moles of ethylene consumed in the process) is normally 70–80% depending on catalyst type, per pass conversion, reactor design, and a large number of process operating variables (97).
Technological innovations in catalyst development and process design and engineering have enabled ethylene oxide manufacturers to meet the commercial needs for larger facilities without using a great number of reactors (102,115). For example, in the Shell oxygen-based process, it is claimed that individual reactor capacities have increased from a modest 9,000 t/yr in 1958 to 25,000 t/yr in 1968, to ca 150,000 t/yr in recent designs (115). There is a pronounced trend in both the United States and Europe toward larger single-train plant sizes. In the late 1950s, a 30,000 t/yr ethylene oxide unit was considered large, whereas 10 years later plant sizes of 100,000–150,000 t/yr were typical (116). Today some producers have plant capacities in excess of 250,000 t/yr.

**Air-Based Direct Oxidation Process.** A schematic flow diagram of the air-based ethylene oxide process is shown in Figure 2. Published information on the detailed evolution of commercial ethylene oxide processes is very scanty, and Figure 2 does not necessarily correspond to the actual equipment or process employed in any modern ethylene oxide plant. Precise information regarding process technology is proprietary. However, Figure 2 does illustrate all the salient concepts involved in the manufacturing process. The process can be conveniently divided into three primary sections: reaction system, oxide recovery, and oxide purification.
In the first section, compressed air is filtered, purified (if necessary), and fed separately with ethylene into a recycle gas stream. This recycle stream feeds a bank of one or more primary multitubular reactors that operate in parallel. The number of primary reactors used depends chiefly on the plant capacity, size of the individual reactors, and the activity and the selectivity of the catalyst used. The ethylene is oxidized to ethylene oxide, carbon dioxide, and water in the packed-bed converters, and the heat of reaction is removed by circulating or boiling an organic oil on the shell side (108) (see HEAT EXCHANGE TECHNOLOGY), eg, Dowtherm, Tetralin, or other high boiling materials. The hot oil is cooled in a steam generator, producing considerable amounts of high pressure steam for the ethylene oxide and other processes at the plant site (96,109).

The per pass ethylene conversion in the primary reactors is maintained at 20–30% in order to ensure catalyst selectivities of 70–80%. Vapor-phase oxidation inhibitors such as ethylene dichloride or vinyl chloride or other halogenated compounds are added to the inlet of the reactors in ppm concentrations to retard carbon dioxide formation (107,120,121). The process stream exiting the reactor may contain 1–3 mol % ethylene oxide. This hot effluent gas is then cooled in a shell-and-tube heat exchanger to around 35–40 °C by using the cold recycle reactor feed stream gas from the primary absorber. The cooled crude product gas is then compressed in a centrifugal blower before entering the primary absorber.

The second important step of the process is ethylene oxide recovery from the crude product gas. This is accomplished in the primary absorber by countercurrent scrubbing with cold water in a column ca 18–20 m high. The ethylene oxide produced in the reactor is dissolved in the absorber water along with some nitrogen and carbon dioxide, and traces of ethylene, ethane, and aldehydes (102). The aqueous stream is removed from the base of the absorber and sent to a desorber. The unabsorbed gas from the main absorber overhead gas stream is heat-exchanged to raise its temperature, and it is then fed as the main stream to the secondary or purge reactor system. In the purge reactor, more air may be added to increase the oxygen content of the feed gas. The gases leaving the purge reactor are heat-exchanged against the feed gas to the same reactor, and then enter a purge absorber. In the purge absorber, ethylene oxide is removed with water in the same manner as in the main absorber.

The chief purpose of the purge reactor system is to allow reaction of a substantial portion of the ethylene content of the purge gas, which must be vented from the main reactor system in order to prevent accumulation of inert gases, primarily nitrogen and carbon dioxide (109). Figure 2 shows a two-stage, air-based plant with a single-purge reactor. In larger plants, three or more stages of reaction may be used to improve overall yield of product (109,113). In such cases the flow scheme is virtually the same, except additional purge reactor absorber systems are added in series to the first purge reactor. The scrubbed gas from the last purge absorber may be partly recycled to the same purge reactor inlet or vented from the system.

In some cases, the ethylene content of the vent gas leaving the last purge reactor makes it economical to further process this gas for energy recovery (109). Such a scheme not only extracts valuable power from the vent gas, but also reduces considerably the hydrocarbon emissions from the process. Several such schemes have been described in References 108 and 122–125. The basic scheme involves heating the ethylene lean gas (<1.5 mol %) to ca 200 °C, and then passing it into a catalytic combustion chamber filled with an active oxidation catalyst containing a noble metal, eg, platinum. Such an active catalyst should burn virtually all of the ethylene and ethane in the vent gas, thereby raising its temperature to 400–600 °C. The hot, pressurized gas expands in a turbine that is coupled to the feed gas compressor in the main process. The hot exhaust gases

![Diagram](https://example.com/diagram.png)

**Fig. 2.** Air-based direct oxidation process for ethylene oxide (96,102,109,117 119).
from the turbine are used to generate steam. Using such a scheme, a 10% reduction in the overall cost is claimed for the manufacture of ethylene oxide by the air-based process (125).

The third key section of the process deals with ethylene oxide purification. In this section of the process, a variety of column sequences have been practiced. The scheme shown in Figure 2 is typical. The ethylene oxide-rich water streams from both the main and purge absorbers are combined, and after heat exchange are fed to the top section of a desorber where the absorbate is steam stripped. The lean water from the lower section of the desorber is virtually free of oxide, and is recirculated to the main and purge absorbers. The concentrated ethylene oxide vapor overhead is fed to the ensuing stripper for further purification. If the desorber is operated under vacuum, a compressor is required.

The ethylene oxide recovered in the desorber contains some carbon dioxide, nitrogen, aldehydes, and traces of ethylene and ethane. In the stripper the light gases are separated overhead and vented, and the partially purified ethylene oxide is sent from the bottom of the stripper to the mid-section of a final refining column. The ethylene oxide from the refining section should have a purity of >99.5 mol %. The final product is usually stored as a liquid under an inert atmosphere.

The overall economics of the process are strongly dictated by the design of the reaction system and the actual operating conditions used. The catalyst properties, as they influence reactor design and operating variables are, therefore, of the greatest significance. Specific information on actual conditions employed in the manufacture is not disclosed. However, the general ranges suggested by literature and patent reviews are summarized in Table 10.

Table 10. Ranges of Reaction System Variables in the Direct Oxidation Process for Ethylene Oxide

<table>
<thead>
<tr>
<th>Variable</th>
<th>Air oxidation</th>
<th>Oxygen oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene, mol %</td>
<td>2 10</td>
<td>20 35</td>
</tr>
<tr>
<td>oxygen, mol %</td>
<td>4 8</td>
<td>4 8</td>
</tr>
<tr>
<td>carbon dioxide, mol %</td>
<td>5 10</td>
<td>5 10</td>
</tr>
<tr>
<td>ethane, mol %</td>
<td>0 1.0</td>
<td>0 1.0</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>220 277</td>
<td>220 235</td>
</tr>
<tr>
<td>pressure, MPa</td>
<td>1 3</td>
<td>2 3</td>
</tr>
<tr>
<td>space velocity, m/s</td>
<td>2000 4500</td>
<td>2000 4500</td>
</tr>
<tr>
<td>pressure drop, kPa</td>
<td>41 152</td>
<td>41 152</td>
</tr>
<tr>
<td>conversion, %</td>
<td>20 65</td>
<td>8 12</td>
</tr>
<tr>
<td>selectivity or yield (%)</td>
<td>63 75</td>
<td>75 82</td>
</tr>
</tbody>
</table>

a Refs. 102, 111, and 113.
b To convert MPa to psi, multiply by 145.
c The space velocity is defined as the standard volume of the reactant stream fed per unit time divided by the volume of reactor space filled with catalyst.
d To convert kPa to mm Hg, multiply by 7.5.

Oxygen-Based Direct Oxidation Process. Even though the fundamental reaction and the ultimate results are the same, there are substantial differences in detail between air- and oxygen-based processes. Virtually all the differences arise from the change in the oxidizing agent from air (ca 20 mol % O2) to pure oxygen (>95 mol % O2). Due to the low per pass conversion, the need for complete removal of ethylene oxide by absorption, and the accumulation of nitrogen in the cycle, the air process requires a substantial purge stream. As a direct consequence of this purge stream, the air-based process requires the staged reaction absorption system described earlier. The oxygen-based process uses substantially pure oxygen, reduces the quantities of inert gases introduced into the cycle, and thereby results in almost complete recycle of the unconverted ethylene oxide (96,106). This eliminates the need for a purge reactor system in an oxygen-based process. However, as in the air-based process, the volume of carbon dioxide formed is about half the volume of ethylene that reacts at a catalyst selectivity of 70–80%. This CO2 must be eliminated on a continuous basis in order to control its concentration at a fixed acceptable level in the cycle. Concentrations of CO2 much in excess of 15 mol % adversely influence catalyst activity (96,102). Therefore, in an oxygen-based system, part of the recycle gas leaving the absorber must be treated in a CO2 removal unit before it is sent back to the main reaction cycle.

In addition to the CO2 removal unit purge stream, an additional process vent is required to prevent accumulation of argon in the cycle. Argon is a significant impurity in the oxygen supply, and can build up to 30–40 mol % in the cycle gas if no deliberate purge is used (102). When this happens, because of the lower heat capacity of the argon, the cycle gas may enter the flammable region, and as a result the oxygen concentration in the cycle has to be lowered. Consequently, the selectivity of the process is substantially lower (126). In spite of this additional purge, the total vent stream in an oxygen-based process is much smaller than in an air-based unit. The operation of the main reactor can be at much higher ethylene concentration than that possible in air-based process due to the smaller purge flow. The high ethylene concentration improves the catalyst selectivity because the per pass conversions are lower for a given ethylene oxide production (96,109). The small purge rates in an oxygen-based system operated with very high purity oxygen (99.0–99.5 mol %) make it possible to use cycle diluents of improved heat capacity other than nitrogen (116). These diluents facilitate the use of higher oxygen concentrations in the cycle and, therefore, improve selectivity.

Figure 3 shows a simple schematic diagram of an oxygen-based process. Ethylene, oxygen, and the recycle gas stream are combined before entering the tubular reactors. The basic equipment for the reaction system is identical to that described for the air-based process, with one exception: the purge reactor system is absent and a carbon dioxide removal unit is incorporated. The CO2 removal scheme illustrated is based on a patent by Shell Oil Co. (127), and minimizes the loss of valuable ethylene in the process.
The main process vent stream generally contains a fairly high hydrocarbon concentration, particularly if the diluent is not nitrogen. In such cases, the purge stream can be readily used in a boiler or incinerated in a furnace without supplemental fuel (106,128). The ethylene oxide recovery and refining sections for both the air- and oxygen-based processes are almost identical. As with the air-based process, specific operating conditions for the reaction system are proprietary; however, the general ranges reported in the literature and patents are summarized in Table 10.

**Process Technology Considerations.** Imnumerable complex and interacting factors ultimately determine the success or failure of a given ethylene oxide process. Those aspects of process technology that are common to both the air- and oxygen-based systems are reviewed below, along with some of the primary differences.

**Ethylene Oxide Catalysts.** Of all the factors that influence the utility of the direct oxidation process for ethylene oxide, the catalyst used is of the greatest importance. It is for this reason that catalyst preparation and research have been considerable since the reaction was discovered. There are four basic components in commercial ethylene oxide catalysts: the active catalyst metal; the bulk support; catalyst promoters used is of the greatest importance. It is for this reason that catalyst preparation and research have been considerable since the reaction was discovered. There are four basic components in commercial ethylene oxide catalysts: the active catalyst metal; the bulk support; catalyst promoters; and inhibitors or anticatalysts that suppress the formation of carbon dioxide and water without appreciably reducing the rate of formation of ethylene oxide (105).

Silver-containing catalysts are used exclusively in all commercial ethylene oxide units, although the catalyst composition may vary considerably (129). Nonsilver-based catalysts such as platinum, palladium, chromium, nickel, cobalt, copper ketenide, gold, thorium, and antimony have been investigated, but are only of academic interest (98,130 135). Catalysts using any of the above metals either have very poor selectivities for ethylene oxide production at the conversion levels required for commercial operation, or combust ethylene completely at useful operating temperatures.

A variety of different procedures have been reported for silver catalyst preparation on relatively inert support materials. The different methods are (1) precipitation of silver oxide from aqueous silver nitrate or other salt solutions by alkali or alkaline-earth compounds (136,137); (2) thermal decomposition of silver salts, in particular silver oxalate, silver carbonate, or organic salts of silver (137,138); (3) reduction of silver salts by hydrogen, formaldehyde, hydrazine, or hydroxylamine (139,140); (4) electrolysis of silver salt solutions (141); and (5) selective removal of secondary metals from silver-containing alloys (142,143). The silver is added to the support either as a coating from a suspension or by impregnation with a solution. The coating procedure is claimed to give a catalyst of higher silver content and initial activity. However, the catalyst is susceptible to silver loss by abrasion and tends to lose selectivity to ethylene oxide after use for several months (144). Impregnation of the support with a silver salt combined with an organic reducing agent appears to be more popular in the patent literature. Some investigators have used a combination of coating and impregnation procedures (144 146).

The chemical and physical properties of the support strongly dictate the performance of the finished catalyst. Although nonsupported silver catalysts have been advocated in some patents (147), it is unlikely that they are used commercially since pure silver tends to sinter at reaction temperatures with a resultant activity loss (102). For commercial operation, the preferred supports are alundum (a-alumina) and silicon carbide (129,131). Other supports are glass wool, quartz, carborundum, and ion-exchange zeolites (see Molecular Sieves). The surface area, porosity, and pore size of the support influence the size of the silver particles on the support and, therefore, affect the performance of the final catalyst (148). High surface area supports (3 100 m²/g) generally yield poor ethylene oxide catalysts presumably because ethylene reacts in the pores from which...
the ethylene oxide is released slowly. The combination of slow product release and poor heat conductivity of high surface area supports is claimed to result in the combustion of ethylene oxide (149). Silver alone on a support does not give rise to a good catalyst (150). However, addition of minor amounts of promoter enhance the activity and the selectivity of the catalyst, and improve its long-term stability. Excess addition lowers the catalyst performance (151,152). Promoter formulations have been studied extensively in the chemical industry. The most commonly used promoters are alkaline-earth metals, such as calcium or barium, and alkali metals such as cesium, rubidium, or potassium (153). Using these metals in conjunction with various counter anions, selectivities as high as 82 87% were reported. Precise information on commercial catalyst promoter formulations is proprietary (154–156).

Many organic compounds, especially the halides, are very effective for suppressing the undesirable oxidation of ethylene to carbon dioxide and water, although not significantly altering the main reaction to ethylene oxide (150). These compounds, referred to as catalyst inhibitors, can be used either in the vapor phase during the process operation or incorporated into the catalyst manufacturing step (102). The inhibitor plays a significant role in the process, although the mechanism of inhibitor action is still a subject of debate (157). Important gas-phase inhibitors are ethylene dichloride, ethylene dibromide, other alkyl halides, aromatic hydrocarbons, amines, and organometallic compounds (150,158). In a study of the effect of ethylene dichloride on catalyst activity, it was found that small amounts improved catalyst performance; however, excess amounts of ethylene dichloride deactivated the catalyst (129).

In order to assure control of the reaction, the vapor-phase inhibitor concentration must be closely controlled in the ppm range. Although several compounds have been claimed to be useful, it is likely that commercial processes use only ethylene dichloride or some of the simpler chlorinated aromatics (102). In general, the choice between inhibitors is not based on their differences in performance, but rather on the designers preference for dealing with the type of control problems each inhibitor system imposes (102).

**Temperature and Thermal Factors.** Temperature is used to control two related aspects of the reaction: heat removal from the reactor bed and catalyst operating temperature. The reactor temperature is controlled through the use of a heat-transfer fluid on the reactor shell. The coolant used in most recent designs is boiling water. Boiling water provides good heat transfer and improved safety over previous reactor designs using either boiling or circulating organic heat-transfer fluids. Control of the catalyst operating temperature is necessary to prevent catalyst damage such as sintering or tube damage resulting from excessive temperatures in the catalyst bed. Localized hot spots of 100 300°C above the coolant temperature can form in the catalyst bed without adequate temperature control.

Heat removal from the reactor is necessary for stable operation. Heat is removed through two processes: sensible heat of the process gas and heat transfer to the coolant. Stable operation of the reactor requires balancing these removal processes with the heat generated in the reaction. The undesired complete oxidation of ethylene is the primary source of heat, with a heat of reaction of 1419.0 kJ/mol of ethylene compared with the partial oxidation heat of reaction of 105.2 kJ/mol (25 kcal/mol). Since the activation energy for complete combustion (16.8 kJ/mol) is greater than for partial oxidation (15.2 kJ/mol), and higher temperatures increase the rate of ethylene oxide combustion, the catalyst selectivity drops as temperature increases (159). These compounds the increased heat generation with increasing catalyst temperature. For example, 25 t/h of ethylene oxide production at 75% selectivity generates 91.3 MW; increasing the temperature to increase production to 30 t/h will decrease the catalyst selectivity, say to 70%, and the heat generated (135 MW) for this 20% increase in production is a 48% increase. Therefore, stable operation of the ethylene oxide reactor requires stability in the coolant temperature control.

The reactor stability is also affected by the internal temperature profile in the tubular catalyst bed. The highest reaction rate occurs near the inlet, where the partial pressure of the components is the highest (160). This results in the highest heat generation rate and therefore the maximum (bed temperature coolant) temperature. Stable operation of the reactor requires keeping this peak temperature difference to less than 30 40°C. Several techniques have been proposed for resolving this problem. For example, a gradient in the catalyst activity down the length of the reactor could result in a uniform temperature profile and improved catalyst selectivity (161). Other solutions propose improving the reactor thermal conductivity (160).

**Space Velocity.** Space velocity has a strong effect on the process economics. It establishes the reactor size and pressure drop, affecting compression costs. The optimum space velocity is a function of energy costs, reaction rate, and selectivity. As space velocity increases, the reactor heat-transfer coefficient, selectivity, and compression costs increase while conversion decreases. The optimization of space velocity is highly integrated into the design of the unit since all of the process variables, pressure, temperature, catalyst, etc, affect the optimum. The literature claims benefits in operating in the range of 1000–4500 h⁻¹ (110,153,162,165).

**Operating Pressure.** Operating pressure has a marginal effect on the economics of the ethylene oxide process. High pressure increases production due to higher gas density, increases heat transfer, increases ethylene oxide and carbon dioxide recovery in the absorbers, and lowers compression costs. Also, since the total number of moles decreases in the formation of ethylene oxide from ethylene and oxygen, high pressure is consistent with high conversion. However, high pressures reduce the flammable limit of the process gas as well as increase equipment costs. Typical commercial pressures are 1 2 MPa (10 20 atm) (110,158,165,167).

**Cycle Diluents.** Air process technology uses nitrogen as the diluent gas. The amount of nitrogen that enters the process in the air feed cannot be economically diluted (97).

The choice of diluent for the oxygen process is based on the thermal properties of the gas. The small process purge makes it economically possible for the process to operate under a wide variety of ballast gases. Several gases have been proposed in the patent literature, including methane (168) and ethane (169). Both of these gases have the advantage of higher specific heat and thermal conductivity than nitrogen, raising the flammable limit and reducing the peak temperature difference in the catalyst bed. However, these diluents lead to less steam generation from the reactor coolant due to more sensible heat loss from the reactor, and increase the risk of forming a flammable vapor cloud following a rupture or leak. They also require additional purification systems to prevent sulfur and other contaminants from poisoning the catalyst (170). Finally, higher ethane concentrations will increase the amount of organic chlorides that are needed. This can result in material of construction and product quality problems, as well as adversely affecting catalyst life.

**Raw Material Purity Requirements.** The oxygen process has four main raw materials: ethylene, oxygen, organic chloride inhibitor, and cycle diluent. The purity requirements are established to protect the catalyst from damage due to poisons or thermal runaway, and to prevent the accumulation of undesirable components in the recycle gas. The latter can lead to increased cycle purging, and consequently higher ethylene losses.

Typical ethylene specifications call for a minimum of 99.85 mol % ethylene. The primary impurities are usually ethane and methane. A
methane limit is largely unnecessary; however, care should be taken to restrict the amount of ethane since high ethane concentration will lead to increased chloride inhibitor concentration, which adversely affects product quality, catalyst life, and materials of construction. Impurities that strongly affect catalyst performance and reactor stability include acetylene, propylene, hydrogen, and sulfur. Acetylene causes catalyst coking at very low concentrations (158). Carbonaceous deposits can also be caused by heavy hydrocarbons if present. Propylene is more reactive than ethylene and will oxidize to a wide range of products, including aldehydes that lower product quality (171,172). Hydrogen and carbon monoxide can lead to hot-spotting of the catalyst, and sulfur is a nonreversible poison for silver-based catalyst (120).

Oxygen specifications can vary depending on the economics of the process. The dominant impurity in oxygen is argon. As the argon concentration in the reactor feed increases, the flammable limit of the gas decreases. Therefore, the cycle gas purge flow rate is established to maintain a given concentration of argon in the recycle stream. The optimization of oxygen purity balances the increased ethylene losses in the cycle gas purge and reduced oxygen concentration in the reactor feed gas against the cost of higher purity oxygen (96). Typical oxygen purity is 95 99.95 mol %. However, several patents have proposed using membranes and adsorption technologies to recover the ethylene in the cycle purge gas and recycle it to the process (173 175). In this case, the economics of the process would lead to reduced oxygen purities.

Organic chloride and cycle diluent specifications are less critical since the flows are significantly less. The organic chloride specifications must prevent gross contamination as well as the potential of solids that would lead to plugging. The cycle diluent must also be free of gross contamination as well as significant catalyst poisons such as sulfur (170).

The air process has similar purity requirements to the oxygen process. The ethane content of ethylene is no longer a concern, due to the high cycle purge flow rate. Air purification schemes have been used to remove potential catalyst poisons or other unwanted impurities in the feed.

**Ethylene Oxide Recovery.** An economic recovery scheme for a gas stream that contains less than 3 mol % ethylene oxide (EO) must be designed. It is necessary to achieve nearly complete removal since any ethylene oxide recycled to the reactor would be combusted or poison the carbon dioxide removal solution. Commercial designs use a water absorber followed by vacuum or low pressure stripping of EO to minimize oxide hydrolysis. Several patents have proposed improvements to the basic recovery scheme (176 189). Other references describe how to improve the scrubbing efficiency of water or propose alternative solvents (180,181).

**Ethylene Oxide Purification.** The main impurities in ethylene oxide are water, carbon dioxide, and both acetaldehyde and formaldehyde. Water and carbon dioxide are removed by distillation in columns containing only rectifying or stripping sections. Aldehydes are separated from ethylene oxide in large distillation columns. The size of the column is related to the high degree of separation required for meeting the product quality demand of poly(ethylene glycol) and detergent ethoxylate manufacturers, typically separated from ethylene oxide in large distillation columns. The size of the column is related to the high degree of separation required for meeting the product quality demand of poly(ethylene glycol) and detergent ethoxylate manufacturers, typically <30 ppm aldehydes. Refining ethylene oxide to meet this specification increases the amount of formaldehyde in the final product relative to acetaldehyde due to its higher volatility (182). In addition to modifications of conventional distillation, other technologies for removing aldehyde from ethylene oxide have been proposed, including molecular sieves and extractive distillation (183 186).

**Process Safety Considerations.** Unit optimization studies combined with dynamic simulations of the process may identify operating conditions that are unsafe regarding fire safety, equipment damage potential, and operating sensitivity. Several instances of fires and deflagrations in ethylene oxide production units have been reported in the past (160). These incidents have occurred in both the reaction cycle and ethylene oxide refining areas. Therefore, ethylene oxide units should always be designed to prevent the formation of explosive gas mixtures.

The safe operating ranges of the unit are dependent on all of the process parameters: temperature, pressure, residence time, gas composition, unit dynamic responses, instrumentation system, and the presence of ignition sources (160). The ethylene oxide reaction cycle operates close to the flammable limit. Higher oxygen concentrations yield higher activity and efficiency but more closely approach the flammable limit. One of the more sensitive areas of the unit's design is oxygen mixing. The oxygen concentration must pass through the flammable region while diluting down to the operating level. This is particularly acute in the oxygen process. Therefore, the oxygen mixing step is highly instrumented, and requires a fairly complicated control scheme to assure safe mixing. Another sensitive area is the final refining of high purity ethylene oxide. As with any reactive chemical, it is prudent to use the lowest temperature heat source practical when refining ethylene oxide. Proper operation of the reboiler, including control of liquid level, is critical. The presence of specific forms of iron oxide in contact with ethylene oxide vapor can lead to highly exothermic reactions that can initiate the explosive decomposition of ethylene oxide. Proper initiation of the distillation is critical. Ethylene oxide leaks in porous insulation can react exothermically with water in the insulation, and the resulting glycol may spontaneously ignite at temperatures greater than 60 C (190,191). The selection of the safe operating conditions and design of effective safety systems is a complex task that requires extensive laboratory testing to determine the effect of the various process parameters on explosibility as well as proven commercial experience.

**Environmental Considerations.** A detailed study of the environmental considerations in the manufacture of ethylene oxide by the direct oxidation of processes is described in Reference 108. The primary air emissions from the formation of ethylene oxide by direct oxidation are ethylene, ethylene oxide, carbon dioxide, and ethane. Traces of NO and SO from pollution control and process machinery operations have also been reported. The largest source of organic emissions to the atmosphere in either the oxygen or air process is the cycle purge. In the oxygen process, this is a low volume, high hydrocarbon stream that can be readily used as boiler fuel since it contains 85 85 mol % hydrocarbons (97). The air process cycle purge is the vent from the last purge reactor. Relative to the oxygen process cycle purge, this is a high volume stream that contains low concentrations of hydrocarbons (<2 mol %). A catalytic converter may be added to this stream to reduce the organic emissions.

Other air emissions occur in the ethylene oxide recovery and purification sections. In the purification section, a light end vent is taken from the ethylene oxide distillation train. This vent contains mainly carbon dioxide with some ethylene and ethylene oxide. In some units this stream is passed through a vent scrubber to remove ethylene oxide, recompressed, and fed back to the reaction cycle to recover the ethylene. The other emission source is the carbon dioxide regenerator vent in the oxygen process. This vent includes ethylene and ethylene oxide that are absorbed from the process gas. Some designs call for the installation of a single-stage flash between the CO2 absorber and regenerator to reduce the ethylene emissions.

Relative to the process streams, emissions from auxiliary equipment and flares are small. Some ethylene oxide units use gas-fired turbines to feed air or ethylene (109). These result in unburned hydrocarbon and possible NO emissions. Also, most ethylene oxide units have flares to vent the process gas during upsets. Data is scarce, but estimates indicate that flaring of process gas occurs once to twice a year (109).

Liquid emissions from ethylene oxide units originate in the recovery section. The water of reaction from complete combustion of ethylene must be purged from the oxide absorber water cycle. This stream contains glycol, organic salts, aldehydes, and ethylene oxide. The location of the
purge stream is selected to minimize ethylene oxide and glycol emissions. This stream is readily biodegradable (109). Direct oxidation processes that operate at lower temperatures generate fewer impurities, and therefore have lower organic loads on the process waste treatment unit. Several technologies have been proposed to reduce the amount of organics in the waste, either by distillation or the use of membranes to recover the contained glycol (187 189,192 194).

**Air vs Oxygen Process Differences and Economics.** The relative economics of the air vs oxygen process are reported (97). Two process characteristics dictate the difference in the capital costs for the two processes. The air process requires additional investment for the purge reactors and their associated absorbers, and for energy recovery from the vent gas. However, this is offset by the need for an oxygen production facility and a carbon dioxide removal system for an oxygen-based unit. In a comparison of necessary investments for medium to large capacity units (>20,000 t/yr), oxygen-based plants have a lower capital cost even if the air-separation facility is included (97). However, for small- to medium-scale plants, the air process investment is smaller than that required for the oxygen process and the air-separation unit, unless the oxygen is purchased from a large air-separation unit serving many customers.

There are also operating cost considerations that differ significantly among the two processes. The costs of silver catalyst, oxygen, and ethylene are critical factors determining the relative economies. For a given catalyst type, the oxygen process operates at a higher selectivity and requires a smaller volume of catalyst. Even though the cost of ethylene comprises ca 60% of the total manufacturing cost in both processes, the incremental cost between the air and oxygen processes is influenced only slightly by changes in the price of ethylene. For example, in 1976 it was estimated that an ethylene price increase of 2.20 \$/kg raised the product cost for air oxidation by only 0.088 \$/kg in excess of that of an oxygen-based unit (96). On the other hand, the price of oxygen has a much more significant effect on the economics of an oxygen unit. A change in the oxygen price by 0.22 \$/kg altered the product cost by 0.243 \$/kg.

The oxygen-process plant has no high pressure purge gas stream of sufficient volume to make energy recovery attractive as in an air process. The process also has a considerable steam requirement for carbon dioxide stripping in the \( \text{CO}_2 \) removal unit. The total compression costs for the air-based process, including the air-separation unit, are slightly higher than for an air-based system (160). Purity of the feedstocks (ethylene and ethylene) also determine the relative economics of the air- and oxygen-based processes. If the ethylene purity is low, the volume of the ethylene-rich purge gas is increased markedly, and the oxygen-based process becomes unattractive. In addition to requiring a high oxygen purity, the ratio of argon to argon plus nitrogen in the oxygen feed is critical to the attainment of high yields in the oxygen process (195). Lower values of the ratio improve yields by ca 1 2%. For large-scale ethylene oxide processes, yield changes of even a fraction of a percent can have an impact on the overall process economics. In general, as the ethylene purity decreases, the air process becomes more attractive (197). However, an air-based process may require an air purification system if contaminants such as sulfur, halogens, and heavier hydrocarbons are present.

Both air and oxygen processes can be designed to be comparable in the following areas: product quality, process flexibility for operation at reduced rates, and on-stream reliability (97,182). For both processes, an on-stream value of 8000 h/yr is typical (196). The reliability of the oxygen-based system is closely linked to the reliability of the air-separation plant, and in the air process, operation of the multistage air compressor and power recovery from the vent gas is crucial (97).

For the same production capacity, the oxygen-based process requires fewer reactors, all of which operate in parallel and are exposed to reaction gas of the same composition. However, the use of purge reactors in series for an air-based process in conjunction with the associated energy recovery system increases the overall complexity of the unit. Given the same degree of automation, the operation of an oxygen-based unit is simpler and easier if the air-separation plant is outside the battery limits of the ethylene oxide process (97).

From the preceding discussion, it is clear that no meaningful generalizations can be made regarding the overall superiority of either the air- or oxygen-based process.

**Other Processes.**

**Chlorohydrin Process.** Ethylene oxide is produced from ethylene chlorohydrin by dehydrochlorination using either sodium or calcium hydroxide (160). The by-products include calcium chloride, dichloroethane, bis-(2-chloroethyl) ether, and acetaldehyde. Although the chlorohydrin process appears simpler, its capital costs are larger, largely due to material of construction considerations (197).

**Arsenic-Catalyzed Liquid-Phase Process.** An arsenic catalyst liquid-phase process for olefin oxides has been patented by Union Carbide (198). The selective epoxidation of ethylene by hydrogen peroxide in a 1,4-dioxane solvent in the presence of an arsenic catalyst is claimed. No solvent degradation is observed. Ethylene oxide is the only significant product detected. The catalyst used may be either elemental arsenic, an arsenic compound, or both.

**Thallium-Catalyzed Epoxidation Process.** The use of \( \text{Tl}(\text{III}) \) for olefin oxidation to yield glycols, carboxyls, or epoxides is well known (199). Because the epoxidation with \( \text{Tl}(\text{III}) \) is stoichiometric to produce \( \text{TlO} \), reoxidation is needed. Halcon has patented processes based on such epoxidation to yield ethylene oxide (200 203). The primary benefits of such a process are claimed to be high yields of ethylene oxide, flexibility to produce either propylene oxide or ethylene oxide, and the potential of a useful by-product (acetaldehyde). Advances using organic hydroperoxides in place of oxygen for reoxidation offer considerable promise, since reaction rates are rapid and low pressures can be used.

**Lummus Hypochlorite Process.** A Lummus patent claims a process for propylene oxide or ethylene oxide using tert-butyl hypochlorite (204). The chemistry for this new process parallels the classical chlorohydrin technology with brine recycle. Advantages claimed are high ethylene yield, reduced reactor size, and lower steam requirements for the saponification step. However, disadvantages include high capital cost for a large chlorine plant, difficult and energy-intensive distillation steps, and losses of tert-butyl alcohol in the process.

**Liquid-Phase Epoxidation with Hydroperoxides.** Molybdenum, vanadium, and tungsten have been proposed as liquid-phase catalysts for the oxidation of the ethylene by hydroperoxides to ethylene oxide (205). \( \text{tert-Butyl} \) hydroperoxide is the preferred oxidant. The process is similar to the arsenic-catalyzed route, and includes the use of organometallic complexes.

**Electrochemical Process.** Several patents claim that ethylene oxide is produced in good yields in addition to faradic quantities of substantially pure hydrogen when water and ethylene react in an electrochemical cell to form ethylene oxide and hydrogen (206 208). The only raw materials that are utilized in the ethylene oxide formation are ethylene, water, and electrical energy. The electrolyte is regenerated in situ, i.e., within the electrolytic cell. The addition of oxygen to the ethylene is activated by a catalyst such as elemental silver or its compounds at the anode or its vicinity (206). The common electrolytes used are water-soluble alkaline metal phosphates, borates, sulfates, or chromates at ca 22 25 C (207). The process can be either batch or continuous (see **Electrochemical Processing**).
Unsteady-State Direct Oxidation Process. Periodic interruption of the feeds can be used to reduce the sharp temperature gradients associated with the conventional oxidation of ethylene over a silver catalyst (209). Steady and periodic operation of a packed-bed reactor has been investigated for the production of ethylene oxide (210). By periodically varying the inlet feed concentration of ethylene or oxygen, or both, considerable improvements in the selectivity to ethylene oxide were claimed.

Fluid-Bed Direct Oxidation Process. The use of a fluidized bed for ethylene oxide production was reported to produce good temperature control and inhibition of side reactions using a granular silver catalyst (211). Several additional fluid-bed processes that claim improved product yields were patented later (212-215). However, only one process, developed by Vulcan Atlantic, was reported to have been successfully demonstrated in pilot-scale equipment (216). The pilot fluid-bed reactor is described as a multitubed converter that produces uniform heat transfer to a fluid circulating in the shell of the converter, and minimizes back-mixing of the fluidized catalyst. A novel circulating fluid-bed process and the associated reaction apparatus have been patented (217-219). By employing high gas velocities, the ethylene oxide productivity per unit catalyst volume is claimed to be three to four times greater than the maximum reported number for conventional fixed-bed tubular reactor (219,220). In spite of the recent rapid advances in fluidization technology, no commercial fluid-bed ethylene oxide processes have been reported.

Biological. Several recent patents have claimed the production of ethylene oxide from a wide variety of raw materials using enzymatic catalysts (221-224).