ETHYLENE OXIDE

1. Introduction

Ethylene oxide [75-21-8] was first prepared in 1859 by Wurtz from 2-chloroethanol (ethylene chlorohydrin) and aqueous potassium hydroxide (1). He later attempted to produce ethylene oxide by direct oxidation but did not succeed (2). Many other researchers were also unsuccessful (3–6). In 1931, Lefort achieved direct oxidation of ethylene to ethylene oxide using a silver catalyst (7,8). Although early manufacture of ethylene oxide was accomplished by the chlorohydrin process the direct oxidation process has been used almost exclusively since 1940. The primary use for ethylene oxide is in the manufacture of derivatives such as ethylene glycol, surfactants, and ethanolamines.

2. Physical Properties

Ethylene oxide (C_2H_4O) is a colorless gas that condenses at low temperatures into a mobile liquid. It is miscible in all proportions with water, alcohol, ether, and most organic solvents. Its vapors are flammable and explosive. The physical properties of ethylene oxide are summarized in Tables 1–7.

Table 1. **Some Physical Constants of Ethylene Oxide**

Property	Value	References
molecular weight	44.05	
bp, °C		
at 101.3 kPa[a]	10.4	9
Δbp/pressure at 100 kPa, K/kPa[b]	0.25	9
coefficient of cubical expansion at 20°C, per °C	0.00158	9
critical pressure, MPa[c]	7.19	9
critical temperature, °C	195.8	10
dielectric constant at 0°C	14.50	11
dipole moment, C·m[d]	6.30×10^{-30}	9
explosive limits in air, %		
upper	100	9
lower	3	9
flash point, Tag open cup, °C	<−18	9
freezing point, °C	−111.7	9
heat of combustion at 25°C, kJ/mol[e]	−1218	12
heat of fusion, kJ/mol[e]	5.17	13
heat of solution in pure water at 25°C and constant pressure, kJ/mol[e]	−6.3	14
heat of reaction with water at 25°C, kJ/mol[e]	−87.9	9
ionization potential, J[e]		
experimental	$1.73 - 1.80 \times 10^{-18}$	15
calculated	1.65×10^{-18}	16
refractive index, n_D^7	1.3597	17

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

[b] To convert K/kPa to K/mm Hg, divide by 7.5.

[c] To convert MPa to atm, multiply by 9.87.

[d] To convert C·m to debyes, multiply by 3.0×10^{29}.

[e] To convert kJ to kcal, divide by 4.184.

2.1. Structure. The strained configuration of ethylene oxide has been a subject for bonding and molecular orbital studies. Valence bond and early molecular orbital studies have been reviewed (28). Intermediate neglect of differential overlap (INDO) and localized molecular orbital (LMO) calculations have also been performed (29–31). The LMO bond density maps show that the bond density is strongly polarized toward the oxygen atom (30). Maximum bond density lies outside of the CCO triangle, as suggested by the bent bonds of valence–bond theory (32). The ^{1}H-nmr spectrum of ethylene oxide is consistent with these calculations (33).

The structural parameters of ethylene oxide have been determined by microwave spectroscopy (34). Bond distances in nm determined are as follows: C–C, 0.1466; C–H, 0.1085; and C–O, 0.1431. The HCH bond angle is 116.6°, and the COC angle 61.64°. Recent *ab initio* studies using SCF, MP2, and CISD have predicted bond lengths that are very close to the experimental values (35,36).

2.2. Clathrate Formation. Ethylene oxide forms a stable clathrate with water (20). It is nonstoichiometric, with 6.38 to 6.80 molecules of ethylene oxide

Table 2. **Physical Properties of Ethylene Oxide Liquid from −40 to +195.8°C**

Temperature, °C	Vapor pressure,[a] kPa[b]	Enthalpy, J/g[c]		Density,[d] kg/L	Heat capacity,[d] J/(kg·K)[c]	Surface tension,[e] mN/m (=dyn/cm)	Viscosity,[e] mPa·s (=cP)	Thermal conductivity, W/(m·K)[f]
		Liquid	Vaporization					
−40	8.35	0	628.6	0.9488	1878	34.2	0.495	0.20
−30	15.05							
−20	25.73	38.8	605.4	0.9232	1912	30.9	0.400	0.18
−10	42.00							
0	65.82	77.3	581.7	0.8969	1954	27.6	0.325	0.16
10	99.54							
20	145.8	115.3	557.3	0.8697	2008	24.3	0.26	0.15
30	207.7							
40	288.4	153.2	532.1	0.8413	2092	21.0[g]	0.23	0.14
50	391.7							
60	521.2	191.8	505.7	0.8108	2247	17.8[g]	0.20	0.14
70	681.0							
80	875.4	232.6	477.4	0.7794	2426	14.7[g]	0.17	0.14
90	1108.7							
100	1385.4	277.8	445.5	0.7443	2782	11.8[g]	0.16	0.13
120	2088	330.4	407.5	0.7052	3293[h]	8.9[g]		
140	3020	393.5	359.4	0.6609	4225[h]	6.2[g]		
160	4224	469.2	297.1	0.608		3.6[g]		
180	5741	551.2	222.5	0.533				
195.8	7191							

[a] Ref. 9.

[b] Calculated, Ref. 24.

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

[d] Refs. 18,19.

[e] Refs. 18–20.

[f] Calculated, Ref. 23.

[g] Calculated, Ref. 22.

[h] Calculated, Ref. 21.

Table 3. **Physical Properties of Ethylene Oxide Vapor from 298 to 800 K**

Temperature, K	Entropy,[a,b] J/(mol·K)[c]	Heat of formation,[b,d] kJ/mol[c]	Free energy of formation,[a,b] kJ/mol[c]	Viscosity,[e] μPa·s[f]	Thermal conductivity,[g] W/(m·K)	Heat capacity,[h] J/(mol·K)[c]
298	242.4	−52.63	−13.10			48.28
300	242.8	−52.72	−12.84	9.0	0.012	48.53
400	258.7	−56.53	1.05	13.5	0.025	61.71
500	274.0	−59.62	15.82	15.4	0.038[i]	75.44
600	288.8	−62.13	31.13	18.2	0.056[i]	86.27
700	302.8	−64.10	46.86	20.9	0.075[i]	95.31
800	316.0	−65.61	62.80		0.090[i]	102.9

[a] Ref. 21.
[b] Calculated, Ref. 24.
[c] To convert J to cal, divide by 4.184.
[d] Refs. 12,24.
[e] Refs. 18–20.
[f] μPa·s = 10^{-5} P.
[g] Refs. 18,19.
[h] Ref. 25.
[i] Calculated, Ref. 21.

to 46 molecules of water in the unit cell (37). The maximum observed melting point is 11.1°C. An x-ray structure of the clathrate revealed that it is a type I gas hydrate, with six equivalent tetrakaidecahedral (14-sided) cavities fully occupied by ethylene oxide, and two dodecahedral cavities 20–34% occupied (38).

Table 4. **Physical Properties of Aqueous Solutions of Ethylene Oxide**

Ethylene oxide				
Wt%	Mol%	Specific gravity at 10/10°C[a]	Freezing point[b], °C	Boiling point[a], °C
0	0	1.000	0.0	100
2.5	1.0	0.9986	−0.9	70
5	2.1	0.9977	−1.6 (eutectic)	58
10	4.4	0.9944	5.6	42.5
15	6.7	0.9888	8.9	38
20	9.3	0.9816	10.4	32
30	14.9	0.9658	11.1 (max)	27
40	21.4	0.9500	10.4	21
50	29.0	0.9356	9.3	19
60	38.0	0.9227	7.8	16
70	48.8	0.9111	6.0	15
80	62.1	0.9005	3.7	13
90	78.6	0.8910	0.0	12
100	100	0.8828	−111.7	10.4

[a] Ref. 9.
[b] Refs. 9 and 20.

Table 5. **Flashpoints of Ethylene Oxide/Water Solutions**[a]

Ethylene oxide concentration		Flash point, °C[b]	
Vol%	Wt%	Closed cup	Open cup
1.2	1.07	26	nd
2.0	1.80	16	nd
2.5	2.22	11	nd
3.0	2.66	5	nd
3.5	3.11	1	nd
4.0	3.53	nd	60
4.5	4.00	nd	43
5.0	4.43	nd	37
6.0	5.32	nd	18

[a] Ref. 9.

[b] nd = not determined.

Table 6. **Solubility of Gases in Ethylene Oxide, Henry's Constants, MPa**[a,b]

Temperature, °C	Nitrogen	Argon	Methane	Ethane
0	289	171	63	8.6
25	221	144	62	11.0
50	189	131	62	13.3

[a] To convert MPa to atm, divide by 0.101.

[b] Ref. 26.

Table 7. **Solubility of Ethylene Oxide in Water, mL Vapor**[a]**/mL Solvent**[b]

	Temperature, °C		
Pressure, kPa[c]	5°C	10°C	20°C
20	45	33	20
27	60	46	29
40	105	76	49
53	162	120	74
67	240	178	101
80		294	134
93			170
101			195

[a] Reduced to 0°C and 101.3 kPa[c].

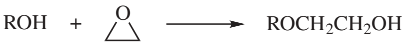
[b] Ref. 27.

[c] To convert kPa to mm Hg, multiply by 7.50.

3. Chemical Properties

Ethylene oxide is a highly reactive compound, and so is used industrially as an intermediate for many chemical products. The three-membered ring is opened in most of its reactions. These reactions are very exothermic because of the tremendous ring strain in ethylene oxide, which has been calculated (39). Reviews of ethylene oxide reactions are given in References 40 and 41.

3.1. Polymerization. The reaction of ethylene oxide with a nucleophile introduces the hydroxyethyl group:



The product of this reaction can also react with ethylene oxide; if this process is repeated many times, a polymer is formed:

Low molecular weight polymers of ethylene oxide, poly(ethylene glycol), are formed by allowing ethylene oxide to react with water or alcohols under the proper conditions (see POLYETHERS). The average molecular weight can be varied from 200 to 14,000 (32,33).

Polymers with much higher average molecular weights, from 90,000 to 4×10^6, are formed by a process of coordinate anionic polymerization (43–45). The patent literature describes numerous organometallic compounds, alkaline-earth compounds, and mixtures as polymerization catalysts. Iron oxides that accumulate in ethylene oxide storage vessels also catalyze polymerization. This leads to the formation of nonvolatile residue (NVR); no inhibitor has been found (46).

3.2. Crown Ethers. Ethylene oxide forms cyclic oligomers (crown ethers) in the presence of fluorinated Lewis acids such as boron trifluoride, phosphorus pentafluoride, or antimony pentafluoride. Hydrogen fluoride is the preferred catalyst (47). The presence of $BF^-;_4$, $PF^-;_6$, or $SbF^-;_6$ salts of alkali, alkaline earth, or transition metals directs the oligomerization to the cyclic tetramer, 1,4,7,10-tetraoxacyclododecane [294-93-9] (12-crown-4), pentamer, 1,4,7,10,13-pentaoxacyclopentadecane [33100-27-6] (15-crown-6), and hexamer, 1,4,7,10,13,16-hexaoxacyclooctadecane [17455-13-9] (18-crown-6) by a template effect. Each cation maximizes the formation of the crown ether that best encircles its ionic radius (48,49).

3.3. Other Chemical Reactions. *With Water.* Wurtz was the first to obtain ethylene glycol by heating ethylene oxide and water in a sealed tube (1). Later, it was noted that by-products, namely diethylene and triethylene glycol, were also formed in this reaction (50). This was the first synthesis of polymeric compounds of well-defined structure. Hydration is slow at ambient temperatures and neutral conditions, but is much faster with either acid or base catalysis (Table 8). The type of anion in the catalyzing acid is relatively unimportant (58) (see GLYCOLS).

With Alcohols. These reactions parallel those of ethylene oxide with water. The primary products are monoethers of ethylene glycol; secondary products are monoethers of poly(ethylene glycol) (42). Most are appreciably water-soluble.

With Organic Acids and Anhydrides. The carboxyl group of an organic acid reacts with ethylene oxide to give the corresponding ethylene glycol monoester. This product can also react with ethylene oxide to yield a poly(ethylene glycol) ester, or with another acid to produce a glycol diester. Ethylene glycol

Table 8. **Rate Constants for the Hydrolysis of Ethylene Oxide**[a]

Temperature, °C	Acidic, k_a, L/(mol·min)[b]	Neutral,[c] 10^4 k_w, min^{-1}	Basic, $10^2 k_b$, L/(mol·min)[b]
20	0.32	0.22	0.34
30	1.00	0.55	1.0
40	2.5	1.9	3.06
60		11.9	17.0
80		60.6	77

[a] Refs. 51–57.

[b] Extrapolated to zero salt concentration.

[c] Rate increases dramatically above 100°C. $k_w = 510$, 1170, and $1730 \times 10^4\ \text{min}^{-1}$ at 113, 123, and 131°C, respectively.

diesters may be obtained directly by the reaction of ethylene oxide with the acid anhydride.

With Ammonia and Amines. Ethylene oxide reacts with ammonia to form a mixture of mono-, di-, and triethanolamines. Nitrogen is a stronger nucleophile than oxygen (59). A small amount of water is essential for the reaction (60).

Complex nitrogen compounds are formed from the reaction of alkylamines with ethylene oxide (61). Thus diethylamine and ethylene oxide react to yield diethylaminoethanol. The dialkylaminoethanols can react with ethylene oxide to give amino poly(ethylene glycols):

Primary and secondary aromatic amines react with ethylene oxide to give the corresponding arylaminoethanols.

With Hydrogen Sulfide and Mercaptans. Ethylene oxide reacts with hydrogen sulfide to yield 2-mercaptoethanol and thiodiglycol (bis-2-hydroxyethyl sulfide) (62,63). Reaction conditions determine the proportions of each derivative. Three moles of ethylene oxide react with one mole of hydrogen sulfide in water to give the strong base tris(hydroxyethyl)sulfonium hydroxide, $(HOCH_2CH_2)_3S^+OH^-$;. The reaction of ethylene oxide with long-chain alkyl mercaptans yields polyoxyethylene mercaptans, some of which are nonionic surfactants (64).

p-Oxathiane and *p*-dithiane are formed from ethylene oxide and hydrogen sulfide at 200°C in the presence of an aluminum oxide catalyst (65).

With Grignard Reagents. Ethylene oxide reacts with Grignard reagents (66), RMgX, to yield the corresponding two carbon homologue, RCH_2CH_2OH (67–69).

With Acyl Halides, Hydrogen Halides, and Metallic Halides. Ethylene oxide reacts with acetyl chloride at slightly elevated temperatures in the presence of hydrogen chloride to give the acetate of ethylene chlorohydrin (70). Hydrogen halides react to form the corresponding halohydrins (71). Aqueous solutions of ethylene oxide and a metallic halide can result in the precipitation of the metal hydroxide (72,73). The halides of aluminum, chromium, iron, thorium, and zinc in dilute solution react with ethylene oxide to form sols or gels of the metal oxide hydrates and ethylene halohydrin (74).

Phosphorus oxychloride reacts with ethylene oxide in the presence of aluminum chloride to give tris-2-chloroethyl phosphate, a valuable plasticizer (75). Phosgene reacts with ethylene oxide and other alkylene oxides to form esters of chlorocarbonic acid (76) (see CARBONIC AND CARBONOCHLORIDIC ESTERS).

With Compounds Containing Active Methylene or Methine Groups. Compounds containing active $-CH_2-$ or $-CH-$ groups, such as malonic and monosubstituted malonic esters, ethyl cyanoacetate, and β-keto esters, react with ethylene oxide under basic conditions (72,77). Ethylene oxide and diethyl malonate react in the presence of sodium ethoxide to give diethyl (2-hydroxyethyl)malonate, which cyclizes to form α-carboethoxy-γ-butyrolactone.

The sodium salt of ethyl acetoacetate in ethanol at 0°C reacts with ethylene oxide to give 2-acetyl-4-butyrolactone, an intermediate for vitamin B_1 and antimalarials (75).

With Phenols. The 2-hydroxylethyl aryl ethers are prepared from the reaction of ethylene oxide with phenols at elevated temperatures and pressures (78,79). 2-Phenoxyethyl alcohol is a perfume fixative. The water-soluble alkylphenol ethers of the higher poly(ethylene glycol)s are important surface-active agents. They are made by adding ethylene oxide to the alkylphenol at ca 200°C and 200–250 kPa (>2 atm), using sodium acetate or hydroxide as a catalyst. The properties of these alkylphenol ethers can be varied over a wide range of solubility and performance characteristics by changing the alkyl chain(s) and the number of ethylene oxides added (80).

With Hydrogen Cyanide. Ethylene oxide reacts readily with hydrogen cyanide in the presence of alkaline catalysts, such as diethylamine, to give ethylene cyanohydrin. This product is easily dehydrated to give acrylonitrile in 80–90% yield:

Ethylene cyanohydrin can be hydrolyzed to acrylic acid or esterified to give the corresponding alkyl acrylates (81) (see CYANOHYDRINS).

Miscellaneous Reactions. Ethylene oxide is considered an environmental pollutant. A study has determined the half-life of ethylene oxide in the atmosphere (82,83). Autodecomposition of ethylene oxide vapor occurs at ~500°C at 101.3 kPa (1 atm) to give methane, carbon monoxide, hydrogen, and ethane (84–86).

Isomerization of ethylene oxide to acetaldehyde occurs at elevated temperatures in the presence of catalysts such as activated alumina, phosphoric acid, and metallic phosphates (75). Iron oxides also catalyze this reaction. Acetaldehyde may be found as a trace impurity in ethylene oxide.

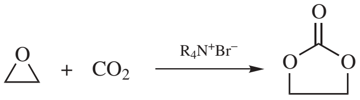
Disproportionation of ethylene oxide to ethylene and carbon dioxide also occurs at temperatures higher than about 150°C in the presence of high surface area iron oxides (87).

$$5\ C_2H_4O \longrightarrow 4\ C_2H_4 + 2\ CO_2 + H_2 + H_2O$$

Diborane reacts with ethylene oxide at −80°C to form diethoxyborane and a solid polymer containing approximately eight ethylene oxide units per molecule (88).

Potassium thiocyanate or thiourea react in aqueous solution with ethylene oxide to give ethylene sulfide (89).

Ethylene carbonate (1,3-dioxolan-2-one) is commercially prepared from ethylene oxide by the addition of carbon dioxide to ethylene oxide with either ammonium or alkali metal salts as catalysts (87):



Carbon disulfide reacts with ethylene oxide to give ethylene trithiocarbonate (90), and isocyanates yield derivatives of 2-oxazolidinone (91).

Ethylene oxide reacts with phosphonium halides to give ylides, which are used to synthesize olefins from carbonyl compounds, such as aldehydes and ketones (92).

Many other reactions of ethylene oxide are only of laboratory significance. These include nucleophilic additions of amides, alkali metal organic compounds, and pyridinyl alcohols (93), and electrophilic reactions with orthoformates, acetals, titanium tetrachloride, sulfenyl chlorides, halo-silanes, and dinitrogen tetroxide (94).

4. 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 chlorohydrin 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 chlorohydrin 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 mol%) 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. All the ethylene oxide plants that were built during the late 1990s 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 chlorohydrin and direct oxidation processes are reported in Reference 98.

4.1. 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 chlorohydrin 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 (99). 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:

$$C_2H_4 + \frac{1}{2}\ O_2 \xrightarrow{Ag} C_2H_4O$$

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

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

or by further oxidation of ethylene oxide:

$$C_2H_4O + 2\frac{1}{2}\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

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 (100). 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:

$$O_2 + 4\ Ag \longrightarrow 2\ O^{2-}_{ads} + 4\ Ag^+$$

The second is nondissociative, and is more weakly bonded:

$$O_2 + Ag \longrightarrow O^{2-}_{ads} + Ag^+$$

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 (100).

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 (100). Monoatomic chemisorbed oxygen reacts with ethylene to form carbon dioxide and water. Since $O^{2-};_{ads}$ must be removed from the silver surface before more O^{2-}_{ads} can form, the two reactions must be combined. The stoichiometry for the complete reaction is:

$$7\ C_2H_4 + 6\ O_2 \longrightarrow 6\ C_2H_4O + 2\ CO_2 + 2\ H_2O$$

This leads to a limiting ethylene selectivity of 6/7 or 85.7%, which has been exceeded, as reported in several patents (101–103).

More recent studies provided the evidence for a different theory (104). 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 (105).

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 (105).

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 (96,99,106). 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 (96,99,106–111). These tubes are filled with a silver-based catalyst ca 3–10 mm dia supported on a carrier material with a surface area usually $<1\ m^2/g$ (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

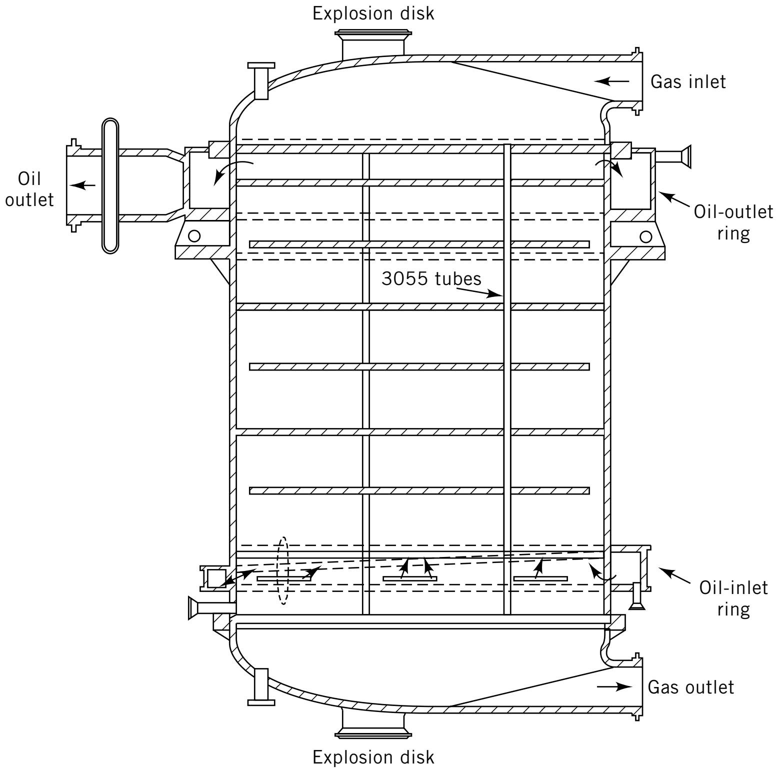


Fig. 1. Oil-cooled reactor for the oxidation of ethylene to ethylene oxide.

needs for larger facilities without using a great number of reactors (99,112). 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 (113). Later some producers had 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

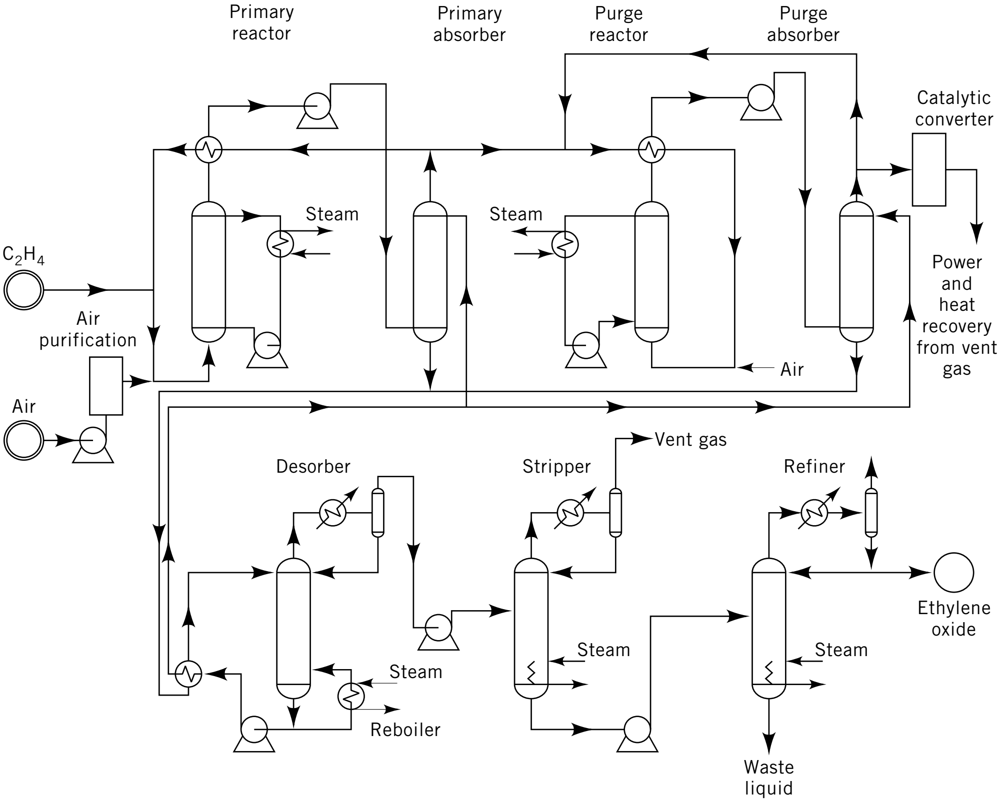


Fig. 2. Air-based direct oxidation process for ethylene oxide (96,99,106,114–116).

the packed-bed converters, and the heat of reaction is removed by circulating or boiling an organic oil on the shell side (105) (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 (96,106).

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 (104,117,118). 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 (99). The aqueous stream is removed from the base of the absorber and sent to a desorber. The unabsorbed gas from the main absorber overhead is split into two portions. The largest portion is recycled to the primary reactor after it cools the hot product gas in the shell-and-tube heat exchanger, and the circulation cycle is repeated. A much smaller fraction of the primary adsorber 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 (106). 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 (106,110). 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 (106). 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 105 and (119–122). 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 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 (122).

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 9.

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% O_2) to pure oxygen (>95 mol% O_2). 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 (96,103). 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 CO_2 must be eliminated on a continuous basis in order to control its concentration at a fixed acceptable level in the cycle. Concentrations of CO_2 much in excess of 15 mol% adversely influence catalyst activity (96,99). Therefore, in an oxygen-based system, part of the recycle gas leaving the absorber must be treated in a CO_2 removal unit before it is sent back to the main reaction cycle.

Table 9. **Ranges of Reaction System Variables in the Direct Oxidation Process for Ethylene Oxide**[a]

Variable	Air oxidation	Oxygen oxidation
ethylene, mol%	2–10	20–35
oxygen, mol%	4–8	4–8
carbon dioxide, mol%	5–10	5–10
ethane, mol%	0–1.0	0–1.0
temperature, °C	220–277	220–235
pressure, MPa[b]	1–3	2–3
space velocity[c], h^{-1}	2000–4500	2000–4500
pressure drop, kPa[d]	41–152	41–152
conversion, %	20–65	8–12
selectivity or yield (mol basis, %)	63–75	75–82

[a] Refs. 99,108, and 110.

[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.

In addition to the CO_2 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 (99). 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 (123). 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 (96,106). 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 (113). 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

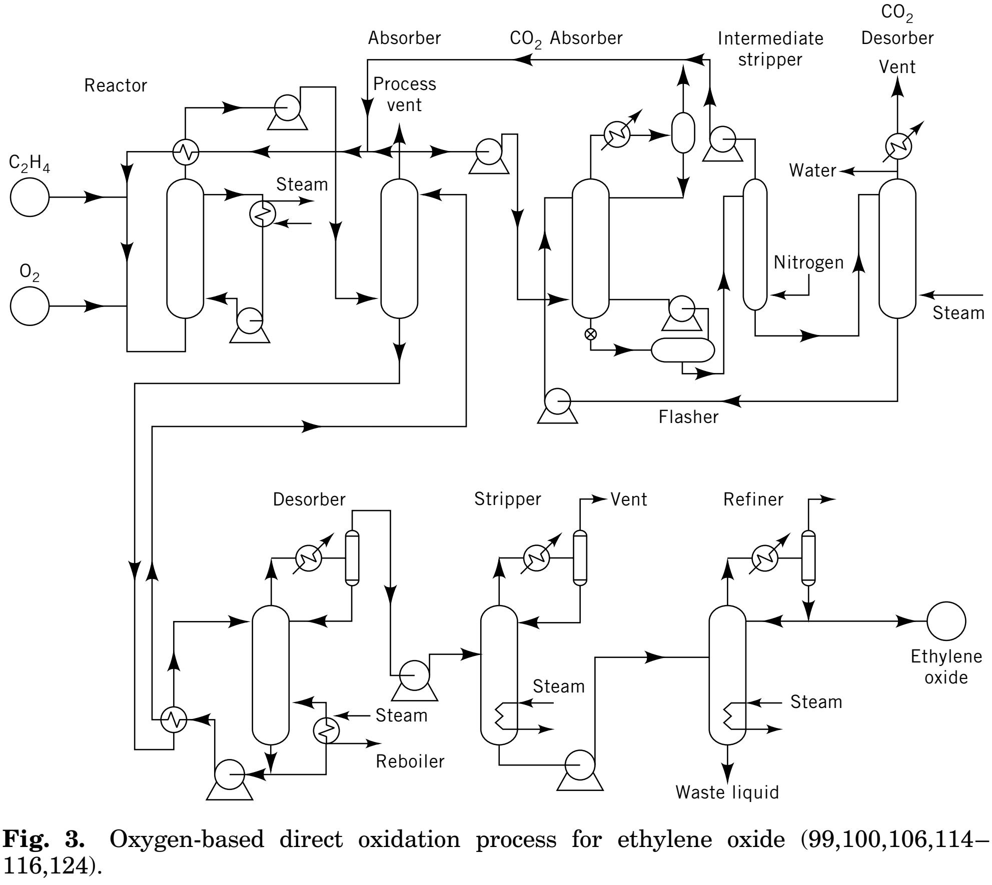


Fig. 3. Oxygen-based direct oxidation process for ethylene oxide (99,100,106,114–116,124).

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 CO_2 removal scheme illustrated is based on a patent by Shell Oil Co. (124), 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 (103,125). 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 9.

4.2. Process Technology Considerations. Innumerable 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 that increase selectivity and/or activity and improve catalyst life; and inhibitors or anticatalysts that suppress the formation of carbon dioxide and water without appreciably reducing the rate of formation of ethylene oxide (102).

Silver-containing catalysts are used exclusively in all commercial ethylene oxide units, although the catalyst composition may vary considerably (127). 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 (98,128–133). 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 (134,135); (*2*) thermal decomposition of silver salts, in particular silver oxalate, silver carbonate, or organic salts of silver (135,136); (*3*) reduction of silver salts by hydrogen, formaldehyde, hydrazine, or hydroxylamine (137,138); (*4*) electrolysis of silver salt solutions (139); and (*5*) selective removal of secondary metals from silver containing alloys (140,141). 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 (142). 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 (142–144).

A patent describes the use of a silver-alumina catalyst which has been treated to remove 25% of sulface sodium ions and replaces the removed sodium with up to 10 ppm lithium ions (126).

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 (145), it is unlikely that they are used commercially since pure silver tends to sinter at reaction temperatures with a resultant activity loss (99). For commercial operation, the preferred supports are alundum (a-alumina) and silicon carbide (126,128). 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 (146). High surface area supports (3–100 m^2/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 (147).

Silver alone on a support does not give rise to a good catalyst (148). 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 (149,150). 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 (151). A patent describe the use of elements from Group Ib and IIb (152). 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 (101–103).

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 (148). 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 (99). Important gas-phase inhibitors are ethylene dichloride, ethylene dibromide, other alkyl halides, aromatic hydrocarbons, amines, and organometallic compounds (148,153,154). 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 (99). 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 (99).

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 (155). This 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 (88). 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 gradation in the catalyst activity down the length of the reactor could result in a uniform temperature profile and improved catalyst selectivity (156). Other solutions propose improving the reactor thermal conductivity (88).

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} (107,151,157–160).

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) (107,153,160–162).

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 (163) and ethane (164). 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 (165). 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 (153). 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 (166,167). Hydrogen and carbon monoxide can lead to hot-spotting of the catalyst, and sulfur is a nonreversible poison for silver-based catalyst (117).

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 (168–170). 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 (165).

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 (171–184). Other references describe how to improve the scrubbing efficiency of water or propose alternative solvents (175,176).

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 <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 (177). In addition to modifications of conventional distillation, other technologies for removing aldehyde from ethylene oxide have been proposed, including molecular sieves and extractive distillation (178–181).

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 (88). 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 (88). 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 selection of insulation 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 (185,186). The selection of the safe operating conditions and design of effective process 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 105. The primary air emissions from the formation of ethylene oxide by direct oxidation are ethylene, ethylene oxide, carbon dioxide, and ethane. Traces of NO_x and SO_x 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 80–85 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 mostly 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 CO_2 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 (106). These result in unburned hydrocarbon and possible NO_x emissions. Also, most ethylene oxide units have flares to vent the process gas during upsets. Data are scarce, but estimates indicate that flaring of process gas occurs once to twice a year (106).

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 (106). 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 (182–184,187–189).

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 economics. 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 product 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 oxygen process also has a considerable steam requirement for carbon dioxide stripping in the CO_2 removal unit. The total compression costs for an oxygen-based process, including the air-separation unit, are slightly higher than for an air-based system (88).

Purity of the feedstocks (oxygen and ethylene) also determine the relative economics of the air- and oxygen-based processes. If the oxygen 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 (190). 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 (97). 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 (97,177). For both processes, an on-stream value of 8000 h/yr is typical (191). 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.

4.3. Other Processes.

Chlorohydrin Process. Ethylene oxide is produced from ethylene chlorohydrin by dehydrochlorination using either sodium or calcium hydroxide (88). The by-products include calcium chloride, dichloroethane, bis(2-chloroethyl) ether, and acetaldehyde. Although the chlorohydrin process appears simpler, its capital costs are higher, largely due to material of construction considerations (192).

Arsenic-Catalyzed Liquid-Phase Process. An arsenic catalyst liquid-phase process for olefin oxides were patented by Union Carbide (193). 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 Tl(III) for olefin oxidation to yield glycols, carbonyls, or epoxides is well known (194). Because the epoxidation with Tl(III) is stoichiometric to produce Tl(I), reoxidation is needed. Halcon patented processes based on such epoxidation to yield ethylene oxide (195–198). 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 (199). 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 (200). *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 (201–203). The only raw materials that are utilized in the ethylene oxide formation are ethylene, water, and electrical energy. The electrolyte is regenerated *in situ*, ie, 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 (201). The common electrolytes used are water-soluble alkali metal phosphates, borates, sulfates, or chromates at ca 22–25°C (202). 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 (204). Steady and periodic operation of a packed-bed reactor has been investigated for the production of ethylene oxide (205). 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 (206). Several additional fluid-bed processes that claim improved product yields were patented later (207–210). However, only one process, developed by Vulcan Atlantic, was reported to have been successfully demonstrated in pilot-scale equipment (211). 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 (212–214). 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 (214,215). 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 (216–219). However, no commercial production routes based on biological mechanisms have been proposed.

5. Shipment and Storage

Small shipments of ethylene oxide are made in either compressed gas cylinders up to ~0.1 m^3 (30 gal) or in 1A1 steel drums (61 gal). Very large shipments

$>40\ m^3$ (10,000–25,000 gal) are made in insulated, type 105J100W or other DOT approved tank cars. For further information on the shipping and handling of ethylene oxide, see References 9 and 220.

5.1. Storage. Carbon steel and stainless steel should be used for all equipment in ethylene oxide service. Ethylene oxide attacks most organic materials (including plastics, coatings, and elastomers); however, certain fluoroplastics are resistant and can be used in gaskets and O-rings. See Reference 9 for a list of materials that are compatible with ethylene oxide.

Storage tanks should be designed in accordance with the ASME code for unfired pressure vessels. All-welded construction is recommended. Ethylene oxide storage tanks should be electrically grounded, isolated from potential fire hazards, and equipped with pressure relief devices. New equipment should be cleaned of iron oxide and immediately purged with inert gas.

Ethylene oxide storage tanks are pressurized with inert gas to keep the vapor space in a nonexplosive region and prevent the potential for decomposition of the ethylene oxide vapor. The total pressure that should be maintained in a storage tank increases with liquid temperature, since the partial pressure of ethylene oxide will also increase. Figure 4 shows the recommended minimum storage pressures for liquid ethylene oxide under nitrogen or methane blanketing gas.

Polymerization of ethylene oxide can occur during storage, especially at elevated temperatures. Contamination with water, alkalies, acids, amines, metal oxides, or Lewis acids (such as ferric chloride and aluminum chloride) can lead to runaway polymerization reactions with a potential for failure of the storage vessel. Therefore, prolonged storage at high temperatures or contact with these chemicals must be avoided (9).

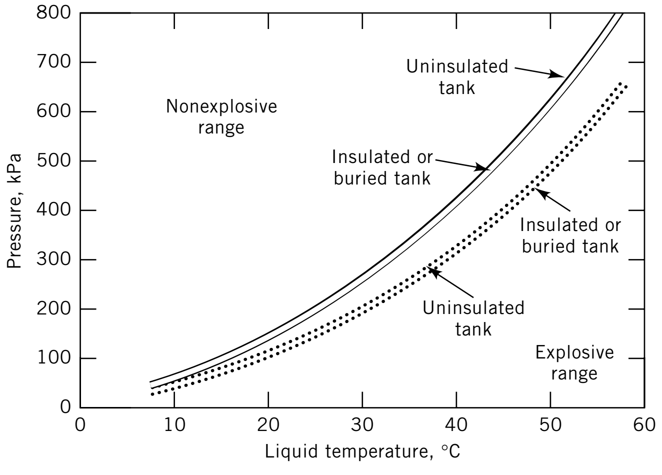


Fig. 4. Recommended safe storage pressures for liquid ethylene oxide under nitrogen (—) or methane (· · ·) blanketing (9). To convert kPa to psi, multiply by 0.145.

Table 10. **U.S. Producers of Ethylene Oxide and Their Capacities**

Producer	Capacity, $\times 10^3$ t
BASF, Geismar, La.	285
Dow, Seadrift, Tex.	422
Taft, La.	662
Plaquemine, La.	281
Eastman, Longview, Tex.	104
Equistar, Bayport, Tex.	340
Formosa, Point Comfort, Tex.	249
Huntsman, Port Neches, Tex.	544
Old World Industries, Clear Lake, Tex.	318
PD Glycol, Beaumont, Tex.	290
Shell, Geismar, La.	572
Sunoco, Brandenburg, Ky.	50
Claymont, Del.	50
Total	4167

6. Economic Aspects

In 2002, world consumption of ethylene oxide was 14.7×10^6 t, 73% of which was used to make ethylene glycols. The percentage for domestic use varied: North America, 66%; Western Europe, 43%; Japan, 68%; Other Asia, 89%; and the Middle East, 99% (221).

The second largest use of ethylene oxide is in surface active agents. Ethylene oxide is used in the production of nonionic alkylphenols ethoxylates and detergent ethoxylates. Domestic use varied by region. Consumption by percentage of total use was North America, 10%; Western Europe, 27%; Japan 20%; Other Asia, 6%; and other regions, 3% (221).

United States producer and their capacities for the year 2001 are listed in Table 10. Commercial production is by the catalytic oxidation of ethylene using oxygen (222).

Demand for 2004 is projected at 4073×10^3 t, demand in 2000 was 3807×10^3 t. Growth is expected at a rate of 1.7%/yr through 2004. Price range in December 2003 was \$0.12–0.22/kg (\$0.27–0.50/lb) tanks fob.

7. Specifications and Analytical Methods

Ethylene oxide is sold as a high purity chemical, with typical specifications shown in Table 11. This purity is so high that only impurities are specified. There is normally no assay specification. Proper sampling techniques are critical to avoid personal exposure and prevent contamination of the sample with trace levels of water. A complete review and description of analytical methods for pure ethylene oxide is given in Reference 223.

The near-ir spectrum of ethylene oxide shows two peaks between 1600–1700 nm, which are characteristic of an epoxide. Near-ir analyzers have been used for verification of ethylene oxide in railcars. Photoionization detectors are

Table 11. **Specifications for Ethylene Oxide**[a]

Property	Value
acidity	0.002 wt% max, calculated as acetic acid
aldehydes	0.003 wt% max, calculated as acetaldehyde
water	0.03 wt% max
residue	0.005 g/100 mL max
color	10 Pt–Co max
suspended matter	substantially free

[a] Ref. 9.

used for the determination of ethylene oxide in air (224–227). These analyzers are extremely sensitive (lower limits of detection are ~0.1 ppm) and can compute 8-h time-weighted averages (TWA_8).

8. Health and Safety Factors

8.1. Toxicology. An excellent review of the toxicity and health assessment of ethylene oxide has been compiled (228). Ethylene oxide (EO) can be relatively toxic as both a liquid and gas. Inhalation of ethylene oxide in high concentrations may be fatal. Estimates of lethal ethylene oxide inhalation levels in animals depend on the duration of exposure. The reported 4-h LC_{50} values for rats, mice, and dogs are 1460, 835, and 960 ppm, respectively (229). More recent information (230) indicates that the 1-h LC_{50} in rats is approximately 5000 ppm.

Inhalation exposure to high concentrations of ethylene oxide has been reported to result in respiratory system irritation and edema (231). Depending on the degree of exposure, there may be stinging of the nose and throat, coughing, and chest tightness. Also, exposure may cause lung injury and delayed onset of pulmonary edema. In long-term studies of animals exposed to less than 100 ppm of ethylene oxide and in human studies, no evidence of injury has been reported for the cardiovascular system, liver, or kidney. There is some evidence that occupational exposure to high levels of ethylene oxide can result in cataracts (232). Neurological effects have also been reported in association with recurrent human (233) and animal (234) inhalation exposures to ethylene oxide. Again, depending on the degree of exposure, headache, nausea, vomiting, diarrhea, dizziness, loss of coordination, convulsion, or coma may occur. The onset of illness is rapid in severe exposures, but may be delayed after moderate exposure. In the reports of human peripheral neurotoxic effects or central nervous system toxicity, most cases have shown a marked improvement on removal from further exposure.

Ethylene oxide has been shown to produce mutagenic and cytogenic effects in a variety of test systems (235). An increased frequency of chromosomal aberrations in peripheral lymphocytes of monkey exposed to ethylene oxide for 104 weeks has been reported (236). In mice, it is an effective inducer of chromosome breaks leading to dominant-lethal mutations. In addition, ethylene oxide has been shown to induce heritable effects in the heritable translocation test conducted in mice exposed to ethylene oxide by inhalation (237,238). In this study, male mice were exposed to ethylene oxide ranging from 165 to 300 ppm for 6 h per day 5 or 7 days/week for 8.5 weeks. Ethylene oxide has also been shown to bind to proteins (239) as well as to DNA (240). Several studies on ethylene oxide-exposed workers have demonstrated an increased incidence of chromosomal aberrations and sister chromatid exchanges; the relevance of such effects to human health evaluation is currently uncertain.

In an animal study of rats exposed by inhalation to ethylene oxide at 10, 33, or 100 ppm for approximately two years (241), and in a separate chronic rat study in which rats were exposed to 50 or 100 ppm of ethylene oxide (236), increased incidences of mononuclear cell leukemia, peritoneal mesothelioma, and various brain tumors have been reported. In an NTP (242) two-year inhalation study of mice at 50 and 100 ppm, alveolar/bronchiolar carcinomas and adenomas, papillary cystadenomas of the harderian gland, and malignant lymphomas, uterine adenocarcinomas, and mammary gland tumors were increased in one or both exposure groups.

When the data as a whole are reviewed for studies on humans exposed to ethylene oxide, no conclusion can be made that there is an increase in mortality associated with those exposed to ethylene oxide. Two Swedish studies (243,244) indicated an increase in leukemia for workers exposed to multiple chemicals including ethylene oxide; however, in a recent larger Swedish study (245) of workers exposed to only ethylene oxide, there was no association of any type of cancer increase for these workers. In a recent study sponsored by NIOSH, there was no significant increase in mortality observed for cancer when all types are combined or for certain individual types of cancer, even for those people who worked the longest and were observed the longest. However, a statistically significant increase in mortality from certain types of lymphoma was observed for male workers. This is contrary to the results observed for female workers. In addition, four other cohort studies of ethylene oxide-exposed workers have been published (246–249), but no unequivocal increase in the risk of cancer was observed.

Developmental toxicity inhalation tests have been conducted using rats or rabbits (250,251). No teratogenic effects were observed. The only developmental effect noted was decreased fetal weights and delayed ossification. In a one-generation inhalation study (252) at the highest concentration tested (100 ppm), there were signs of embryo- or fetotoxicity, as demonstrated by a decrease in the number of implantation sites and a decrease in litter size. Dominant lethal mutagenic effects in rodents have also been reported at high vapor concentrations (253,254). Testicular atrophy in guinea pigs and slight degeneration of seminiferous tubules in rats exposed to high vapor concentrations of ethylene oxide has been observed (234). Data in humans are limited. In an epidemiologic study (255), the spontaneous abortion rates in ethylene oxide sterilizer hospital personnel were reported to be increased; however, because of a number of problems with this study, both in design and analysis, the results are difficult to interpret at best (228).

Dermal exposure information has been collected from case reports of industrial accidents. Concentrated ethylene oxide evaporates rapidly from the skin and produces a freezing effect, often compared to frostbite, leaving burns ranging from first to third degree severity (256,257). A 50% aqueous solution of ethylene oxide is the most irritating combination. The onset of the skin burn can be delayed. Skin sensitization in ethylene oxide plant workers who were challenged with a single dermal application of ethylene oxide was not noted (258). However, some evidence has been reported of contact dermatitis in a small proportion of exposed workers (259,260). Skin sensitization studies in guinea pigs are negative (261).

Swallowing ethylene oxide is a highly unlikely route of exposure. However, harmful effects, including coma, death, and severe irritation and ulceration of the mouth and throat, could occur.

OSHA PEL; TWA = 1 ppm and listed as a cancer hazard, ACGIH (TLV) = 1 ppm and is listed as a suspected human carcinogen (262).

8.2. Explosibility and Fire Control. As in the case of many other reactive chemicals, the fire and explosion hazards of ethylene oxide are system-dependent. Each system should be evaluated for its particular hazards including start-up, shut-down, and failure modes. Storage of more than a threshold quantity of 5000 lb (~2300 kg) of the material makes ethylene oxide subject to the provisions of OSHA 29 CFR 1910 for “Highly Hazardous Chemicals.” Table 12 summarizes relevant fire and explosion data for ethylene oxide, which are at standard temperature and pressure (STP) conditions except where otherwise noted.

8.3. Liquid Hazards. Pure liquid ethylene oxide will deflagrate given sufficient initiating energy either at or below the surface, and a propagating flame may be produced (263,264). This requires certain minimum temperatures and pressures sensitive to the mode of initiation and system geometry. Under fire exposure conditions, an ethylene oxide pipeline may undergo internal decomposition either by direct initiation of the liquid, or by formation and subsequent decomposition of a vapor pocket (185).

Liquid mists of ethylene oxide will decompose explosively in the same manner as the vapor. Burning rate increases with decreased droplet size. While the deflagration pressure ratio for ethylene oxide vapor is about 11 or less, liquid mist decomposition can give much greater pressures and very fast rates of pressure rise (185).

Liquid ethylene oxide under adiabatic conditions requires about 200°C before a self-heating rate of 0.02°C/min is observed (185,186). However, in the presence of contaminants such as acids and bases, or reactants possessing a labile hydrogen atom, the self-heating temperature can be much lower (185). In large containers, runaway reaction can occur from ambient temperature, and destructive explosions may occur (265,266).

Ethylene oxide is an electrically conductive liquid that does not accumulate static electricity in grounded equipment. Static electricity can, however, accumulate in liquid mist produced by splashing and spraying. Although the vapor alone has a large minimum ignition energy, mixtures with oxidants such as air can be very sensitive to ignition (185).

8.4. Vapor Hazards. Ethylene oxide vapor can decompose explosively and propagate a decomposition flame when its pressure is greater than about 300 mm Hg (depending on temperature). To prevent decomposition, dilution using an inert gas (N_2 or CO_2) or an extinguishant such as a halocarbon have

Table 12. **Fire and Explosion Hazard Evaluation Data**

Property	Value
Liquid properties	
electrical conductivity (−25°C), pS/m	4×10^6
reaction threshold temperature (ARC, 0.02°C/min, $\phi = 1$), °C	$\sim$200
Vapor properties	
standard heat of formation, kJ/mol[a]	−52.63
heat of decomposition (max), kJ/mol[a]	−134.3
minimum decomposition pressure, kPa[b]	40
decomposition flame temperature (P constant), K	1277
decomposition pressure ratio (V constant)	$\sim$11.0
autodecomposition temperature, K	$\sim$773
fundamental burning velocity, m/s	2.7×10^{-2}
minimum ignition energy, J[a]	$\sim$1
heat capacity, C_p, J/(mol·K)[a]	48.28
thermal conductivity, W/(mol·K)	0.124
Properties of vapor–air mixtures	
lower flammable limit, mol%	3.0
upper flammable limit, mol%	100
deflagration K_G index[c] J, (MPa·m)/s[d]	18.8⟶24.6
deflagration $P_{\max}$ index[c], kPa	968⟶975
minimum deflagration pressure ($\sim$5 – 60 mol%), kPa[b]	1.3–2.6
stoichiometric composition, mol %	7.72
detonable range, mol%	5–30
recommended TNT efficiency, %	10
low heat of combustion, kJ/mol[a]	1217
high heat of combustion, kJ/mol[a]	1305
theoretical flame temperature (P constant), K	2402
theoretical deflagration pressure ratio (V constant)	9.91
autoignition temperature, K	718
fundamental burning velocity, m/s	1.08
minimum ignition energy (10.4 mol %), J[a]	6×10^{-5}

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

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

[c] (20⟶1000 – L spheres).

[d] $1\text{bar} = 10^2$ kPa $= 10^{-1}$ MPa.

been used. The amount of dilution required depends on temperature, pressure, and the anticipated ignition source (267). It is found that considerably more inert component is required for long duration ignition such as by a flame than would be needed for a short duration spark or fused wire igniter (268).

Similarly, the minimum ignition energy of the vapor is found to be substantially less using inductance sparks of long duration than with capacitance sparks (268). This behavior is typical of many decomposition flames and some slow-burning gases in air. Ignition sources of high power tend to distort the flame kernel, and the energy cannot be absorbed as efficiently as from a longer- duration ignition source of optimized characteristics (269).

Safe dilution requirements can be given for the gas phase in a flammability diagram or equation (267,270). Alternatively, safe vapor dilution can be given in terms of the liquid storage conditions where allowance can be made for solubility of the inert gas in liquid ethylene oxide (270).

As an alternative to inert operation, either the enclosure can be designed to withstand the overpressure due to a decomposition, or the enclosure can be fitted with a deflagration suppression system (268). Inert operation is usually preferred. To prevent a decomposition flame propagating into an enclosure, special flame arrestors comprising tube bundles might be considered (185). It is essential that the design be tested under worst-case practical conditions, and anticipates "burn through" should a flame stabilize at the end of the arrestor. As the arrestor heats, its ability to prevent flame propagation may be compromised. This situation may be detected by temperature sensors, and appropriate action taken to remove the flame.

At a sufficient temperature, EO vapor will autodecompose. The minimum autodecomposition temperature decreases with increased volume and pressure (185,186). The vapor is susceptible to local catalysis by certain high surface area metal oxides such as γ-Fe_2O_3 and γ-FeO(OH). The catalyst may cause rapid local heating and vapor ignition under near-adiabatic conditions. The most rapid rate of self-heating occurs when conditions promote EO disproportionation rather than isomerization or polymerization. The catalysts may accumulate on polyethylene oxide or other polymers in a system, and may have migrated considerable distances from the original metal oxide source. These polymers may also trap significant quantities of EO, which serve as fuel for propagating decomposition in proximity to the catalyst.

8.5. Hazards of Mixtures with Air.

Pools of liquid ethylene oxide will continue to burn until diluted with at least 22 parts of water by volume. This must be increased to about 100 parts water if the vapor is confined, such as in a sewer.

Mixtures of ethylene oxide with air are far easier to ignite and burn much faster than the pure vapor. Flames may propagate at low pressures, 1.3–2.6 kPa (10–20 mm Hg), over a wide range of compositions. The burning velocity (or K_G index) is much larger than that of propane, and under the provisions of NFPA 68 (271) there is no design basis for venting an optimum ethylene oxide deflagration in weak enclosures such as buildings. In the open air, partial confinement of vapor clouds may cause significant blast overpressures (185). A TNT equivalence of 10% has been suggested (272).

When ethylene oxide vapor or liquid leaks into porous refractory insulation such as mineral wool or calcium silicate, it reacts with water contained in the insulation forming low molecular weight poly(ethylene glycol)s. Whereas ethylene oxide is volatile, the glycols can accumulate and self-heat in the presence of air. Runaway self-heating requires temperatures above ~60°C and typically ~80°C (186). The event may lead to a fire in the insulation that might overheat small diameter lines causing internal decomposition. To prevent this, cellular glass insulation may be used since it is nonporous and cannot accumulate glycols (186).

Catalysts such as iron oxides cause isomerization of the ethylene oxide to acetaldehyde with the evolution of heat. The acetaldehyde has a much lower autoignition temperature in air than does ethylene oxide, and the two effects may lead to hot-spot ignition (185,186).

9. Uses

The largest use of ethylene oxide is in the production of ethylene glycols. Its second largest use is in the production of surface active agents incldluing nonionic alkylphenol ethoxylates and detergent alcohol ethoxylates. Ethanolamines and glycol ethers are also important derivatives.

Ethylene oxide is an excellent fumigant and sterilizing agent (226). Ethylene oxide is used as an antimicrobial pesticide to fumigate spices and to sterilize medical devices, such as sutures, bandages, catheters, endoscopes, and cardiac pacemakers. Ethylene oxide has been used as a fumigant for corrosion promoting microbes, particularly in fire protection sprinkler systems (273). Over half the medical devices made in the United States are sterilized using ethylene oxide; every hospital performing surgery has at least one ethylene oxide sterilizer. Ethylene oxide gas sterilants permit convenient sterilization of delicate instruments and supplies made of almost any material. Ethylene oxide readily penetrates deep pores and narrow crevices, and passes through wrappings of most polymers, paper, and cloth. The ethylene oxide sterilization process requires relatively low temperatures and pressures, and does not damage the materials or packaging being sterilized.

Ethylene oxide sterilant gases are supplied as liquified compressed gases, either pure or as a mixture with a flame retardant. When supplied as a pure gas, the ethylene oxide is shipped in special insulated containers. For safety reasons, nitrogen gas is added to the vapor phase up to a total pressure of 345 kPa (50 psig) at 21°C. When used in a sterilizing chamber, the flammability of ethylene oxide is usually controlled by purging the sterilization chamber with nitrogen gas at the beginning and the end of the sterilization process. In some cases, the effects of a potential deflagration are moderated by operating under great vacuum or, in the case of small hospital sterilizers, by using very small quantities of ethylene oxide. During 1960–1990, the most common flame retardants used for ethylene oxide mixtures were CO_2 and dichlorodifluoromethane (CFC-12). CFC-12 causes depletion of stratospheric ozone and can no longer be used. Nonflammable sterilizing gas compositions of ethylene oxide, pentafluoroethane, and heptafluoropropane have been described. These gas compositions are environmentally acceptable and are more efficient to use than convetional sterilant compositions (274).

Ethylene oxide has been studied for use as a rocket fuel (275) and as a component in munitions (276). It has been reported to be used as a fuel in FAE (fuel air explosive) bombs (277).

10. Derivatives

10.1. Ethylene Glycol.

Well over 73% of the ethylene oxide produced worldwide is used in the manufacture of ethylene glycols. Ethylene glycol [107-21-1]is used in two significant applications: as a raw material for poly(ethylene terephthalate) for use in polyester fiber, film, and containers, and as an automotive antifreeze. Other important uses for ethylene glycol are in heat-transfer fluids, deicing fluids (aircraft, runway, and coal), latex paints (to provide freeze–thaw stability), natural gas dehydration, and many others (278) (see ANTIFREEZES AND DEICING FLUIDS; GLYCOLS).

Di-, tri-, and tetraethylene glycols are coproducts of ethylene glycol. Diethylene glycol is used as an intermediate for polyester resins, polyurethanes, and for tri- and tetraethylene glycols (by reaction with ethylene oxide). It is used for the drying of natural gas, as a component in antifreeze and deicers, and a variety of other applications. Triethylene glycol is primarily used as a liquid drying agent for natural gas. It is also used as a humectant and a solvent, and in the manufacture of plasticizers and unsaturated polyester resins. Tetraethylene glycol has an important value in the extraction of aromatic hydrocarbons from nonaromatic hydrocarbons (279) (see GLYCOLS).

10.2. Nonionic Surface-Active Agents. Approximately 11% of the ethylene oxide consumed in the United States is used in the manufacture of nonionic surfactants. These are derived by addition of ethylene oxide to fatty alcohols, alkylphenols (qv), tall oil, alkyl mercaptans, and various polyols such as poly(propylene glycol), sorbitol, mannitol, and cellulose. They are used in household detergent formulations, industrial surfactant applications, in emulsion polymerization, textiles, paper manufacturing and recycling, and for many other applications (280).

10.3. Ethanolamines. These are produced by the reaction of ethylene oxide and ammonia (see ALKANOLAMINES). Approximately one-third of the production is used in detergents. Other applications include natural gas purification, cosmetics, metalworking, textiles, and chemical intermediates (281).

10.4. Glycol Ethers. These are made by reaction of ethylene oxide with various alcohols. They are used for solvents, detergents, brake fluids, and jet fuel deicing.

10.5. Poly(ethylene Glycol)s. These relatively low molecular weight ethylene oxide polymers are made by reaction of ethylene oxide with water or glycols. Molecular weights range from 200 to 14,000 (42). Poly(ethylene glycol)s of molecular weight 200–600 are water-white liquids. The higher molecular weight polymers range in consistency from a soft white grease-like petrolatum to hard waxy solids. They are used in cosmetics, ointments, pharmaceuticals, and as a food additive. They are also used as water-soluble lubricants for molds, textile processing, and ceramics, and as a wood preservative (43,280).

10.6. Poly(ethylene Oxide). High molecular weight ethylene oxide polymers are made by coordinative anionic polymerization (43,280) on alkyls or alkoxides of Group IIA or IIIA metals. Commercially available materials are available in a molecular weight range of 90,000–3,800,000. These polymers have diverse applications. A very dilute (<100 ppm) solution in water greatly reduces viscous drag. Agriculturally, it is used to encapsulate seeds at regular spacings in a tape leading to regular plant spacing and elimination of thinning. It is also used for warp sizing, coagulation, and as a water-soluble packing material (43,280) (see POLYETHERS). Flushable fiber compositions comprising modified polypropylene and modified poly(ethylene oxide) for use in personal care products have been described in the patent literature (282).

10.7. Other Derivatives. Ethylene carbonate, made from the reaction of ethylene oxide and carbon dioxide, is used as a solvent. Acrylonitrile (qv) can be made from ethylene oxide via ethylene cyanohydrin; however, this route has been entirely supplanted by more economic processes. Urethane intermediates can be produced using both ethylene oxide and propylene oxide in their structures (280) (see URETHANE POLYMERS).

BIBLIOGRAPHY

"Ethylene Oxide" in *ECT* 1st ed., Vol. 5, pp. 906–925, by R. S. Aries, Consulting Chemical Engineer, and H. Schneider, R. S. Aries & Associates; in *ECT* 2nd ed., Vol. 8, pp. 523–558, by H. C. Schultze, Union Carbide Corp.; in *ECT* 3rd ed., Vol. 9, pp. 432–471, by J. N. Cawse, J. P. Henry, M. W. Swartzlander, and P. H. Wadia, Union Carbide Corp.; in *ECT* 4th ed., Vol. 9, pp. 915–959, by J. P. Dever, K. F. George, W. C. Hoffman, and H. Soo, Union Carbide Corporation; "Ethylene Oxide" in *ECT* (online), posting date: December 4, 2000, by J. P. Dever, K. F. George, W. C. Hoffman, H. Soo, Union Carbide Corporation.

CITED PUBLICATIONS

1. A. Wurtz, *Ann.* **110**, 125 (1859); *Ann. Chem. Phys.* **55**, 433 (1859).
2. A. Wurtz, *Ann. Chim. Phys.* **69**, 335 (1863).
3. W. Bone and R. Wheeler, *J. Chem. Soc.* **85**, 1637 (1904).
4. L. Reyerson and L. J. Swearingen, *J. Am. Chem. Soc.* **50**, 2872 (1928).
5. R. Willstater and M. Bommer, *Ann.* **422**, 136 (1921).
6. Ger. Pat. 168,291; Fr. Pat. 360,785 (1905–1906); Brit. Pat. 21,941 (Oct. 4, 1906), J. Walter.
7. Pat 729,952 (Mar. 27, 1931), and additions 41,254 (July 4, 1931), 41,724 (Sept. 10, 1931), 41,484 (Sept. 25, 1931), 41,810, 41,811 (Apr., 1933); Fr. Pat. 739,562 (Oct. 3, 1931), T. E. Lefort (to Societe Francaise de Catalyse Generalisee).
8. Brit. Pats. 402,438 and 402,749 (Dec. 4, 1933), T. E. Lefort (to to Societe Francaise de Catalyse Generalisee); U.S. Pat. 1,998,878 (Apr. 23, 1935), T. E. Lefort (to Carbide and Carbon Chemicals Corp.); reissued as U.S. Pats. 20,370 (May 18, 1937), 22,241 (Dec. 29, 1942).
9. *Ethylene Oxide, Brochure F-ICD23*, Union Carbide Corp., Danbury, Conn., 1993.
10. C. J. Walters and J. M. Smith, *Chem. Eng. Prog.* **48**, 337 (1952).
11. D. W. Davidson and G. J. Wilson, *Can. J. Chem.* **41**, 1424–1434 (1963).
12. B. J. Zwolinski and R. Wilhoit in D. E. Gray, ed., *American Institute of Physics Handbook*, 3rd ed., McGraw-Hill Book Co., Inc., New York, 1972, pp. 316–342.
13. W. F. Giauque and J. Gordon, *J. Am. Chem. Soc.* **71**, 2176 (1949).
14. F. S. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances*, Reinhold Publishing Corp., New York, 1936, p. 46.
15. F. H. Field and J. L. Franklin, *Electron Impact Phenomena*, Academic Press, Inc., New York, 1957.
16. R. Rein and co-workers, *J. Chem. Phys.* **45**, 4743 (1966).
17. G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.* **8**, 618 (1940).
18. R. W. Gallant, *Hydrocarbon Process.* **46**(3), 143 (1967).
19. C. L. Yaws, *Physical Properties*, McGraw-Hill Book Co., Inc., New York, 1977, pp. 167–176.
20. O. Maass and E. H. Boomer, *J. Am. Chem. Soc.* **44**, 1709 (1922).
21. Ref. 19, pp. 8, 85, and 175.

22. Ref. 19, pp. 135 and 175.
23. Ref. 19, pp. 145 and 175.
24. D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, 1969, p. 419.
25. K. A. Kobe and R. E. Pennington, *Pet. Refiner* **29**(9), 135 (1950).
26. J. D. Olson, *J. Chem. Eng. Data* **22**, 326 (1977).
27. A. Seidell, *Solubilities of Organic Compounds*, D. van Nostrand Co., Inc., New York, 1941.
28. R. E. Parker and N. S. Issacs, *Chem. Rev.* **59**, 737 (1959).
29. R. Bonacorsi, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* **52**, 5270 (1970).
30. G. Franking and co-workers, *Bull. Chem. Soc. Jpn.* **48**, 2769 (1975).
31. H. Fujimoto and co-workers, *Bull. Chem. Soc. Jpn.* **49**, 1508 (1976).
32. C. A. Coulson, *Valence*, Oxford University Press, New York, 1976, 215–216.
33. L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.* **75**, 4567 (1953).
34. C. Hirose, *Bull. Chem. Soc. Jpn.* **47**, 1311 (1974).
35. A. Komornicki, F. Pauzat, and Y. Ellinger, *J. Phys. Chem.* **87**, 3847 (1983).
36. E. D. Simandiras and co-workers, *J. Am. Chem. Soc.* **110**, 1388 (1988).
37. D. N. Glew and N. S. Rath, *J. Chem. Phys.* **44**, 1710 (1965).
38. R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.* **42**, 2725 (1965).
39. R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Standards* **48**, 206 (1952).
40. A. Rosowsky in A. Weissberger, ed., *Heterocyclic Compounds*, Vol. 19, pt. 1, Wiley-Interscience, New York, 1964.
41. M. S. Malinovskii, *Epoxides and Their Derivatives*, Daniel Davey & Co., Inc., New York, 1965 (especially for references from Eastern European countries).
42. *Glycols, Brochure F-41515B*, Union Carbide, New York, 1978.
43. F. E. Bailey and J. V. Koleske, *Poly(ethylene Oxide)*, Academic Press, Inc., New York, 1976.
44. J. Farakawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Wiley-Interscience, New York, 1963.
45. K. C. Frisch and S. L. Reegen, *Ring Opening Polymerization*, Marcel Dekker, Inc., New York, 1969.
46. T. H. Baize, *Ind. Eng. Chem.* **53**, 903 (1961).
47. J. Dale, G. Borgen, and K. Daasvatn, *Acta Chem. Scand.* **B28**(3), 378 (1974); U.S. Pat. 3,928,386 (Dec. 23, 1975), J. Dale, G. Borgen, and K. Daasvatn.
48. J. Dale and K. Daasvatn, *J. Chem. Soc., Chem. Commun.*, 295 (1976); U.S. Pat. 3,997,563 (Dec. 14, 1976), J. Dale and K. Daasvatn.
49. R. M. Izatt and co-workers, *Chem. Rev.* **85**, 271 (1985).
50. A. Lourenco, *Ann. Chem. Phys.* **67**, 275 (1863).
51. J. N. Bronsted, M. Kilpatrick, and M. Kilpatrick, *J. Am. Chem. Soc.* **51**, 428 (1929).
52. J. Koskihallio and E. Whalley, *Trans. Faraday Soc.* **55**, 815 (1959).
53. F. A. Long, J. G. Pritchard, and F. E. Stafford, *J. Am. Chem. Soc.* **79**, 2362 (1957).
54. A. M. Eastham and G. A. Latremouille, *Can. J. Chem.* **30**, 169 (1952).
55. P. O. I. Virtanen, *Suomen Kemistilehti* **34B**, 62 (1961).
56. H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.* **44**, 905 (1948).
57. J. Koskihallio and E. Whalley, *Can. J. Chem.* **37**, 783 (1959).
58. L. Smith, G. Wode, and I. Widhe, *Z. Physik. Chem.* **130**, 154 (1927).
59. R. F. Goldstein, *The Petroleum Chemicals Industry*, John Wiley & Sons, Inc., New York, 1958, p. 352.
60. L. Knorr, *Chem. Ber.* **32**, 729 (1899).
61. Ref. 56, pp. 354–355.
62. Ref. 37, pp. 327–328.
63. C. C. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 278 (1949).

64. H. Lemaire in M. J. Schick, ed., *Nonionic Surfactants*, Marcel Dekker, Inc., New York, 1966, pp. 177–179.
65. Ref. 37, p. 330.
66. Ref. 37, pp. 386–417.
67. N. G. Gaylord and E. J. Becker, *Chem. Rev.* **49**, 413 (1951).
68. M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954.
69. V. Grignard, *Bull. Soc. Chim. Fr.* **29**, 944 (1903); *Compt. Rend.* **136**, 1260 (1903).
70. Ref. 37, pp. 350, 432–440.
71. E. L. Gustus and P. G. Stevens, *J. Am. Chem. Soc.* **55**, 378 (1933).
72. W. Deckert, *Angew. Chem.* **45**, 559 (1932).
73. O. F. Lubatti, *J. Soc. Chem. Ind. (London)* **54**, 424T (1935).
74. W. Zeise, *Chem. Ber.* **66B**, 1965 (1933).
75. Ref. 56, p. 358.
76. M. S. Malinovski and N. D. Medjanzema, *J. Gen. Chem. USSR* **23**, 221 (1953).
77. Ref. 37, pp. 418–428.
78. Ref. 37, pp. 308–315.
79. Ref. 56, pp. 348–352.
80. C. R. Enyeart in Ref. 61, pp. 80–81.
81. Ref. 56, p. 357.
82. S. Jaffe in H. M. England and W. T. Beery, eds. *Proceedings, Second International Clean Air Congress*, Academic Press, Inc., New York, 1971, pp. 316–324.
83. H. Güsten, L. Klasinc, and D. Maric, *J. Atmos. Chem.* **2**(1), 83–93 (1984).
84. S. A. Greene and L. J. Gordon, *Jet Propul.*, 798 (July, 1957).
85. F. A. Burden and J. H. Burgoyne, *Nature* **163**, 723 (1949); *Proc. Roy. Soc. London Ser. A* **199**, 328 (1949).
86. G. B. Shah, E. P. Chock, and R. G. Rinker, *Ind. Eng. Chem. Fundam.* **10**(1), 13 (1971).
87. Union Carbide Chemicals and Plastics Company, Inc., *Ethylene Oxide Producer's Technology Conference, Executive Summary*, Atlanta, Ga., Jan. 22, 1992.
88. F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 567–576, 2755 (1950).
89. R. Landau and R. E. Lidov in S. A. Miller, ed., *Ethylene: Its Industrial Derivatives*, Ernest Benn Ltd., London, 1969, p. 613.
90. Ref. 37, pp. 453–454.
91. Ref. 37, pp. 343–344.
92. J. Buddrus, *Chem. Ber.* **107**, 2050–2061 (1974).
93. Ref. 86, pp. 567–576.
94. Ref. 86, pp. 576–580.
95. J. F. Norris, *J. Ind. Eng. Chem.* **11**, 817 (1919).
96. I. Kiguchi, T. Kumazawa, and T. Nakai, *Hydrocarbon Process.* **55**(3), 69 (1976).
97. B. J. Ozero and J. V. Procelli, *Hydrocarbon Process.* **63**(3), 55 (1984).
98. G. O. Curme and F. Johnston, *Glycols, ACS Monograph No. 114*, Reinhold Publishing Corp., New York, 1952, Chapts. 2 and 5.
99. Ref. 88, pp. 521–563.
100. W. M. H. Sachtler, C. Backy, and R. A. Van Santen, *Catalysts Review-Sci. Eng.* **23**(182), 127–149 (1981).
101. Eur. Pat. Appl. 176,253 A1 (Apr. 2, 1986), (to ICI).
102. Eur. Pat. Appl. 266,852 A1 (May 11, 1988), (to Shell Oil Co.).
103. Eur. Pat. Appl. 266015 A1 (May 4, 1988) (to Shell Oil Co.).
104. P. B. Grant and R. M. Lambert, *J. Catal.* **92**, 364–375 (1985).
105. G. H. Twigg, *Trans. Faraday Soc.* **42**, 284, and 657 (1946); *Proc. Roy. Soc. (London) Ser. A* **188**, 92 (1946).

106. M. Gans and B. J. Ozero, *Hydrocarbon Process.* **55**(3), 73 (1976); B. DeMaglie, *Hydrocarbon Process.* **55**(3), 78 (1976); D. E. Field and co-workers, *Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry*, Vol. 6, EPA Report No. EPA-450/3-73-006-f, Environmental Protection Agency, Washington, D.C., June, 1975.
107. Ger. Pat. 2,300,512 (July 26, 1973), R. P. Nielsen and co-workers (to Shell International Research); Ger. Pat. 2,448,449 (Apr. 30, 1975), P. A. Kilty (to Shell International Research).
108. Belg. Pat. 638,319 (Oct. 8, 1964), R. S. Davis (to Halcon International).
109. Dutch Pat. Appl. 6,502,927 (Sept. 23, 1964), (to The Dow Chemical Co.).
110. Brit. Pat. 1,075,454 (July 12, 1967), (to Halcon International).
111. U.S. Pat. 4,012,425 (Mar. 15, 1977), R. P. Nielsen and J. H. LaRochelle (to Shell Oil Co.).
112. K. R. Barker and J. C. Zomerdijk, *Eur. Chem. News Chemscope* **24**, 28 (Oct. 12, 1973).
113. R. Landau and co-workers, *Chem. Eng. Prog.* **64**(3), 17 (1968).
114. C. H. Chilton, *Chem. Eng.* **65**(15), 100 (1958).
115. *Hydrocarbon Process.* **54**(11), 145 (1975).
116. *Hydrocarbon Process.* **52**(11), 129 (1973).
117. P. W. Sherwood, *Chim. Ind. (Paris)* **70**, 1078 (1953); *Pet. Process.* **9**, 1592 (1954).
118. W. E. Vaughan and R. M. Goepp, Jr., *U.S. Dept. Comm. Off. Tech. Serv.*, PB Rep. 79607 (1947); FIAT Final Report 875, May 2, 1947.
119. U.S. Pat. 3,552,122 (Jan. 5, 1971), M. Parmegiani, S. D. Milanese, and O. Bellofatto (to Snam Progetti).
120. R. J. Ruff, *Chem. Eng. Prog.* **53**(8), 377 (1957).
121. U.S. Pat. 3,603,085 (Sept. 7, 1971), M. Parmegiani and S. D. Milanese (to Snam Progetti).
122. N. Y. Step, O. N. Dyment, and B. B. Chesnokov, *Khim. Prom. (Moscow)* **48**, 645 (1972).
123. U.S. Pat. 3,083,213 (Mar. 26, 1963), M. L. Courter (to Shell Oil Co.).
124. U.S. Pat. 3,878,126 (Apr. 15, 1975), E. G. Foster (to Shell Oil Co.).
125. U.S. Pat. 3,119,837 (Jan. 28, 1964), H. A. Kingsley and F. A. Cleland (to Shell Oil Co.).
126. U.S. Pat. Appl. 20030191019 (Oct. 9, 2003), N. Rizkalla, E. Bornn, and C. W. Zulauf.
127. E. T. McBee, H. B. Haas, and P. A. Wiseman, *Ind. Eng. Chem.* **37**, 432 (1945).
128. L. Y. Margolis and O. M. Todes, *Isv. Akad. Nauk SSSR Otd. Khim. Nauk*, 52, (1952); *Chem. Abstr.* **46**, 5413 (1952).
129. P. H. Emmett, *Catalysis*, Vol. 7, Reinhold Publishing Corp., New York, 1960, p. 246.
130. L. Y. Margolis, *Usp. Khim.* **28**, 615 (1959).
131. Brit. Pat. 1,329,252 (Sept. 5, 1973), D. Bryce-Smith and co-workers.
132. A. Ayame and co-workers, *Nippon Kagaku Kaishi* **8**, 1189 (1974).
133. O. Svajgl and co-workers, *Chem. Prum.* **22**, 493 (1972).
134. U.S. Pat. 2,605,239 (July 29, 1952), G. W. Sears (to E. I. du Pont de Nemours & Co., Inc.).
135. U.S. Pat. 2,831,870 (Apr. 22, 1958), W. J. McClements and B. E. Elliott (to Allied Chemical & Dye Corp.).
136. Brit. Pat. 754,593 (Aug. 8, 1956), (to N. V. de Bataafasche Petroleum Maatschappij).
137. U.S. Pat. 2,805,207 (Sept. 3, 1957), F. J. Metzger.
138. Brit. Pat. 811,828 (Apr. 15, 1959), (to The Dow Chemical Co.).
139. Brit. Pat. 501,278 (Feb. 21, 1939), (to N. V. de Bataafasche Petroleum Maatschappij).
140. U.S. Pat. 2,686,762 (Aug. 17, 1954), E. L. C. Tollefson (to National Research Council of Canada).

141. A. Cambron and W. A. Alexander, *Can. J. Chem.* **34**, 665 (1956).
142. Jpn. Pat. 46 40,256 (Nov. 17, 1971), S. Ishii and co-workers (to Nippon Shokubai Kagaku Kogyo).
143. U.S. Pat. 3,793,231 (Feb. 19, 1974), H. Bergmann and co-workers (to Huels).
144. Brit. Pat. 1,300,971 (Dec. 29, 1972), (to Huels).
145. U.S. Pat. 3,843,491 (Oct. 22, 1974), M. Piro and co-workers (to Snam Progetti).
146. P. Hariott, *J. Catal.* **21**, 56 (1971).
147. R. Wolf and co-workers, *Chem. Tech. (Berlin)* **14**, 600 (1962).
148. U.S. Pats. 2,279,469 and 2,279,470 (Apr. 14, 1942), G. H. Law and H. C. Chitwood (to Carbide and Carbon Chemicals Corp.).
149. J. Barthory and co-workers, *Proc. Conf. Appl. Phys. Chem* **2**, 279 (1971).
150. J. J. Carberry and co-workers, *J. Catal.* **26**, 247 (1972).
151. U.S. Pat. 3,962,136 (June 8, 1976), R. P. Nielsen (to Shell Oil Co.).
152. U.S. Pat. 6,281,370 (Aug. 28, 2001), M. Shima and H. Takada (to Nippon Shokubai Co., Ltd).
153. P. W. Sherwood, *Oil Gas J.* **39**, 80 (1957); **40**, 150 (1957).
154. U.S. Pat. Appl. 20010007035 (July 5, 2001), Y. Oka and K. Takematsu (to Nippon Shokubai Co., Ltd.).
155. L. Akella, Ph.D. dissertation, University of Florida, University Microfilms International, Ann Arbor, Mich., 1983.
156. G. K. Boreskov and co-workers, *Kinet. Katal.* **3**, 214 (1962).
157. Dutch Pat. Appl. 6,502,927 (Sept. 23, 1964), (to the Dow Chemical Co.).
158. U.S. Pat. 3,758,418 (Sept. 11, 1973), W. J. Leonard (to Shell Oil Co.).
159. Brit. Pat. 1,411,315 (Oct. 22, 1975), A. L. Gelbshtein (to the USSR).
160. Rom. Pat. 55,800 (Sept. 15, 1973), I. Oprescu and co-workers (to Institutul Petrochim).
161. Belg. Pat. 638,319 (Oct. 8, 1964), R. S. Davis (to Halcon International).
162. Brit. Pat. 748,957 (May 15, 1956), R. B. Egbert (to Chempatents Inc.).
163. U.S. Pat. 3,119,837 (Jan. 28, 1964), H. A. Kingsley and F. A. Cleland (to Shell Oil Co.).
164. Belg. Pat. 707,567 (June 5, 1968), D. Brown (to Halcon International).
165. U.S. Pat. 4,582,950 (Apr. 15, 1986), P. J. Busse and D. B. Taggart (to InterNorth).
166. F. L. W. McKim and A. Cambron, *Can. J. Res.* **27B**, 813 (1949).
167. L. M. Kaliberdo and co-workers, *Kinet. Katal.* **8**, 463 (1967).
168. Eur. Pat. Appl. 0200518-A2 (Nov. 5, 1986), B. J. Ozero (to The Halcon SD Group).
169. U.S. Pat. 4,879,396 (Nov. 7, 1989), B. J. Ozero (to Scientific Design Co., Inc.).
170. U.S. Pat. 4,769,047 (Sept. 6, 1988), R. F. Dye (to Shell Oil Co.).
171. U.S. Pat. 3,766,714 (Oct. 23, 1973), J. W. Cunningham (to Shell Oil Co.).
172. Eur. Pat. Appl. 181,273 (May 14, 1986), H. Neel and F. Delannoy (to Atochem SA).
173. U.S. Pat. 4,437,938 (July 17, 1981), V. S. Bhise and R. Hoch (to Halcon SD Co.).
174. U.S. Pat. 4,437,939 (Nov. 16, 1981), V. S. Bhise and R. Hoch (to Halcon SD Co.).
175. Jpn. Pat. 60 126,278 (July 5, 1985), (to Mitsui Toatsu Chemical Co.).
176. USSR Pat. 1,570,743 (June 15, 1990), V. A. Kurbatov and co-workers (to USSR).
177. K. R. Barker and J. C. Zomerdijk, *Eur. Chem. News Chemscope* **24**, 28 (Oct. 12, 1973).
178. Eur. Pat. Appl. 322,323 (June 28, 1989), F. Delannoy and G. Letray (to Atochem SA).
179. U.S. Pat. 3,3355,547 (Aug. 15, 1967), D. Garrett (to Halcon International).
180. Fr. Pat. 1,330,900 (May 20, 1963), Paire and co-workers (to Kuhlmann Co.).
181. U.S. Pat. 3,265,593 (Aug. 9, 1966), D. G. Leis (to Union Carbide Corp.).
182. U.S. Pat. 5,034,134 (Aug. 26, 1991), K. F. George and co-workers (to Union Carbide Corp.).

183. Jpn. Pat. 1,163,142 (June 27, 1989), H. Sugawara and T. Okawa (to Mitsui Toatsu Chemicals, Inc.).
184. U.S. Pat. 4,802,988 (Feb. 7, 1989), C. R. Bartels and J. Reale (to Texaco Inc.).
185. L. G. Britton, *Plant/Operations Progress* **9**(2) (Apr., 1990).
186. L. G. Britton, *Plant/Operations Progress* **10**(1) (Jan., 1991).
187. Brit. Pat. 1,463,324 (Feb. 2, 1977), (to FarbWerke Hoechst AG).
188. U.S. Pat. 4,822,926 (Apr. 18, 1989), R. F. Dye (to Shell Oil Co.).
189. U.S. Pat. 3,904,656 (Sept. 9, 1975), S. E. Broz (to PPG Industries, Inc.).
190. U.S. Pat. 3,083,213 (Mar. 26, 1963), M. L. Courter (to Shell Oil Co.).
191. B. DeMaglie, *Hydrocarbon Process*. **55**(3), 78 (1976).
192. R. Landau, *Pet. Refiner* **32**(9), 146 (1953).
193. U.S. Pat. 3,993,673 (Nov. 23, 1976), C. H. McMullen (to Union Carbide Corp.).
194. A. G. Lee, *The Chemistry of Thallium*, Elsevier, New York, 1971.
195. U.S. Pat. 4,021,453 (May 3, 1977), W. F. Brill (to Halcon International).
196. Belg. Pat. 853,864 (Oct. 24, 1977), N. Rizkalla and A. N. Naglieri (to Halcon International).
197. U.S. Pat. 4,058,542 (Nov. 15, 1977), N. Rizkalla and A. N. Naglieri (to Halcon International).
198. Belg. Pat. 855,127 (Nov. 28, 1977), (to Halcon International).
199. Ger. Pat. 2,541,526 (Apr. 1, 1976), A. P. Gelbein (to Lummus Co.).
200. Eur. Pat. Appl. 84,301,864 9 (Nov. 7, 1984), R. L. Kelly (to Brit. Pet. Chemicals).
201. U.S. Pat. 3,427,235 (Feb. 11, 1979), J. A. M. Le Duc (to Pullman Inc.).
202. U.S. Pat. 3,288,692 (Nov. 29, 1966), J. A. M. Le Duc (to Pullman Inc.).
203. U.S. Pat. 3,723,264 (Mar. 27, 1973), J. A. M. Le Duc and co-workers (to Pullman Inc. and Farbenfabriken Bayer Aktiengesellschaft).
204. A. Renken, M. Muller, and C. Wandrey, *Proc. 4th Intl. Conf. Chem. Reac. Eng.*, Heidelberg, 107, 1976.
205. Ger. Pat. 2,605,991 (Aug. 25, 1977), A. Renken, C. Wandrey, and M. Muller (to Hoechst AG).
206. U.S. Pat. 2,430,443 (Nov. 11, 1947), S. B. Becker (to Standard Oil Co.).
207. U.S. Pat. 2,578,841 (Dec. 18, 1951), N. C. Robertson and R. T. Allen (to Celanese Corp.).
208. U.S. Pat. 2,600,444 (June 17, 1952), F. W. Sullivan, Jr. (to GAF Corp.).
209. U.S. Pat. 2,628,965 (Feb. 17, 1953), F. W. Sullivan, Jr. (to GAF Corp.).
210. U.S. Pat. 2,684,967 (July 27, 1954), C. H. O. Berg (to Union Oil Co.).
211. T. E. Corrigan, *Pet. Refiner* **32**(2), 87 (1953).
212. U.S. Pat. 3,948,609 (Apr. 6, 1976), N. M. Guseinov and co-workers (to the USSR).
213. Brit. Pat. 1,379,797 (July 28, 1972), N. M. Guseinov and co-workers (to the USSR).
214. USSR Pat. 562,555 (June 25, 1977), N. M. Guseinov and co-workers (to the USSR).
215. *Processing* **21**(11), 54 (1973).
216. F. B. Abeles and L. J. Dunn, *J. Plant Growth Regul*. **4**, 123–128 (1985).
217. Eur. Pat. Appl. 83 303,695 (Jan. 11, 1982), C. H. Hou, A. I. Laskin, and R. N. Patel (to Exxon Research and Engineering Co.).
218. Eur. Pat. Appl. 98,138 (Jan. 11, 1984), C. H. Hou, A. I. Laskin, and R. N. Patel (to Exxon Research and Engineering Co.).
219. J. A. M. DeBont and co-workers, *Enzyme Microb. Technol*. **5**(1), 55 (1983).
220. *U.S. Code of Federal Regulations*, Title 49, paragraph 173.323.
221. J. Lacson, "Ethylene Oxide," *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., Oct. 2003.
222. "Ethylene Oxide, Chemical Profile," *Chemical Market Reporter*, Aug. 13, 2001.
223. R. L. Anderson in F. D. Snell and L. S. Ettre, eds., *Encyclopedia of Industrial Chemical Analysis*, Vol. 12, John Wiley & Sons, Inc., New York, 1971, pp. 317–340.

224. E. J. Bond and T. Dumas, *J. Agric. Food Chem.* **30**, 986 (1982).
225. M. Collins and M. J. Barker, *Am. Lab.* **72** (1983).
226. *Gas Sterilants, Brochure L-2085-A*, Linde Division, Union Carbide Corp., Danbury, Conn., 1985.
227. M. Adams and M. Collins, *Anal. Proc.* **25**, 190 (1988).
228. L. Golberg, *Hazard Assessment of Ethylene Oxide*, CRC Press, Boca Raton, Fla., 1986.
229. K. H. Jacobson and co-workers, *AMA Arch. Ind. Health* **13**, 237–244 (1956).
230. Union Carbide Corp. internal laboratory report.
231. A. M. Thiess, *Archiv. Toxiko.* **20**, 127–140 (1963).
232. W. M. Jay and co-workers, *Am. J. Ophthalmol.* **93**, 727–732 (1982).
233. P. F. Finelli and co-workers, *Arch. Neurol.* **40**, 419–421 (1983).
234. R. L. Hollingsworth and co-workers, *AMA Arch. of Ind. Health* **13**, 217–227 (1956).
235. International Agency for Research on Cancer, *Ethylene Oxide in IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man* **11**, 157 (1976).
236. D. W. Lynch and co-workers, *Toxicol. Appl. Pharmacol.* **76**, 69–84 (1984).
237. W. M. Generoso and co-workers, *Environ. Mutagen.* **8**, 1–7 (1986).
238. W. M. Generoso and co-workers, *Mutat. Res.* **199**, 175–181 (1988).
239. Osterman-Golkar and co-workers, *Mutat. Res.* **34**, 2 (1976).
240. L. Ehrenberg and co-workers, *Mutat. Res.* **24**, 83–103 (1974).
241. W. M. Snellings and co-workers, *Toxicol. Appl. Pharmacol.* **75**, 105–117 (1984).
242. *National Toxicology Program Technical Report*, National Institutes of Health publication number 88-2582, U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, Washington, D.C., 1987.
243. C. Hogstedt and co-workers, *J. Am. Med. Assoc.* **24**, 1132–1133 (1979).
244. C. Hogstedt and co-workers, *J. Am. Med. Assoc.* **255**, 1575–1578 (1986).
245. L. Hagmar and co-workers, *Ind. Arch. Environ. Health* **63**, 271–277 (1991).
246. M. J. Gardner and co-workers, *Br. J. Ind. Med.* **47**, 860–865 (1990).
247. H. L. Greenberg and co-workers, *Br. J. Ind. Med.* **47**, 221–230 (1990).
248. N. Kiesselback and co-workers, *Br. J. Ind. Med.* **47**, 182–188 (1990).
249. R. W. Morgan and co-workers, *J. Occup. Med.* **23**, 767–769 (1981).
250. P. L. Hackett and co-workers, *NTIS No. PB83-258038*, U.S. Department of Health and Human Services, Public Health Services, Centers for Disease Control, National Institute for Occupational Safety and Health, Washington, D.C., 1982.
251. W. M. Snellings and co-workers, *Toxicol. Appl. Pharmacol.* **64**, 476–481 (1982).
252. W. M. Snellings and co-workers, *Toxicol. Appl. Pharmacol.* **63**, 382 (1982).
253. J. W. Embree and co-workers, *Toxicol. Appl. Pharmacol.* **40**, 261–267 (1977).
254. R. B. Cumming and T. A. Michaud, *Environ. Mutagen.* **1**, 166–167 (1979).
255. K. Hemminki and co-workers, *Br. Med. J.* **285**, 1461–1463 (1982).
256. J. S. Taylor, *Dermatologic Hazards from Ethylene Oxide* **19**, 189–192 (1977).
257. R. J. Sexton and E. Henson, *J. Ind. Hyg. Toxicol.* **31**, 297–300 (1949).
258. A. M. Thiess, *Archiv. Toxico.* **20**, 127–140 (1963).
259. R. J. Sexton and E. Henson, *Ind. Hyg. Occup. Med.* **32**, 549–564, (1950).
260. J. L. Shupack and co-workers, *J. Lab. Clin. Med.* **98**, 723–729 (1981).
261. G. Woodard and M. Woodard, *Proc. Health Ind. Assoc. Tech. Symp.*, Washington, D.C., 1971, pp. 140–161.
262. R. J. Lewis, Sr., *Sax's Dangerous Properties of Industrial Materials*, 10th ed., Vol. 2, John Wiley & Sons, Inc., New York, 2000.
263. B. Pesetsky and co-workers, *AIChE Loss Prevention* **13** (1980).
264. L. D. Chen and G. M. Faeth, *Combustion and Flame* **40**, 13–28 (1981).
265. J. E. Troyan and R. Y. LeVine, *AIChE Loss Prevention* **2**, 125–130 (1968).
266. R. G. Vanderwater, *Chem. Eng. Prog.* **85**(12) (Dec., 1989).

267. R. K. June and R. F. Dye, *Chem. Eng. Prog.* **85**(12) (Dec., 1989).
268. R. Siwek and E. Rosenberg, *Paper 52, 6th Int. Symp. Loss Prevention and Safety Promotion in the Process Industries*, Oslo, June 19–22, 1989.
269. L. G. Britton, *Plant/Operations Prog.* (Apr., 1992).
270. J. L. Brockwell, *Plant/Operations Prog.*, (Apr., 1992).
271. *Venting of Deflagrations*, NFPA 68, 1986 ed., National Fire Protection Association, Quincy, Mass.
272. *The Effects of Explosions in the Process Industries, Loss Prevention Bulletin 068*, Overpressure Working Party, Major Hazards Assessment Panel, Institution of Chemical Engineers, Apr., 1986.
273. U.S. Pat. 6,605,254 (Aug. 12, 2003), A. M. Aguilera and co-workers (to AlliedSignal Inc.).
274. U.S. Pat. 6,432,357 (Aug. 13, 2002), R. G. Richard, B. R. Decaire, and S. A. Conviser (to Honeywell International Inc.).
275. B. Kit and D. S. Evered, *Rocket Propellant Handbook*, The MacMillan Co., New York, 1960, 220–225.
276. U.S. Pat. 3,940,443 (Feb. 24, 1976), C. A. Glass (to U.S.A. represented by the Secretary of the Navy).
277. *New York Post*, 5, (Apr. 25, 1975).
278. *Ethylene Glycol, Brochure F-49193B-ICD*, Union Carbide Corp., Danbury, Conn., 1991.
279. *Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol; Brochures* F-49181A-ICD, F-49191A-ICD, F-80066-ICD, Union Carbide Corp., Danbury, Conn., 1990.
280. F. E. Bailey and J. V. Koleske, *Alkylene Oxides and Their Polymers*, Marcel Dekker, Inc., New York, 1991.
281. *Ethanolamines, Brochure F-41175C*, Union Carbide Corp., Danbury, Conn., 1990.
282. U.S. Pat. 6,585,922 (July 1, 2003), J. H. Wang and D. M. Schertz (to Kimberly-Clark Worldwide, Inc.).

J. P. Dever
K. F. George
W. C. Hoffman
H. Soo
Union Carbide Corporation