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1. Introduction	547	7. Analysis	561
2. Physical Properties	547	8. Handling, Storage, and Transportation	561
3. Chemical Properties	549	9. Uses	564
4. Production	553	10. Economic Aspects	565
4.1. Catalysts	553	11. Toxicology and Occupational Health	565
4.2. Mechanism of Catalysis	554	12. Acknowledgement	568
4.3. Technology	556	References	568
5. Environmental Protection and Ecology	560		
6. Quality Specifications	561		

1. Introduction

Ethylene oxide (oxirane) [75-21-8], M_r 44.05, is the simplest cyclic ether. It is a colorless gas or liquid and has a sweet, etheric odor. The ethylene oxide molecule with its short C–C bond and strained angles is shown in Figure 1 [6]. Theoretical calculations of the structure are in good agreement with experimental results [7].

Ethylene oxide is very reactive because its highly strained ring can be opened easily, and is thus one of the most versatile chemical intermediates. Because of its reactivity and toxicity it is also a hazardous compound that has been involved in a number of serious incidents. A good understanding of its properties is a necessary prerequisite for its safe handling. Ethylene oxide was first described in 1859 by WURTZ [8], who prepared it by eliminating hydrochloric acid from ethylenechlorohydrin, using potassium hydroxide solution. Industrial production by the chlorohydrin process began in 1914 and was based on WURTZ'S discovery. Since then the production and importance of ethylene oxide have steadily grown.

In 1931, LEFORT [9] discovered the direct catalytic oxidation of ethylene [74-85-1], which gradually superseded the chlorohydrin process. Currently, ethylene oxide is produced by direct oxidation of ethylene with air or oxygen; annual

worldwide production capacity is ca. 15×10^6 t, making it an important industrial chemical. Ethylene oxide itself is used as a disinfectant, sterilizing agent, and fumigant. Its most important derivative is ethylene glycol [107-21-1], which is used in antifreeze (car radiators) (\rightarrow Antifreezes) and for the manufacture of polyester fibers (\rightarrow Fibers, 5. Polyester Fibers; \rightarrow Polyesters). Other ethylene oxide derivatives, amines and poly(ethylene glycols), are used in surfactants, solvents, etc.

There is some endogenous formation from ethylene in humans [10], and it has been discovered in an interstellar source [11].

As atmospheric pollutant it is present in natural gas, cigarette smoke, and diesel exhaust. Though ethylene oxide in nature is rare its biological action may have a fundamental impact on DNA and RNA evolution of whole biological systems [12].

2. Physical Properties

Some physical properties of ethylene oxide are summarized in Table 1.

In the pressure range 0 – 101.3 kPa and at 40 and 60 °C, the solubility of ethylene oxide in water obeys Henry's law. The Henry constants for these temperatures are 2.875 and 1.448,

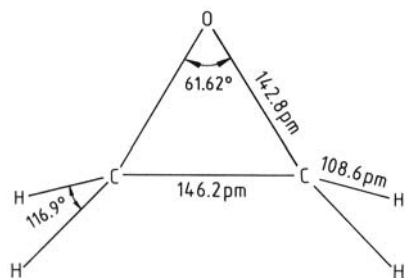


Figure 1. The ethylene oxide molecule

respectively. However, at 20 °C a more than proportional increase in solubility occurs with the partial pressure [15].

Liquid ethylene oxide and water are completely miscible in all proportions. Table 2 shows some of the properties of aqueous ethylene oxide solutions. Of particular note are the relatively high melting points, which are due to clathrate formation [17]. Clathrates consist of organic molecules that are enclosed in a cage

Table 1. Physical properties of ethylene oxide [5], [13], [14]

<i>mp</i> at 101.3 kPa	-112.5 °C
<i>bp</i> at 101.3 kPa	10.8 °C
Critical temperature	195.8 °C
Critical pressure	7.2 MPa
Critical density	314 kg/m ³
Refractive index, n_D^{20}	1.3597
Explosive limits in air at 101.3 kPa	
lower	2.6 vol %
upper	100.0 vol %
Electrical conductivity	4×10^{-6} S/m
Dielectric constant	
at -1 °C (liquid)	13.9
at 15 °C (vapor)	1.01
Heat of combustion at 25 °C,	
101.3 kPa	29.648 kJ/kg
Entropy of the vapor at 101.3 kPa	
10.5 °C	5.439 kJ kg ⁻¹ K ⁻¹
25.0 °C	5.495 kJ kg ⁻¹ K ⁻¹
Ignition temperature in air at	
101.3 kPa	429 °C
Ignition energy in air at	
101.3 kPa and 25 °C	0.087 mJ
Minimum ignition energy of the gas at	
220 kPa and 100 °C	64 mJ
Decomposition temperature of	
the vapor at 101.3 kPa	571 °C
Heat of polymerization	2091 kJ/kg
Heat of fusion	117.86 kJ/kg
Heat of decomposition of the vapor	1901 kJ/kg
Coefficient of cubic expansion	
at 22 °C	0.00161
at 55 °C	0.00170
Heat of solution in water at 25 °C	142.57 kJ/kg

Table 2. Physical properties of aqueous ethylene oxide solutions [3], [5], [16]

Ethylene oxide content, wt %	<i>mp</i> , °C	<i>bp</i> , °C	Density at		Flash point, °C
			10 °C, g/L		
0	0.0	100	0.9991		
0.5					41.5
1	-0.4				31
2					3
3	-1.3				
5	-1.6	58	0.9988		-2
10	5.6	42.5	0.9980		
20	10.4	32	0.9945		-21
30	11.08 (max)	27	0.9882		-28
40	10.4	21	0.9792		-35
60	7.8	16	0.9534		-45
80	3.7	13	0.9194		-53
100	-112.5	10.4	0.8826		-57

structure. In this case, the cage is an ice lattice which is composed of unit cells, each containing 46 water molecules, and two types of cavities: six larger ones (14-sided, tetradecahedra) and two smaller ones (12-sided, dodecahedra). If the clathrates are made to crystallize from increasingly concentrated aqueous solutions of ethylene oxide, their density and ethylene oxide content also increase. Ethylene oxide first fills the six tetradecahedral cavities of the water lattice, followed by 20 – 40 % of the dodecahedral cavities [18].

The temperatures for the formation of ice and hydrate from mixtures of ethylene oxide and water for concentrations of 0 to 97.89 wt % ethylene oxide gave a highest hydrate formation temperature of 11.08 °C at an ethylene oxide concentration of 26.15 wt %. The hydrate corresponds to a composition of 6.91 molecules of water per molecule ethylene oxide. The unit cell consists of 46 water molecules and 6.66 ethylene oxide molecules. The eutectic point of the mixture has been determined to lie at 2.107 °C and 4.75 wt % ethylene oxide (Fig. 2) [19].

There are also mixed clathrates, in which the small cages are occupied by ethylene oxide and the big cages by molecules with an higher space requirement, e.g., tetrahydrofuran [20].

The solubilities of gases in ethylene oxide vary, increasing in the order nitrogen, argon, methane, ethane. Earlier data [21] have been revised [22]. The Henry constants for these gases in ethylene oxide at different temperatures are given in Table 3.

Table 4 shows other temperature-dependent physical properties of gaseous and liquid ethylene oxide.

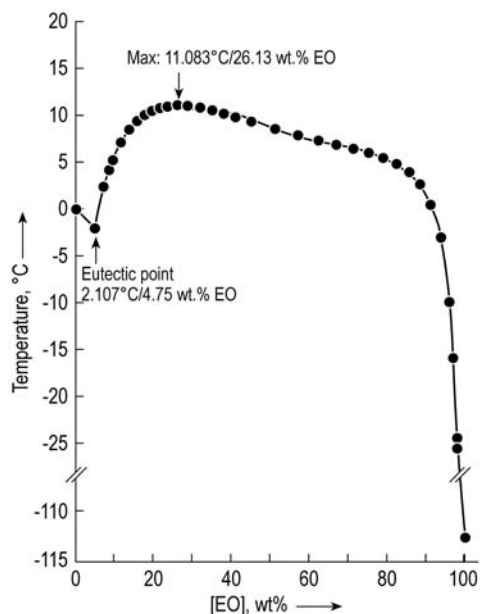


Figure 2. Hydrate-formation temperature as a function of ethylene oxide concentration

3. Chemical Properties

Ethylene oxide is a very reactive, versatile compound. Its reactions proceed mainly via ring opening and are highly exothermic. Explosive decomposition of the ethylene oxide vapor may occur at higher temperatures if heat dissipation is inadequate. Only the most important types of the

Table 3. Solubility of gases in ethylene oxide (Henry constants in MPa) [22], [23]

Temperature, °C	Solubility in ethylene oxide			
	Nitrogen	Argon	Methane	Ethane
0	284	169	62.1	8.5
25	221	144	62.2	11.0
50	184	129	62.3	13.0

large number of possible reactions are briefly discussed here. More detailed information can be found in [25–29].

Decomposition. Gaseous ethylene oxide starts to decompose at ca. 400 °C to form mainly CO, CH₄, as well as C₂H₆, C₂H₄, H₂, C, and CH₃CHO. The first step in the decomposition is presumed to be the isomerization of ethylene oxide to acetaldehyde [30]. Once the decomposition reaction has been initiated (ignition source), it can be propagated through the gas phase and, under certain conditions, may be explosive (see Chap. 8).

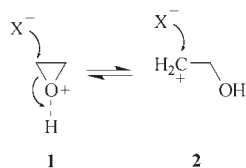
Addition to Compounds with a Labile Hydrogen Atom. Ethylene oxide reacts with compounds containing a labile hydrogen atom to form a product containing a hydroxyethyl group:xs



Table 4. Physical properties of ethylene oxide at various temperatures [3], [24]

Temperature °C	Density		Heat of Vaporization kJ/kg	Vapor pressure kPa	Specific heat		Thermal conductivity		Surface tension mN/m	Dynamic viscosity	
	Vapor g/L	Liquid kg/m ³			Vapor kJ kg ⁻¹ K ⁻¹	Liquid kJ kg ⁻¹ K ⁻¹	Vapor 10 ⁻⁴ J cm ⁻¹ s ⁻¹ K ⁻¹	Liquid 10 ⁻⁴ J cm ⁻¹ s ⁻¹ K ⁻¹		Vapor mPa · s	Liquid mPa · s
	-40	0.2	946	647	7.6	1.88		17.7	33.8		0.50
-30	0.3	931	634	16.2			17.2	32.3		0.44	
-20	0.5	919	621	24.6	1.91		16.8	30.7		0.39	
-10	0.9	909	607	40.3			16.4	29.1		0.34	
0	1.3	899	592	65.4	1.00	1.95	1.03	16.0	27.6	0.0090	0.31
+10	1.8	888	578	99.2	1.06		1.10	15.6	26.7		0.28
+20	2.9	876	563	145.6	1.10	2.00	1.18	15.3	24.5		0.25
+30	3.9	862	547	208.0	1.15		1.25	15.0			0.23
+40	5.25	847	531	287.1	1.19	2.06	1.34	14.7	22.0		0.21
+50	6.85	831	515	391.0	1.23		1.43	14.3		0.0104	0.19
+60		814	498	534.6	1.28	2.15	1.52	14.0	17.5		0.18
+70		796	481	694.6	1.32		1.62	13.7			0.16
+80		779	463	912.8	1.36	2.27	1.72	13.4	14.5		0.15
+100		745	424	1464.0	1.45	2.40	1.93	12.5	12.0	0.0118	0.14

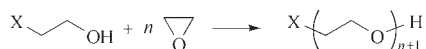
Examples of XH are: HOH, H₂NH, HRNH, R₂NH, RCOOH, RCONH₂, HSH, RSH, ROH, N≡CH, and B₂H₆ (R = alkyl, aryl). The reaction is accelerated by acids and bases. During acid catalysis, the ethylene oxide is first protonated to form an epoxonium ion (**1**), which is in equilibrium with the corresponding hydroxycarbenium ion (**2**). The anion X⁻ can then react with **1** or **2** in an S_N2 or S_N1 reaction, respectively. In an alkaline medium, the S_N2 mechanism is favored. A detailed discussion of reaction mechanisms can be found in [27], [31].



The protonation of ethylene oxide by various H-active compounds in tetrachloromethane can be detected by IR spectroscopy. Broadening and shift of the IR bands in the region of 530 to 740 cm⁻¹ depend on the type of H-active compound (OH, NH, CH) [32]. Analogous protonated intermediates have been postulated in gas-phase S_N2 reactions of ethylene oxide on the basis of theoretical and experimental results [33].

All common acids and Lewis acids as well as zeolites, ion exchangers [34], and aluminum oxide are effective catalysts. Solid polymeric acids (cation exchangers) are especially recommended for the reaction of ethylene oxide with methanol [35].

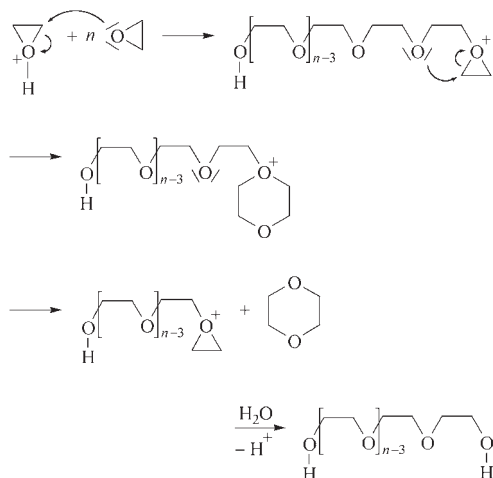
As the end product of the above reaction contains at least one hydroxyl group, it may react successively with further ethylene oxide molecules:



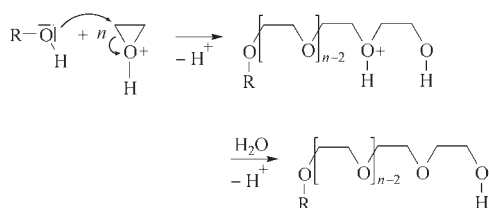
The molecular mass of the resulting polymers depends on the ratio of the reactants, the catalyst used, and the reaction conditions [1], [28].

A byproduct of the acid-catalyzed polymerization is dioxane, which may even be the sole product with a large excess of ethylene oxide. An explanation for this behavior is offered by the assumption that two different reaction mechanisms are effective. The first is the active chain end (ACE) mechanism, which leads to dioxane and poly(ethylene glycol).

The second is the activated monomer (AM) mechanism, which leads exclusively to poly(ethylene glycol).



And the second is the activated monomer (AM) mechanism, which leads exclusively to poly(ethylene glycol).



One of the conditions which favor the ACM mechanism and therefore the formation of dioxane is an increasing excess of ethylene oxide [36].

A large variety of reactions occur between ethylene oxide and compounds containing labile hydrogen atoms; therefore, such compounds are often used to produce derivatives.

Commercially, the most important of this type of reaction is the hydrolysis of ethylene oxide to ethylene glycol. About 60 % of the total ethylene oxide production is converted into ethylene glycol in this way (→ Ethylene Glycol). However, this reaction, which is often referred to as ethoxylation, is also used to produce the bulk of all the other commercially important ethylene oxide derivatives. The ethoxylation products of alkyl

phenols, ammonia, fatty alcohols, fatty amines, and fatty acids have a variety of uses [28]. Although polymer formation according to the above equation is more likely to be an unwanted side reaction, the production of poly(ethylene glycols) of widely varying molecular mass by this route is of some importance [37]. Undesired polymerization may be catalyzed by rust in rusty containers [38].

Reaction with Water. The formation of hydrates is discussed in Chapter 2. Hydrolysis is the most important reaction of ethylene oxide: about 60% of the total ethylene oxide production is transformed into ethylene glycol. The reaction of ethylene oxide with water in the absence of catalysts at 20 °C is relatively slow, as shown by the half-life of 20 d. The dependence of the half-life of a 3 % solution of ethylene oxide in water on pH is shown in Figure 3. The dependence is characterized by a bell-shaped curve with a relatively broad plateau from pH 5 to 11 and a steep slope on both sides. A strong acceleration occurs only below pH 4 and above pH 12. By-products of the hydrolysis are diethylene glycol, triethylene glycol, and higher molecular mass poly(ethylene glycols). The percentage of ethylene oxide converted to these products depends almost solely on the ratio of water to ethylene

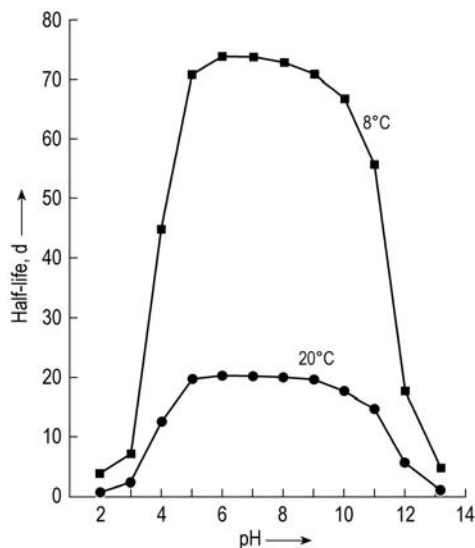


Figure 3. Half-life of 3 wt % ethylene oxide in water as a function of pH at 8 and 20 °C

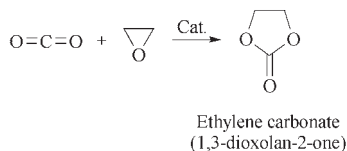
oxide in the starting material and only marginally on pH and temperature.

Reaction with DNA, RNA and Proteins.

The major product of reaction with DNA is 7-(2-hydroxyethyl) guanine. Further reaction products are (2-hydroxyethyl) guanine and 3-(2-hydroxyethyl) adenine [12].

In men exposed to ethylene oxide, adducts with hemoglobin can be found and its level may be evaluated by the concentration of (2-hydroxyethyl) valine [39].

Addition to Double Bonds. Ethylene oxide can add to compounds with double bonds, e.g., carbon dioxide [40], to form cyclic products:

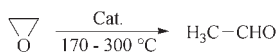


Quaternary ammonium compounds are suitable catalysts for this reaction, which then proceeds at 200 °C and 8 MPa [41]. Use of porphine complexes of aluminum in solvents such as chloroform allows the reaction to take place at normal pressure and at room temperature [42]. Hydrolysis of ethylene carbonate (1,3-dioxolan-2-one) [96-49-1] yields pure ethylene glycol [43]. Therefore, the reaction is of interest for the selective production of ethylene glycol from ethylene oxide, i.e., for avoiding the partly unwanted formation of poly(ethylene glycols) [44].

Ethylene oxide also adds to other double bond systems, e.g., to $\text{R}_2\text{C}=\text{O}$ [45], $\text{SC}=\text{S}$, $\text{O}_2\text{S}=\text{O}$, $\text{RN}=\text{CO}$, and $\text{OS}=\text{O}$.

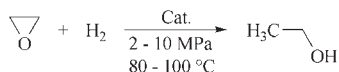
Catalytic Isomerization to Acetaldehyde.

Aluminum oxide (Al_2O_3) [46], phosphoric acid and phosphates [47], and under certain conditions silver [48] catalyze the isomerization of ethylene oxide to acetaldehyde.



Reduction to Ethanol. Reduction of ethylene oxide to ethanol is catalyzed by Ni, Cu, and

Cr on Al_2O_3 [49].

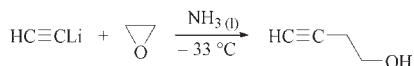
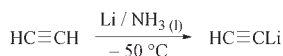


Reaction with Grignard Reagents.

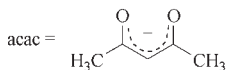
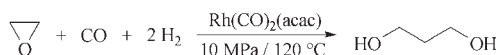
Grignard reagents react with ethylene oxide to produce compounds with a primary hydroxyl group [29], [50].



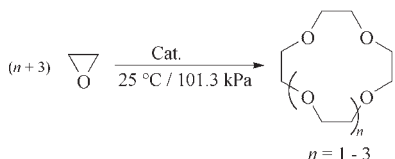
Reaction with Lithium Acetylide. Acetylene is treated with lithium in liquid ammonia to form the lithium salt, which reacts with ethylene oxide at -33°C to give 3-butyne-1-ol in 80% yield [51].



Reaction with Synthesis Gas. Ethylene oxide is carbonylated with CO/H_2 in the presence of rhodium catalysts in tetraethylene glycol dimethyl ether to give 1,3-propanediol in good yields [52].

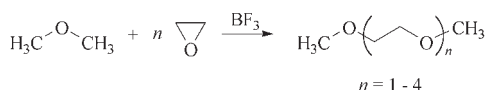


Oligomerization to Crown Ethers. Ethylene oxide oligomerizes to form cyclic polyethers (crown ethers) in the presence of a fluorinated Lewis acid catalyst (\rightarrow Crown Ethers).



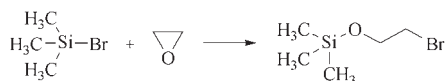
Synthesis is successful when groups that saturate potential terminal hydroxyl groups are absent [53]. Suitable catalysts are the BF_4^- , PF_6^- , or SbF_6^- salts of metal cations. The reaction can be directed to produce a particular oligomer by choosing an appropriate metal cation. The size of the cation determines the size of the crown ether ring by acting as a template [54]. For example, with CsBF_4 , only the cyclic hexamer ($n = 3$), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) [17455-13-9], is produced; if $\text{Cu}(\text{BF}_4)_2$ is used, 90% of the product consists of the pentamer ($n = 2$), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-6) [33100-27-5], and with $\text{Ca}(\text{BF}_4)_2$, a mixture of the tetramer (50%, $n = 1$), 1,4,7,10-tetraoxacyclodecane (12-crown-4) [294-93-9], and the pentamer, 1,4,7,10,13-pentaoxacyclopentadecane (18-crown-6) [17455-13-9], is produced.

Reaction with Dimethyl Ether. Ethylene oxide reacts with dimethyl ether to produce poly(ethylene glycol) dimethyl ethers (\rightarrow Dimethyl Ether); this reaction is used for the industrial production of the lower molecular mass homologues, which are widely used as solvents [55].

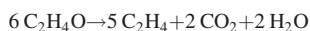
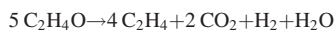


Reaction with Bromotrimethylsilane.

Ethylene oxide adds to bromotrimethylsilane [2857-97-8] in a highly exothermic reaction with excellent yields [56].



Disproportionation in the presence of iron oxides (especially $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$) has been described as the cause of an explosion (see Chap. 8) [57].



4. Production

As mentioned in the introduction, ethylene oxide was produced formerly by the chlorohydrin process (\rightarrow Chlorohydrins, Chap. 4.). However, this method is no longer used on an industrial scale; a description is given in [58]. Although the selectivity of this process (80 %) was satisfactory, practically all of the chlorine that was used was lost as calcium chloride and unwanted chlorine-containing byproducts were generated. This not only was inefficient, but also caused pollution problems so that this method has now been replaced by the direct oxidation process.

WURTZ, who had discovered ethylene oxide, attempted as early as 1863 to produce it by direct oxidation of ethylene with oxygen, but did not succeed [59]. Many other unsuccessful attempts were made [60] before LEFORT made the crucial discovery in 1931 that the formation of ethylene oxide from ethylene and oxygen was catalyzed by metallic silver [9]. Since the catalyst plays a central role in the production process, it is discussed first.

4.1. Catalysts

To date no other metal has been found that can compete with silver in the catalysis of the direct oxidation of ethylene to ethylene oxide. However, the silver catalysts have been substantially improved since their discovery by LEFORT [9].

Only supported catalysts are used, the silver being deposited on a porous *support material* in concentrations of 7 – 20 %. The support material is of critical importance [61]; currently, preference is given to ultrapure (over 99 %) aluminum oxide [57828-03-2] fired at a high temperature that has a defined pore structure (pore diameter 0.5 – 50 μm) and low specific surface area ($<2 \text{ m}^2/\text{g}$). Although supports with higher specific surface areas are very active, their selectivity is low, presumably because ethylene oxide can diffuse only slowly out of the smaller pores and, therefore, can be further oxidized [62]. Supports with chemical activity towards ethylene or ethylene oxide are unsuitable. All support containing hydroxyl groups catalyze the isomerization of ethylene oxide to acetaldehyde. As total oxidation of acetaldehyde is very fast on silver, catalysts consisting of silver and carriers like

γ -alumina, SiO_2 , MgO , SiC , TiO_2 , Y_2O_3 , and ZrO_2 give only poor selectivities or form only CO_2 and H_2O [63]. Silane treatment of supports containing hydroxyl groups improves the performance in ethylene oxide formation, and this confirms the detrimental effect of hydroxyl groups, which result in isomerization of ethylene oxide to acetaldehyde [64].

The impregnation methods used to deposit the silver on the support are being constantly improved. Complexes of silver salts with amino compounds are used which decompose to give evenly and finely distributed silver particles with a diameter of 0.1 – 1 μm [65]. Figure 4 shows a scanning electron micrograph (SEM) of the inner surface of a silver catalyst particle.

In addition, 100 – 500 mg/kg of *promoters* such as salts or other compounds of alkali and alkaline earth metals are added to the catalyst, significantly improving the selectivity. Among the alkali metal salts, those of cesium are especially effective [66]. Promoters are often combined. An especially effective combination consists of rhenium, sulfur, tungsten, molybdenum and results in outstanding selectivities of up to 90 %, albeit at higher temperature and reduced catalyst life [67].

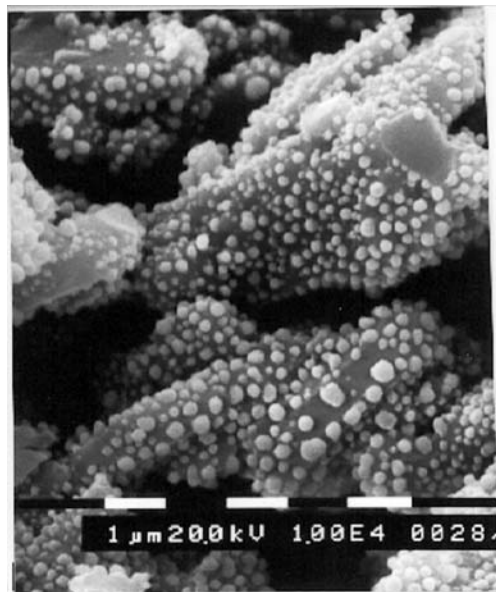


Figure 4. Silver catalyst for ethylene oxide production (SEM, $\times 10\,000$)

Addition of chlorine compounds to the reaction gases improves selectivity [68]. These *inhibitors* (e.g., 1,2-dichloroethane, vinyl chloride [69], ethyl chloride) [70] suppress the combustion of ethylene to carbon dioxide and water; they ensure that the silver surface is covered evenly with a supply of chlorine [71].

The advances made in silver-based catalysts since LEFORT'S original discovery (i.e., optimized support materials, silver distribution, and use of promoters and inhibitors) have improved selectivity from 50 to about 90%. Silver has maintained its position as the only known metal that can catalyze the oxidation of ethylene to ethylene oxide with a commercially viable selectivity.

The silver catalysts used in ethylene oxide production are not suited for the production of epoxides from olefins with allylic hydrogen atoms (e.g., propene); total oxidation is the prevailing reaction. Nonallylic olefins such as butadiene are reported to form epoxides in reasonable yields [72].

Aging of the Catalyst. Modern silver-based catalysts have an initial selectivity of 80 – 90%; a maximum selectivity of 90% is commercially feasible [44]. The disadvantages associated with highly selective catalysts are that they age relatively quickly and less heat is produced. As the catalyst is used, its selectivity and activity gradually deteriorate [73–75] due to

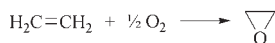
1. Abrasion, dust formation, and blocking of pores.
2. Accumulation of detrimental impurities introduced with the reaction gases (e.g., sulfur from ethylene or methane).
3. Changes in the silver particles, which enlarge, form agglomerates, and become unevenly distributed. Thus, the installed silver surface, which is about 20 km² for 100 t/a ethylene oxide capacity, drops to about 50% of its initial value by sintering during two years on stream. To compensate this reduction in silver surface the reaction temperature (reaction velocity) has to be increased accordingly to maintain the production rate.

Generally applicable methods of regenerating such catalysts are unknown; the only method of any importance is the use of methanolic solutions of cesium salts [76]. If regeneration is impossi-

ble, it becomes economically necessary to replace the catalyst when selectivity has fallen to a critical level or becomes technically necessary because the reaction temperature has reached the maximum design value. The lifetime of a modern catalyst is two to five years, depending on the type of catalyst (high-selectivity catalysts have considerably shorter life times), the rate of ethylene oxide production, and the purity of the reaction gases (sulfur is extremely poisonous). From the spent catalysts silver is recovered in high purity and with only small losses, while the used supports are waste.

4.2. Mechanism of Catalysis

Two reactions take place simultaneously at the silver surface. In addition to ethylene oxide formation (partial oxidation, Eq. 1), complete combustion (total oxidation, Eq. 2) to CO₂ and water also takes place. Small amounts of acetaldehyde and formaldehyde are also formed [77]. The reactions given by Equations (1) and (2) are exothermic, their enthalpies being –106.7 and –1323 kJ/mol, respectively at 250 °C and 1.5 MPa [44].

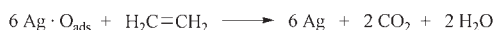
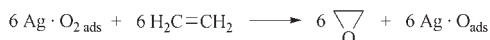


Although many attempts have been made to discover the mechanism responsible for silver's unique action, opinions remain divided [78]. Evaluation of the various studies is difficult because often they were carried out under different conditions that were not always suitable for industrial purposes. It is agreed that silver can adsorb oxygen in a number of ways and that this phenomenon is the basis of its unequalled efficiency in catalyzing the oxidation of ethylene to ethylene oxide. The following adsorption forms of oxygen are of critical importance:

1. Atomic oxygen
2. Molecular oxygen
3. Subsurface oxygen, i.e., dissolved oxygen found below the surface

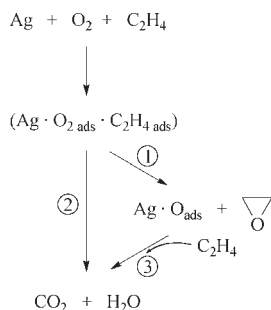
Opinions differ as to the role of these different types of adsorbed oxygen; two conflicting mechanisms have been proposed.

Mechanism 1. Only molecular oxygen reacts with ethylene to form ethylene oxide, whereas atomic oxygen only reacts to form carbon dioxide and water [79]. Chlorine (from the inhibitor) blocks the adsorption of atomic oxygen on the silver surface so that, in the ideal case, the optimally inhibited silver surface only adsorbs molecular oxygen (Eq. 3). The adsorbed molecular oxygen then reacts with ethylene to form ethylene oxide, leaving behind one oxygen atom after desorption (Eq. 4). This atomic oxygen then causes the combustion of ethylene to CO_2 and H_2O (Eq. 5).



Since six oxygen atoms are needed for the complete oxidation of one ethylene molecule, six ethylene oxide molecules must be formed before one ethylene molecule can be completely oxidized. Therefore, if inhibition of atomic oxygen adsorption is optimal, the maximum selectivity is $6/7 \times 100 = 85.7\%$. This mechanism plausibly explains the way in which the inhibitor acts. For a long time the molecular oxygen mechanism was strongly supported by the fact that efforts to improve the catalysts and the process seemed to lead to selectivities approaching the limit of 85.7% predicted by the mechanism, but not exceeding it.

A variant of this mechanism is based on the assumption that molecular oxygen can cause both ethylene oxide formation and total oxidation via a common intermediate [80], [81]:



The effect of the inhibitor is interpreted differently here. Reaction 2 requires a greater space than reaction 1. The inhibitor favors reaction 1 by reducing the available space on the surface of the catalyst. On an optimally inhibited surface, reaction 2 is totally suppressed, so that total oxidation takes place only via reaction 3. This results again in a maximum selectivity of 85.7%.

Mechanism 2. In this mechanism, atomic oxygen, possibly together with the subsurface oxygen, is thought to be responsible for both total and partial oxidation. The contribution of the molecular oxygen, if any, is indirect [82], [83]. The environment of the adsorbed oxygen atom determines whether the reaction with ethylene leads to ethylene oxide or CO_2 and H_2O [84], [85]. Chlorine (inhibitor), promoters, and subsurface oxygen in the proximity of the reacting oxygen atom are thought to influence the latter to favor partial oxidation, e.g., by reducing the negative charge of the adsorbed oxygen [86]. Unlike mechanism 1, the theoretical upper limit of selectivity of 6/7 does not apply for mechanism 2.

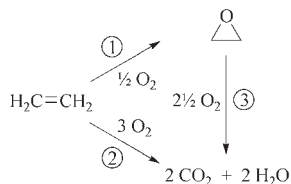
Since with modern catalysts (containing Cs, W, Re, and S in promoting quantities on the silver) maximum selectivities of 90% are feasible even on an industrial scale, mechanism 1 can at least not exclusively be valid with these catalysts. Also, it has been shown that atomic oxygen, formed on the silver surface by decomposition of N_2O , can produce ethylene oxide, though with low selectivities [87], [88]. For the epoxidation of nobornene and styrene it has been shown under ultrahigh-vacuum conditions that the atomic oxygen species on the silver is responsible for the epoxidation [89], [90]. Furthermore, theoretical calculations seem to favor mechanism 2 and can explain the action of inhibitor and promoter [91], [92].

Intermediates of the total oxidation are thought to include acetaldehyde, acetic acid, formic acid, and oxalic acid [84]. Desorption of intermediates from the silver surface produces acetaldehyde when a helium stream is used; ethanol and acetic acid are produced when a hydrogen stream is used [93].

Formate, acetate, and oxalate were detected on a silver surface by ^{13}C NMR spectroscopy after contacting the silver first with oxygen and subsequently with ethylene [94].

Kinetics. Three reactions are usually considered in kinetic models:

1. Partial oxidation
2. Total oxidation
3. Consecutive oxidation



The consecutive combustion of ethylene oxide (3) is negligible only if temperatures are not too high and if the reaction takes place under chemical control. To avoid diffusion control low surface area catalyst supports with high pore diameters are required. The surface reaction leading to ethylene oxide is considered to be of the Langmuir – Hinshelwood type, that is, oxygen and ethylene are both adsorbed on the silver surface before reaction. Ethylene is not adsorbed on a clean, oxygen-free silver surface; this only occurs after preadsorption of oxygen. The reaction of ethylene with oxygen on the silver surface is also thought to be the rate-determining step in the absence of diffusion control. Kinetic data and models are available in the literature [95], [96], but these are usually restricted to very specific reaction conditions and catalysts, far from the complex situation of the industrial production. Ref. [97] describes kinetic studies with an industrial catalyst in different laboratory reactors to clarify the influence of the reaction products but does not take into account the influence of inhibitors, which is crucial to achieve high selectivities on an industrial scale.

4.3. Technology

An overview of the beginnings of commercial ethylene oxide production can be found in [1]. Production technologies for ethylene oxide plants based on the direct oxidation process are licensed by Shell, Scientific Design (SD), UCC, Japan Catalytic, Snam Progetti, and Hüls. Due to improved catalysts and production technology, large plants with capacities of up to 400 000 t/a can now be built.

The technologies are very similar, but differences exist, depending on whether air or pure oxygen is used for oxidation [44]. Shell plants use only pure oxygen, while Scientific Design and UCC have developed air-based oxidation plants as well. Figure 5 shows a simplified scheme for both the air- and oxygen-based processes. They both employ a recycle gas stream, which is continuously circulated through the reactors by compressors. The reactors consist of large bundles of several thousand tubes that are 6 – 13 m long and have an internal diameter of 20 – 50 mm. The catalyst is packed in the tubes in the form of spheres or rings with a diameter of 3 – 10 mm; the initial selectivity of modern catalysts is ca. 80 – 90%, depending on the type of catalysts used. The catalysts are either very active, operating at an initial temperature of about 200 °C but with relatively low selectivities of 80 – 84 %, or they are highly selective but then need an initial temperature that is ca. 40 °C higher. Ethylene is converted at 200 – 300 °C and 1 – 3 MPa to produce ethylene oxide, CO₂, H₂O, and heat, as well as traces of acetaldehyde and formaldehyde; these products must be removed or separated from the recycle gas stream. The recycle gas is then reloaded with oxygen and ethylene and returned to the reactor.

Oxygen-Based Oxidation Process. At present, ethylene oxide is produced mainly by the oxygen-based process. The reactor tubes filled with the catalyst are surrounded by a coolant (water or a high-boiling hydrocarbon) that removes the reaction heat and permits temperature control. Heat is extracted either by pumping or by evaporating the coolant. If organic heat transfer media are used, the extracted energy is used to generate steam in secondary cycles, which is then employed for heating. The reaction heat also heats the recycle gas during its passage through the reactor. After leaving the reactor, the gas is likewise cooled by means of steam generation and/or used directly to heat the reactor inlet gases. Because of the different enthalpies of the partial and total oxidation reactions (see Section 4.1), the total available heat depends on the selectivity for the former (S) and amounts to 47 250 – (434×S) kJ/kg ethylene.

Consequently, the quantity of energy released increases rapidly with decreasing selectivity.

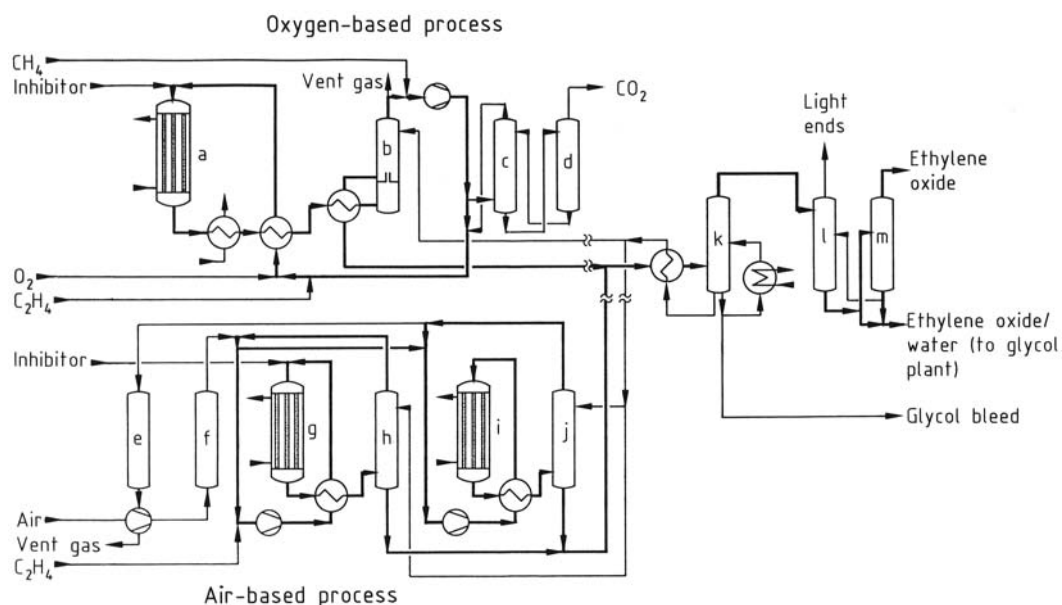


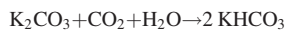
Figure 5. Flow scheme for ethylene oxide production by the oxygen-based or air-based oxidation of ethylene
 a) Reactor; b) Ethylene oxide scrubber; c) CO₂ scrubber; d) CO₂ desorber; e) Off-gas purification; f) Air purification; g) Primary reactor; h) Primary ethylene oxide scrubber; i) Secondary reactor; j) Secondary ethylene oxide scrubber; k) Ethylene oxide desorber; l) Stripping column; m) Ethylene oxide distillation

Therefore, the heat removal system must be sufficiently adaptable to cope with growing heat release in the reactor at rising reaction temperatures during the aging process of the catalyst, which is characterized by a decrease in its selectivity and activity in the course of its on-stream time. Temperatures on the coolant side (water or organic) of the catalyst tubes are restricted by the maximum design pressure, which usually does not allow temperatures higher than 300 °C. When the maximum temperature is reached the catalyst must be replaced.

After the gas from the reactor has been cooled, the ethylene oxide (1 – 2 %) and CO₂ (5 – 10 %) must be removed by scrubbing first with water and then with an aqueous potassium carbonate solution. In the ethylene oxide scrubber, virtually all of the ethylene oxide and small amounts of the other constituents of the recycle gas (CO₂, N₂, CH₄, CH₂CH₂, and aldehydes) dissolve in the water. The resulting aqueous ethylene oxide solution then passes to the ethylene oxide desorber. The ethylene oxide recovered as the head product in the desorber is subsequently stripped of its low-boiling components (i.e., the above-mentioned components of the recycle gas) and

finally distilled, thereby separating into water and ethylene oxide.

A small proportion of the gas leaving the ethylene oxide scrubber (0.1 – 0.2 %) is removed continuously (combusted) to prevent the buildup of inert compounds (N₂, Ar, and C₂H₆), which are introduced as impurities with the reactants: ethylene (C₂H₄) and oxygen (Ar and N₂). The recycle gas from the scrubber is compressed, and a side stream is freed from carbon dioxide by further scrubbing with hot aqueous potassium carbonate solution. This leads to removal of the CO₂ not only by physical dissolution but also by reaction with potassium carbonate to give the hydrogencarbonate.



The potassium carbonate solution, which is enriched with CO₂ is sent to the CO₂ desorber, where the CO₂ is stripped off at atmospheric pressure and is either released into the atmosphere or fed to a CO₂ utilization plant, after optional catalytic treatment (e.g., supported Pd/Pt) to remove residual hydrocarbons. The concentrations of the reactants in the bulk of the

recycle gas, which is free from ethylene oxide and has a reduced CO₂ content, are restored to their starting levels by separate addition of oxygen, ethylene, inhibitor (1,2-dichloroethane, ethyl chloride or vinyl chloride), and if necessary, a diluent (CH₄). The gas is then returned to the reactor.

The oxygen that is used must be extremely pure (> 99%) and is obtained by air separation. Nevertheless, a purge stream of recycle gas is still necessary due to the presence of traces of N₂ and Ar. Oxygen is added in a special mixing device that ensures rapid homogenization with the recycle gas. This is necessary because the explosive limit is locally exceeded at the mixing point.

The ethylene is also usually very pure (> 99.5%) and must be free from the strong catalyst poisons sulfur and acetylene. Methane, used as a diluent, also must be free from sulfur compounds.

Natural gas is used as methane source and usually requires cleaning steps to attain the required purity. Sulfur compounds, which poison the catalyst irreversibly, are removed by adsorption beds. Higher hydrocarbons, which affect the reactor performance, mainly by removing the chlorine inhibitor from the silver surface, are removed by distillation or with molecular sieves.

Air-Based Oxidation Process. The air-based process is similar to the oxygen process, but some differences exist. Air introduces a large amount of nitrogen into the recycle gas, which means that a large amount of purge gas must be vented to maintain a constant nitrogen concentration in the recycle stream. The quantity of gas that is vented removes sufficient CO₂ to make CO₂ scrubbing unnecessary. However, the off-gas leaving the primary reactor still contains so much ethylene that it must be further converted in a subsequent secondary or purge reactor before it can be vented into the atmosphere.

The reaction conditions cannot be tailored to the needs of ethylene oxide formation as optimally as in the oxygen-based process. The conversion of ethylene is higher than in the oxygen-based process, especially in the secondary reactors, so as to obtain an acceptable level of ethylene loss in the purge gas. Since selectivity is inversely related to ethylene conversion, it follows that the air-based process has a lower selectivity.

Table 5. Operating parameters used in the air-based and oxygen-based production of ethylene oxide

Parameter	Air-based process	Oxygen-based process
C ₂ H ₄ concentration, vol %	2 – 10	15 – 40
O ₂ concentration, vol %	4 – 8	5 – 9
CO ₂ concentration, vol %	5 – 10	5 – 15
C ₂ H ₆ concentration, vol %	0 – 1	0 – 2
Ar concentration, vol %		5 – 15
CH ₄ concentration, vol %		1 – 60
Temperature, °C	220 – 277	220 – 275
Pressure, MPa	1 – 3	1 – 2.2
GHSV ^a , h ⁻¹	2000 – 4500	2000 – 4000
Pressure drop, kPa	40 – 200	
C ₂ H ₄ conversion, %	20 – 65	7 – 15
Selectivity, %	80	80 – 90

^aGHSV = gas hourly space velocity.

The conditions and gas compositions used in the oxygen- and air-based processes are listed in Table 5.

Reactor. Since oxidation of ethylene is highly exothermic, reaction in a fluidized bed would appear to be appropriate. However, attempts to develop such a process on a commercial basis have not produced any advantages for selectivity [98], [99] and have led to problems due to abrasion and sintering. As a result, all ethylene oxide plants currently employ fixed-bed tubular reactors. The diameter of the tubes must not be excessive so as to ensure sufficient heat transfer to the heat transfer medium. A tube diameter of 20 – 40 mm is common. The diameter of the catalyst particles has an upper limit determined by the need for satisfactory gas mixing and a lower limit resulting from an increasing drop in pressure. A diameter of 3 – 8 mm is used.

Cooling. Each of the two possible heat extraction systems – circulation or evaporation of the coolant – has its advantages and disadvantages. Coolant circulation requires a large amount of liquid (pumping power), but allows a defined temperature increase in the direction of gas flow. Ethylene and oxygen concentrations in the cycle gas decrease on passage through the reactor; this leads to lower conversion, which can be compensated by controlled temperature increase toward the reactor outlet.

In evaporative cooling, an organic coolant (e.g., isododecane) or water is used. The reaction temperature is controlled very effectively by a

control valve that keeps the pressure of the boiling coolant at the appropriate pressure. The whole temperature range from 190 to 290 °C, required by the aging catalyst, can be covered by evaporative cooling. Organic coolants with a boiling point of about 190 °C at atmospheric pressure are used. The hydrostatic height of the coolant in the reactor results in an unavoidable temperature increase towards the bottom of the reactor. Since evaporation extracts heat more efficiently than circulation, evaporative cooling requires a smaller volume of circulating coolant. The axial temperature differences can be minimized more easily. Large amounts of liquid coolant leave the reactor with the coolant vapor. The liquid is recovered in a separator and returned to the reactor. The coolant present in the reactor and in the separator constitutes a safety reserve during uncontrolled increases in ethylene conversion in the reactor (“runaway”).

The flammability of organic coolants is a clear disadvantage compared to water, especially at the necessary high temperatures. However, water results in much higher pressures on the coolant side and hence higher apparatus costs.

When organic coolants are used, the coolant vapors are condensed in heat exchangers producing steam, after which the liquefied coolant is returned to the reactor. The steam serves to heat distillation columns in the plant. If water is used as coolant the steam leaving the reactors can be used directly. The higher the selectivity of the catalyst, the more steam must be imported into the plant.

Improved catalysts with high activities and selectivities operate at a lower temperature (ca. 220 °C) and allow smaller reactor volumes. This has encouraged the use of water-cooled reactors; however, organic heat transfer media (e.g., Dowtherm) are still widely employed. A detailed discussion of heat transfer with organic heat transfer media in terms of optimum selectivity and safety can be found in [100].

Ethylene Conversion. The selectivity of ethylene oxide formation depends on ethylene conversion. Selectivity decreases more or less linearly with increasing ethylene conversion [101]. Therefore, the highest selectivities are achieved with minimum conversions, but the resulting ethylene oxide concentrations are then too low for commercial purposes. Thus, ethylene

conversion is chosen to achieve ethylene oxide concentrations of 1–3 vol % at the reactor outlet.

Byproducts. Besides large quantities of CO₂ produced by total oxidation of ethylene, ethylene glycols and small amounts of acetaldehyde and formaldehyde are formed and must be processed in ethylene oxide plants. The acetaldehyde stems from isomerization of ethylene oxide, catalyzed by the catalyst support and by rust on apparatus walls. Formaldehyde is produced by oxidation of ethylene oxide with and without participation of the wall surface [102]. Ethylene glycols are unavoidably produced when ethylene oxide is scrubbed from the recycle gas with water and is subsequently stripped from the aqueous solution by heating. Monoethylene glycol [107-21-1], diethylene glycol [111-46-6], triethylene glycol [112-27-6], and higher poly (ethylene glycols) are formed when ethylene oxide comes into contact with water [103] (→ Ethylene Glycol). Some of the cycle water must be bled off continuously and the ethylene glycol removed to prevent it from accumulating (see Fig. 5). This glycol is of inferior quality to that synthesized by ethylene oxide hydrolysis. Special methods for purifying the resulting glycols have been described, e.g., treatment with ion exchangers and activated charcoal [104].

Materials. Since ethylene oxide is noncorrosive, the reactors and the sections of the plant that convey ethylene oxide are usually made of mild steel. To reduce the formation of acetaldehyde by isomerization of ethylene oxide on rust, stainless steel is increasingly being used for the reactors and the ensuing cycle gas lines, where temperatures are highest. The sealing materials for valves, flanges, and pumps must be chosen carefully [105]. Many materials used in chemical industry for O-rings, packings, and gaskets are not resistant to the influence of ethylene oxide and have been the cause of severe incidents [106]. The materials in the system used to remove the carbon dioxide must also be carefully selected because of possible CO₂ corrosion [107].

If rust is present in steel tubes or containers, polymer formation [38], increased viscosity, and brown discoloration are to be expected.

Current plant design is predominantly tailored to the oxygen-based process because this is nor-

mally more economical than the air-based process. In exceptional cases, however, the air-based process may be preferred depending on local factors (e.g., the availability of oxygen) [108].

Possible Developments. Alternative routes from ethylene to ethylene oxide are being studied, e.g., Tl(III)-catalyzed oxidation in solution [108], electrochemical oxidation [109], and enzymatic oxidation [110]. However, these processes appear to be far from industrial application. About half of the ethylene oxide produced is converted into ethylene glycol. Alternative syntheses for ethylene glycol based on carbon monoxide, formaldehyde, and ethylene are being developed [111–114] (\rightarrow Ethylene Glycol); these are more promising than those for ethylene oxide. With increasing raw material prices, the appearance of an economical alternative is foreseeable. Naturally, such an alternative would have an adverse effect on ethylene oxide capacities, but the economics of ethylene oxide production could be improved by

1. Selective production of monoethylene glycol from ethylene oxide, without the formation of higher ethylene glycol homologues, e.g., via glycol carbonate [44]
2. Reducing energy consumption
3. Improving the selectivity, capacity, life-span, and activity of the catalysts

5. Environmental Protection and Ecology

Ethylene oxide plants using the direct oxidation process represent a clear environmental improvement over the chlorohydrin process. Environmental and other important aspects of ethylene oxide production are discussed in EPA studies [115]. Both oxygen- and air-based plants emit two main off-gas streams: recycle vent gas and CO₂. In the oxygen-based process, ca. 70 % of the recycle vent gas consists of hydrocarbons (ethylene and methane), which can be combusted (by torch or in a steam generator). The corresponding off-gas in the air-based process is produced in considerably greater quantities, but contains only up to ca. 2.3 % hydrocarbons. It can be purified by catalytic oxidation. The CO₂-rich vent gas in the oxygen-based process contains ca. 0.2 % hydro-

carbons. This concentration can be reduced substantially by depressurizing the CO₂-rich absorbent in two steps. The gas from the first step is rich in hydrocarbons and is recycled, only the gas from the second step is vented [116]. A catalytic treatment (e.g., supported Pd/Pt) may be required by environmental regulations to remove hydrocarbons before the CO₂ is released to the atmosphere but may also be necessary to ensure the purity of the CO₂ for further use. The CO₂-rich vent gas stream from air-based plants is produced in much smaller quantities and contains ca. 5 % hydrocarbons that can be removed by combustion. Ethylene oxide can be removed from waste gases, such as are generated during sterilization, by combustion with oxygen [117] or by an acid scrub [118], [119], [121]. Biodegradation of the ethylene glycol generated during ethylene oxide hydrolysis presents no difficulties. If ethylene oxide occurs as a mixture with fluorohydrocarbons, recovery by drying and subsequent compression is recommended [120]. Methods for handling ethylene oxide reaction vessels without the release of vent gas have been described [122].

Ethylene oxide is toxic to microorganisms and fish [123]. The LC₅₀ value for fish (*Pimephales promelas*) is 84 mg/L (exposure time 96 h). However, in free-flowing waters the ethylene oxide concentration decreases continually (after 4 h at 25 °C in moving water, the concentration drops by ca. 95 %) due to a combination of evaporation, hydrolysis (half-life at 25 °C ca. 14 d), and biodegradation. The ethylene glycol produced as a result of ethylene oxide hydrolysis is considerably less toxic to aquatic organisms (LC₅₀ > 10 000 mg/L) and is readily biodegradable. Effluents (e.g., from ethylene oxide production plants [115]) containing ethylene oxide are therefore treated biologically after the ethylene oxide has been converted into ethylene glycol.

Degradation of ethylene oxide in air is relatively slow and thought to proceed mainly by a slow reaction with hydroxyl radicals. Disregarding other removal mechanisms, this results in a lifetime of 330 d. The reaction with ozone is too slow to represent a significant removal pathway [124]. Another report indicates a lifetime of 100 – 200 d [125]

According to TA Luft [126], vent gas streams must not contain more than 25 g/h or 5 mg/m³ ethylene oxide.

Table 6. Typical specifications of ethylene oxide

Appearance	clear, colorless
<i>bp</i> at 101.3 kPa	10.8 °C
Water content*	50 mg/kg
CO ₂ content*	10 mg/kg
Aldehyde content*	50 mg/kg
Ethylene oxide content (min.)*	99.5 %

* As determined by gas chromatography.

6. Quality Specifications

Ethylene oxide is a major industrial product that is obtained with a consistently high purity irrespective of the production process used. Typical specifications are given in Table 6.

7. Analysis

An overview of analytical methods for ethylene oxide can be found in [127]. An established method for determining ethylene oxide is based on its reaction with MgCl₂ [128]. In view of the low TRK value (5 mg/m³), accurate methods are needed to determine traces of ethylene oxide in air.

An adsorption chromatography method is reported to be suitable for concentrations exceeding 0.15 ppm [129]. The NIOSH method 1607 [134] with a working range of 0.04 – 1.7 ppm (0.09 – 3 mg/m³) is based on adsorption with charcoal, derivatization with HBr to give 2-bromoethanol, and gas chromatography. The CS₂ used in the NIOSH method can be replaced by *N,N*-dimethylacetamide [130]. Methods using adsorption on charcoal are susceptible to the influence of temperature and humidity [131], [132].

A field comparison of four methods of monitoring ethylene oxide by portable devices – two passive monitors, one sorbent tube (OSHA), and one GC method (NIOSH) – showed their viability for measuring the workplace concentration for short-term and full-shift exposure [133].

Exposition to ethylene oxide can be monitored by the detection of (2-hydroxyethyl) valine in hemoglobin, the method resulting in accurate data of time-integrated exposure [39].

8. Handling, Storage, and Transportation

Ethylene oxide has repeatedly caused serious explosions, fires, and accidents [106], [135], [136]. It is an extremely hazardous substance because it can explode and is both highly flammable and extremely reactive (exothermic reactions). Aqueous solutions containing > 4 wt % ethylene oxide are flammable; flash points are given in Table 2. Furthermore, ethylene oxide is toxic and poses a danger both to health and to the environment. The inherent hazards of the product must be known; all prescribed safety measures and legal requirements must be observed. Personnel handling ethylene oxide must receive appropriate training.

Safety precautions for handling ethylene oxide and its dangerous properties are described in detail in the data sheets provided by the manufacturers (e.g., [106], [137]) and elsewhere (e.g., [105], [138–141]). Therefore, only the most important points are discussed here.

Explosion and Fire Control. Pure ethylene oxide vapor or ethylene oxide vapor mixed with air or inert gases can decompose explosively. Explosiveness depends on pressure, temperature, concentration, the type, form, and energy of the ignition source, and the type of container. High pressure can be generated on explosion of ethylene oxide; therefore, for safe handling the exact explosive limits must be known. Pure ethylene oxide vapor at 101.3 kPa decomposes when passed through a heated platinum coil [142]. The temperature at which decomposition starts (decomposition temperature) was calculated to be 571 °C. Calculations were based on the temperature at the tube exit and the thermodynamic data for ethylene oxide and its decomposition products. The thermal decomposition of ethylene oxide and ethylene oxide – nitrogen mixtures has been investigated [143]. If ethylene oxide vapor is introduced into a preheated vessel at 101.3 kPa, explosive decomposition takes place at ca. 500 °C [143]. The decomposition temperature is reduced by an increase in the pressure (e.g., ca. 450 °C at 1 MPa) but is increased by the addition of nitrogen. Explosive thermal decomposition is still possible below atmospheric pressure, but the necessary temperature then increases above 500 °C.

The ignition properties of ethylene oxide and its mixtures with air and inert gases have been studied by several authors. Pure ethylene oxide vapor can ignite even at a pressure as low as 48 kPa (electric spark) or 20.2 kPa (mercury fulminate) [144]. The maximum theoretical explosive pressure is ca. 10 times the initial pressure, but can increase to 20 times the initial pressure if liquid ethylene oxide is present. This phenomenon occurs because liquid ethylene oxide evaporates and participates in the decomposition reactions that take place in the vapor phase [145]. Mixtures of ethylene oxide with N_2 , CO_2 , methane, and air do not ignite over certain concentration ranges; the upper explosive limit is always 100% ethylene oxide, since pure ethylene oxide also decomposes if ignited. In the presence of oxygen (air), combustion and decomposition take place simultaneously and the ignition temperature (or energy) is reduced. The ignition temperature of ethylene oxide in air at 101.3 kPa is 429 °C [146]. As the ethylene oxide concentration increases, the proportion destroyed by decomposition also increases [21], [147]. The minimum value cited for the lower explosive limit of ethylene oxide – air mixtures is 2.6% [148]; the explosive range of ethylene oxide – air mixtures is accordingly 2.6 – 100%. Figures for an upper explosive limit of ca. 80% at 101.3 kPa are probably due to differences in the apparatus and methods used [149–151].

Explosive decomposition of ethylene oxide in closed containers can be suppressed by blanketing with an inert gas until the total pressure of the nonexplosive range is reached. Blanketing agents with higher thermal conductivities suppress explosions more effectively. Quotation of the minimum total pressure necessary for inert gas blanketing is important; values cited in [21] were obtained without consideration of the pressure and temperature dependence and, therefore, do not apply at higher pressures. Figure 6 shows the total pressure currently recommended for inert gas blanketing of ethylene oxide with nitrogen as a function of temperature [105]. The explosive limits of other mixtures of ethylene oxide with inert gases and air can be found in the literature, e.g., ethylene oxide with H_2O [152]; N_2 [143], [152]; $N_2 - H_2O$ [144]; $CO_2 - H_2O$ [144]; CH_4 [145]; CO_2 [21], [152], [153]; C_3H_6 [154]; C_4H_9 [154]; $N_2 - air$ [21]; $CH_4 - air$ [21]; $CO_2 - air$ [148]; $CF_2Cl_2 - air$ [151], [155].

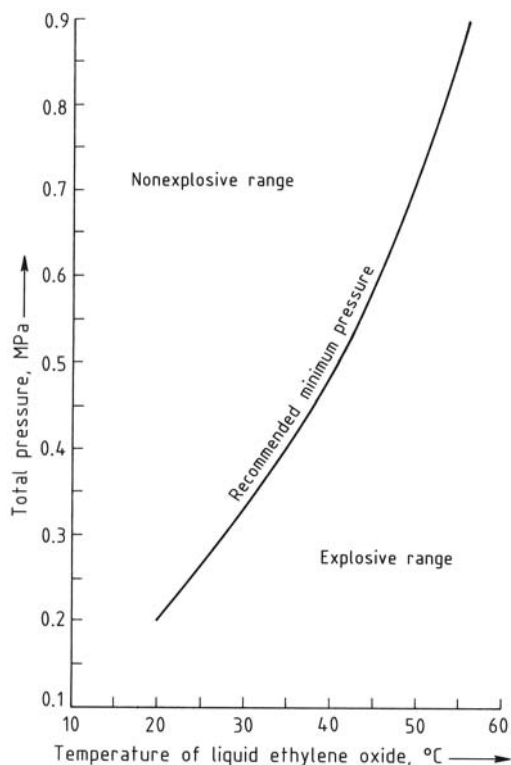


Figure 6. Recommended total pressure for the safe storage of ethylene oxide as a function of the temperature of liquid ethylene oxide after blanketing with nitrogen

As has already been explained, liquid ethylene oxide can participate in the decomposition that is initiated in the vapor phase. Explosion of liquid ethylene oxide initiated by an ignition source within the liquid was first described in 1980 [156], [157], but once again, the decomposition reaction is thought to take place in the gas phase created by the source of ignition and is maintained by the subsequent evaporation of ethylene oxide. Figure 7 shows the temperature limits for ignition of liquid ethylene oxide as a function of the pressure. At pressures between 10 and 15 MPa, the ignition temperature decreases rapidly. This phenomenon is presumed to be due to the fact that the critical state is reached. The conditions under which liquid ethylene oxide is usually produced, stored, or processed lie within the nonexplosive range (Fig. 7).

The highly exothermic reactions of ethylene oxide represent a further hazard [135]. If traces of polymerization initiators (e.g., amines) find their way into a large supply of ethylene oxide (e.g., in

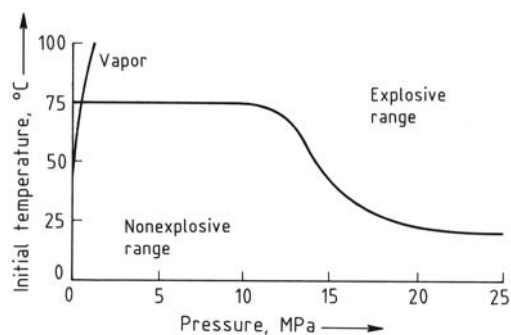


Figure 7. Explosive limits for pure liquid ethylene oxide as a function of pressure and temperature

a tank), polymerization starts slowly and then accelerates because of the resulting temperature increase. Polymerization proceeds quasi-adiabatically, leading to sudden and rapid increases in temperature and pressure that can rupture the container [158], [159], which may be followed by explosive decomposition of the released ethylene oxide vapor (see Fig. 8).

Although rust is only a mild catalyst for ethylene oxide polymerization, its presence in heat exchangers or other hot equipment can lead to ignition of the ethylene oxide vapor by a combination of polymerization and disproportionation to C_2H_4 , CO_2 , H_2 , and H_2O (explosion in the UCC plant, Seadrift, 1991). γ - Fe_2O_3 and γ - $FeOOH$ are the active species in this reaction [160].

Insulation fires can occur if ethylene oxide leaks into insulating material such as asbestos, magnesium silicate, calcium silicate, and mineral

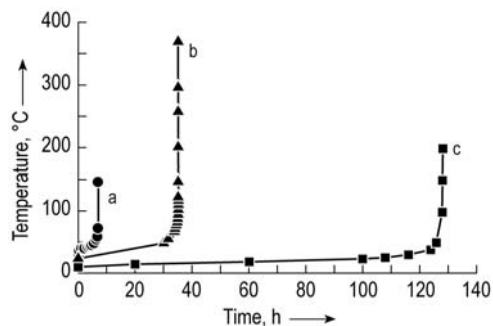


Figure 8. Runaway reactions of ethylene oxide (EO) [169] a) Dewar polymerization of EO (10 ml)/NaOH (0.02 g)/ H_2O [167]; b) Calculated adiabatic reaction of EO (40%) in H_2O (initial temperature 27 °C) [168]; c) Polymerization of EO/ NMe_3 (0.184 %)

wool by a combination of effects and reactions. Like other organic compounds, ethylene oxide can have considerably lower autoignition temperatures in insulation material than otherwise [161], [162]. Isomerization of ethylene oxide to acetaldehyde in the presence of rust results in an additional decrease in the autoignition temperature [141]. In the presence of water, ethylene oxide may be hydrolyzed to ethylene glycol and subsequently polymerize to poly(ethylene glycols) with evolution of heat. Eventually, the organic material collected in the insulation (ethylene oxide, acetaldehyde, glycols) may be oxidized by air. The resulting hot spots on the surface of the apparatus can trigger an explosive decomposition of ethylene oxide vapor in the column (explosion in the BP plant, Antwerp, 1987 [163] and in the BASF plant, Antwerp, 1989 [164]). To avoid these risks, special insulating material with a low specific surface and closed cells (glass foam) is used, and special methods for insulation have been developed. A gap between the outer wall of the apparatus and the insulation prevents accumulation of organic material in the insulation and allows monitoring of organic compounds in the gap.

The accidents in ethylene oxide plants also initiated a fundamental reevaluation of the distillation section. The use of structured packing instead of trays can prevent the propagation of ethylene oxide decomposition. A beginning decomposition in the column can be recognized in time to be quenched with water [165], [166].

Because of the above-mentioned hazards, the following potentially dangerous situations must be prevented:

1. Leakage of liquid or gaseous ethylene oxide
2. Entry of air, oxygen, or reactive impurities into ethylene oxide containers
3. Ignition sources in danger areas
4. Overheating of ethylene oxide (chemical reaction, fire, etc.)

Leaks or spills should be promptly diluted with sufficiently large volumes of water to reduce the ethylene oxide concentration to less than 4 wt %. Mixtures of ethylene oxide and water will still burn if the ethylene oxide concentration exceeds 4 wt %. Fires should also be extinguished with large volumes of water, carbon dioxide extinguishers can be used for small fires.

Storage and Transportation. Ethylene oxide is transported in tank cars and containers and can be conveyed by rail or by sea and, in many countries, also by road. In Germany, conveyance by road is possible with special permission and under certain conditions (GGVS/ARD § 7). Hazard classifications for ethylene oxide follow:

Water hazard class	WGK 2 (no. 235)
CFR 49	no. 172.101, flammable liquid
GGVS/GGVE/RID/ADR	class 2, no. 4 ct
ADNR	class 2, no. 8 AF
EMS	2-06
MFAG	365
GGVSee, IMDG Code	class 2
UN no.	1040
JATA no.	722
Temperature class (DIN 57 165)	2
Explosion limit (DIN 57 165)	IIB

Storage and transport containers for ethylene oxide are usually made from steel, but steel is suitable only if special measures have been taken to prevent rust formation [38]. Rust acts as a mild polymerization catalyst and is dispersed in the ethylene oxide by polymerization starting on available surfaces. Polymer concentrations as low as ca. 110 mg/kg produce an increase in viscosity, may cause brown discoloration, may block filters, valves etc., and form deposits on the container walls. Therefore, steel containers should be blasted before first use, the blasting residues carefully removed, and the container flushed with nitrogen. Stainless steel is increasingly being used to avoid these problems. When aqueous solutions of ethylene oxide are handled, precipitation of solid hydrates (cf. Table 2) may cause blockages.

In Europe, tank cars are tested at a pressure of 1.6 MPa and they must be protected from the sun by a protective roof or insulation (GGVE). Ethylene oxide – nitrogen mixtures can be transported at a maximum pressure of 1 MPa at 50 °C (GGVS/RID). The proportion of nitrogen in the vapor phase must be high enough to ensure that explosion cannot occur at or below this temperature. In the United States railroad tanks are insulated and equipped with pressure-release valves.

Safety measures that should be observed when reactions with ethylene oxide are performed or when it is used for sterilization can be found in [105].

Personal Protective Equipment. To avoid skin contact with ethylene oxide, goggles as well as protective clothing (gloves, boots, suits, aprons) have to be used. As ethylene oxide permeates easily through most materials, the choice of an adequate material is crucial. Butyl rubber is normally a suitable material, but as quality and thickness play an important role, a test of the permeation resistance against ethylene oxide is recommended before use.

Leather clothing and footwear represent an often neglected risk when contacted with ethylene oxide or its aqueous solution, because the severe and slowly healing damage to the skin appears only after a induction period of many hours. Therefore leather articles must be discarded at once when contaminated with ethylene oxide. Other clothing contaminated with ethylene oxide must be taken off immediately and discarded or decontaminated. Immediate flushing with copious water can avoid detrimental action on eyes and skin.

If ethylene oxide concentrations of 0.25 ppm in the air are reached, respiratory equipment must be used [170]. Gas masks are permitted only up to certain exposure limits, and their duration of use is restricted according to the ethylene oxide concentration [171]. Beyond a certain concentration level, equipment has to be used which is independent of the ambient atmosphere (e.g., positive-pressure self-contained breathing apparatus) [172]. Also above ethylene oxide concentrations of 0.25 ppm restrictions in the employment of juveniles and pregnant women are effective [170].

9. Uses

Ethylene oxide is an excellent disinfectant, sterilizing agent, and fumigant when it is used as a nonexplosive mixture with N₂, CO₂, or dichloro-fluoromethane. The gas penetrates into pores and through packaging or clothing. It can be used, for example, to sterilize surgical instruments in hospitals or to remove pests and microorganisms from spices, furs, etc.

However, most ethylene oxide is converted into other products. Figure 9 shows the percentages of ethylene oxide used in these derivatives in the United States. Although this distribution was determined in 1978, it still applies today and is typical of the world market.

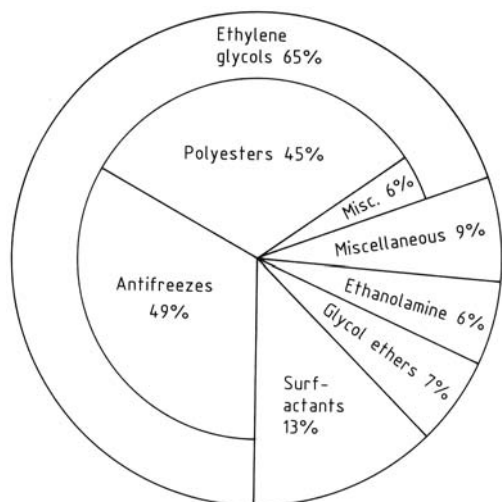


Figure 9. Uses of ethylene oxide

Products derived from ethylene oxide have many different uses, only the most important ones are listed here:

Monoethylene Glycol[107-21-1] [173]: Antifreeze for engines, production of poly(ethylene terephthalate) (polyester fibers, foils, and bottles), and heat transfer liquids.

Diethylene Glycol[111-46-6] [174]: Polyurethanes, polyesters, softeners (cork, glue, casein, and paper), plasticizers, gas drying, solvents, and deicing of aircraft and runways.

Triethylene Glycol[112-27-6] [175]: Lacquers, solvents, plasticizers, gas drying, and humectants (moisture-retaining agents).

Poly(ethylene Glycols) [176]: Cosmetics, ointments, pharmaceutical preparations, lubricants (finishing of textiles, ceramics), solvents (paints and drugs), and plasticizers (adhesives and priinks).

Ethylene Glycol Ethers [177]: Brake fluids, detergents, solvents (paints and lacquers), and extractants for SO₂, H₂S, CO₂, and mercaptans from natural gas and refinery gas.

Ethanolamine [141-43-5] : Chemicals for textile finishing, cosmetics, soaps, detergents, gas purification (H₂S, SO₂, and CO₂).

Ethoxylation Products of fatty alcohols, fatty amines, alkyl phenols, cellulose, poly(propylene glycol) [28]: Detergents and surfactants (nonionic), biodegradable detergents, emulsifiers, and dispersants.

Ethylene Carbonate[96-49-1]: Solvents.

10. Economic Aspects

In 1980, ca. 16 % of world ethylene production was used to synthesize ethylene oxide; this use was second only to polyethylene production (44 %). World production of ethylene oxide in 2000 was ca. 15×10^6 t/a. Ethylene oxide is an important raw material for major consumer goods in virtually all industrialized countries. Table 7 gives an overview of worldwide ethylene oxide capacities. Excess capacities were already apparent in 1984 [178]

11. Toxicology and Occupational Health

The toxicological properties of ethylene oxide are mainly determined by its reactivity with nucleophilic groups such as carboxyl, amino, phenolic hydroxide, or sulfhydryl groups.

In humans, acute inhalative poisoning causes headache, nausea, and vomiting within a few minutes [179–181]. Local irritation results in dyspnea [182]. Myocardial damage [183], excitation, numbness, and finally coma [179] follow. After dermal exposure, blisters are formed on the skin, and symptoms similar to those found after inhalation appear due to skin absorption [184]. Sensitization has been reported after repeated dermal contact [185]. Repeated inhalation of ethylene oxide leads to sensory-motor polyneuropathy and impaired memory [186], [187]. Cataracts may be formed after chronic exposure [188].

Oral Toxicity. The acute oral toxicity (LD₅₀) of ethylene oxide in the rat is 330 mg/kg [189].

Inhalation. The 4-h LC₅₀ value is 835 mL/m³ in the mouse and 1460 mL/m³ in the rat [190]. Acute symptoms largely resemble those observed

Table 7. World ethylene oxide capacities in 2000

Country	Company	Location	Licensor*	Capacity, 10 ³ t/a
Australia	ICI	Botany	SD	40
Canada				775
	Dow	Saskatchewan	Dow	285
	UCC	Prentiss I	UCC	220
		Prentiss II	UCC	270
W. Europe				2615
Belgium	BASF	Antwerp	Shell, s	350
	Ineos	Antwerp	Shell, s	350
Germany	BASF	Ludwigshafen	Shell, s	215
	Erdölchemie	Dormagen	Shell, s	200
	Clariant	Gendorf	Shell, s	200
	RWE/DEA	Marl	Hüls, Shell, s	150
France	BP	Lavera	Shell, s	200
Great Britain	UCC	Wilton	Shell, s	300
Italy	Enichem	Priolo	SD	30
		Gela		40
Netherlands	Dow	Terneuzen	Dow, s	150
	Shell	Moerdijk		250
Sweden	Akzo Nobel	Stenungsund	Nippon Sh./SD, s	80
Spain	La Seda	Tarragona	Shell, s	100
E. Europe				950
Bulgaria	Neftochim	Burgas	SD	80
Slovakia	Slovnaft	Bratislava	Shell, s	40
Poland	Petrochemia	Plock	Shell, s	60
			Snam	30
Romania	Romchim	Brazi	SD	35
	Arpechim	Pitesti	SD	35
Ukraine	Nephtekhim	Dzherzhinsk	SD	200
Russia	Techmashimp.	Khazan	Japan Catalytic	100
		Nishnekamsk	SD	200
		Nishnekamsk	SD	120
	Salavat Neft Org.	Salsvat		50
Asia				3845
China	CNPC	Liaoyang	Hüls, l	60
		Fushun		50
		Jilian		40
		Jilin	SD	80
		Dushanzi		30
	Sinopec	Maoming		80
		Yanshan		65
		Yangzi		240
		Jinshan		130
		Tianjin		55
	Zhejiang Chem. Pet	Zhejiang		20
		Beijing		50
India	Glycols India	Kashipur		20
	Indian PC	Kojali	SD	20
		Vadodana		5
		Nagothane		45
	SM Deyechem Ltd.	Pune	SD/Toyo	20
	Reliance Ind.	Hazira		265
	NOCIL	Bombay	Shell, s	20
Indonesia	O.T. Yasa Ganesha Pura	Merak	SD, s	185
Japan	Nippon Shokubai	Kawasaki	Japan Catalytic	240
	Mitsubishi PC	Yokkaichi	Shell, s	90
	Kashima	Shell, s		240
	Mitsui PC	Chiba	Shell, s	120
	Nisso Murazen	Chiba	SD, s	120
	Nisso Yuka	Yokkaichi	Shell, s	85
	Semppoku EO Daesan	Osaka	Shell, s	130
North Korea		Puyangtang	Japan Catalytic	10

Table 7 (Continued)

Country	Company	Location	Licensor*	Capacity, 10 ³ t/a	
South Korea	Honam PC	Yeochon	Shell, s	115	
		Yeochon	Shell, s	100	
		Yeochon	Shell, s	100	
	Hyundai PC	Daesan	SD, s	90	
		Daesan		160	
		Daesan	SD, s	80	
Singapur	Ethylenegl. Sing.	Merbau	Shell, s	125	
Taiwan	Orient. UCC	Koahsiung	UCC, s	190	
		Koahsiung	SD	40	
	CMFC	Koahsiung	SD	60	
		Mailiao		240	
				720	
Latin America					
Brasil	Oxiteno	Camacari, Bahia	SD, s	130	
			SD, s	105	
		Maua, Sao Paulo	SD, s	45	
Mexico	Pemex	La Cangrejera	SD	110	
		Pajaritos	SD	40	
		Morelos	SD	220	
		Santa Rita	SD, s	70	
Venezuela	Pralca			1370	
Middle East					
Saudi Arabia	Sharq	Al Jubail	Shell, s	360	
		Al Jubail	Shell, s	360	
		Yanbu	SD, s	310	
Kuwait	Equate	Shuiaba		270	
Turkey	Petkim Petro.	Aliaga	Shell, s	70	
United States				4083	
	BASF Wyandotte	Geismar, LA	Shell, s	140	
		Geismar, LA	Shell, s	160	
	Celanese	Clear Lake, TX	Shell, s	305	
		Plaqemine, TX	Dow, l	260	
	Eastman	Longview, TX	Shell, s	100	
	Huntsman	Port Neches, TX	SD, l	455	
	Sun	Brandenburg, KY	Shell, s	55	
	Marcus Hook, PA	Shell, s		55	
		Equistar	Bayport, TX	Shell, s	340
	Shell	Beaumont, TX	SD	308	
		Geismar, LA	Shell, s	165	
	Geismar, LA	Geismar, LA	Shell, s	240	
		Shell, s		180	
	UCC	Seadrift, TX	UCC, l	420	
		Taft, LA	UCC, s	350	
	Nan-Ya	Taft, LA	UCC, l	310	
		Point Comfort, TX	SD, s	240	
	Total				14 396

*l = air process; s = oxygene process; SD = Scientific Design.

in humans. Subchronic administration of ethylene oxide (100 and 200 mL/m³) to cats by means of inhalation for a period of 22 days produced anorexia, apathy, atoxia, and paralysis of the hind quarters [191]. Lethalities also occurred, postmortem examination revealed liver and kidney damage accompanied by hyperemia and perivascular bleeding in various organs (e.g., the brain) [191]. Rodents that inhaled air containing ethylene oxide at a concentration of 300 – 400 mL/m³ displayed additional local

irritation and severe, primary neurotoxic atrophy of the musculature in their hind quarters [190]. Hemotoxic effects have also been observed in rodents [192]. Monkeys exposed to inhalative concentrations of 204 mL/m³ for up to 226 days showed impaired reflexes, reduced sensitivity to pain, and neurotoxic muscular atrophy of their hind quarters [193].

Teratogenicity. In studies on rats exposed to maximum inhalative concentrations of 100

[195] or 150 mL/m³ [195], symptoms of intolerance were observed in the dams but no malformations were observed in the fetuses. Ethylene oxide does not produce teratogenic effects in rabbits [195].

Mutagenicity. Ethylene oxide is mutagenic due to its alkylating properties. It alkylates the germ cells of male rats [196] and produces mutations in *Drosophila melanogaster* [197], *Neurospora crassa* [198], and *Salmonella typhimurium* (Ames test) [199], [200]. Dominant lethal mutations and chromosome aberrations are induced in male rats [201]. Increased numbers of micronuclei are found in the polynuclear erythrocytes of rats [202] and mice [203], [204]. Chromosomal defects are induced in cultured amniotic cells from humans [205]. Increased exchange between sister chromatids is found in monkeys and rats [206], [207]; the same effect is observed in workers who have been exposed to ethylene oxide (cumulative dose 0.5 – 50 g) [208–211].

Carcinogenicity. A large number of reports have been published on the carcinogenic properties of ethylene oxide in animals. Dilute ethylene oxide applied to the skin of rats did not induce tumor formation [212]. Subcutaneous injection of ethylene oxide in rats did not have any systemic carcinogenic effects [213], [214]. However, intragastric administration led to an increase in the incidence of epithelial carcinomas in the gastric mucosa [215]. An increased incidence of brain tumors and mononuclear cell leukemia was found in rats that had inhaled ethylene oxide at concentrations of 10, 33, or 100 mL/m³ over a period of two years [216]. An increased incidence of peritoneal mesotheliomas was also observed in the animals exposed to concentrations of 33 and 100 mL/m³. Results of human epidemiological studies on workers exposed to ethylene oxide differ [217–220]. Ethylene oxide is classified as a “putative human chemical carcinogen” [221].

Permissible Exposure Limits. Ethylene oxide is classified as a class 2 carcinogen by the German MAK commission (TRK = 1 mL/m³ = 2 mg/m³) and as a class A2 carcinogen by the ACGIH (TLV-TWA = 1 mL/m³ = 2 mg/m³) [222].

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