

AIR



LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF ETHYLENE OXIDE



L & E

EPA- 450/4-84-007L

September 1986

**LOCATING AND ESTIMATING AIR EMISSIONS
FROM SOURCES OF ETHYLENE OXIDE**

U.S. Environmental Protection Agency
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication as received from the contractor. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

EPA - 450/4-84-007L

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1	Purpose of Document	1
2	Overview of Document Contents	3
3	Background	5
	Nature of Pollutant	5
	Overview of Production and Use	7
	References for Section 3	14
4	Emissions from Ethylene Oxide Production	16
	Ethylene Oxide Production	16
	References for Section 4	33
5	Emissions from Industries Which Use Ethylene Oxide	35
	Ethylene Glycol and Its Homologs	35
	Glycol Ethers	41
	Ethanolamines	45
	Ethoxylation	48
	Fumigation/Sterilization	49
	References for Section 5	59
6	Source Test Procedures	61
	Sampling and Analysis	61
	Direct Instrumentation Methods	64
	References for Section 6	66

APPENDICES

A	Derivation of Emission Estimates for Fugitive Equipment Leaks Based on EPA Emission Factors	A-1
---	--	-----

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Physical and Chemical Properties of Ethylene Oxide	6
2	Producers of Ethylene Oxide in the United States in 1986	8
3	Major Users of Ethylene Oxide as a Chemical Feedstock in 1986	12
4	Descriptions of Streams and Vents Illustrated in Figure 3 for the Air Oxidation of Ethylene to Ethylene Oxide	20
5	Descriptions of Streams and Vents Illustrated in Figure 4 for the Oxygen Oxidation of Ethylene to Ethylene Oxide	23
6	Emission Factors for the Release of Ethylene Oxide from an Air-Oxidation Ethylene Oxide Production Plant	31
7	Emission Factors for the Release of Ethylene Oxide from an Oxygen-Oxidation Ethylene Oxide Production Plant	32
8	Types of Ethylene Oxide Sterilization/Fumigation Equipment Used at Different Sites	50
9	Miscellaneous Uses and Use Rates of Ethylene Oxide as a Fumigant and Sterilant	54
10	Selected Procedures for Ethylene Oxide Monitoring	62
11	Selected Ethylene Oxide Direct Monitoring Methods	65
A-1	Fugitive Equipment Leak Parameters - Air Oxidation Model Ethylene Oxide Production Plant	A-2
A-2	Fugitive Equipment Leak Parameters - Oxygen Oxidation Model Ethylene Oxide Production Plant	A-3
A-3	Fugitive Equipment Leaks Control Techniques	A-4

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Locations of Plants Which Manufacture Ethylene Oxide	9
2	End Use Distribution of Ethylene Oxide	11
3	Basic Operations that may be Used in the-Production of Ethylene Oxide by Air Oxidation	19
4	Basic Operations that may be Used in the Production of Ethylene Oxide by Oxygen Oxidation	22
5	Basic Operations that may be Used in the Production of Ethylene Glycol, Diethylene Glycol, and Triethylene Glycol by Conventional Noncatalyzed Hydration of Ethylene Oxide	38
6	Process Operations for Transfer of Ethylene Oxide to the Ethylene Glycol Plant	39
7	Basic Operations that may be Used in the Production of Glycol Ethers from Ethylene Oxide	43
8	Production of Ethanolamines by the Ethylene Oxide-Ammonia Process	47

SECTION 1
PURPOSE OF DOCUMENT

EPA, States and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with ethylene oxide. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of ethylene oxide and making preliminary estimates of the potential for air emissions therefrom.

Because of the limited amounts of data available on ethylene oxide emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about 1) the type of sources that may emit ethylene oxide, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for ethylene oxide to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact

assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions for any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment and operating practices. Thus, in situations where an accurate assessment of ethylene oxide emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2 OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State and local air pollution agencies and others who are interested in locating potential air emitters of ethylene oxide and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of ethylene oxide, its commonly occurring forms and an overview of its production and uses. A chemical use tree is shown along with a table summarizing the quantities of ethylene oxide consumed in various end uses. This background section provides a general perspective on the nature of the substance and where it is manufactured and consumed.

The fourth and fifth sections of this document focus on major industrial sources of ethylene oxide air emissions. Section 4 discusses the production of ethylene oxide and Section 5 discusses the use of ethylene oxide as an industrial feedstock in the production of ethylene glycols, glycol ethers, ethoxylates, and ethanolamines. For each major industrial source category described in Sections 4 and 5, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor information is summarized. The emission factors show the potential for ethylene oxide emissions for uncontrolled

operations as well as operations using controls typically employed in industry. Also presented are names and locations of all major facilities reported to be producing ethylene oxide or using it as a feedstock in other production processes.

Also in Section 5 is a description of the use of ethylene oxide as a fumigant and sterilant. Much of the ethylene oxide used for this purpose is released directly to the atmosphere. Various equipment and procedures for this use of ethylene oxide are described. Use rates are given for the various industries which use ethylene oxide for this purpose.

The final section of this document summarizes available procedures for source sampling and analysis of ethylene oxide. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA has generally not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of ethylene oxide, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 3 BACKGROUND

NATURE OF POLLUTANT

Ethylene oxide (EO) is one of the epoxide family of chemicals. In addition to its International Union of Pure and Applied Chemistry (IUPAC) name, oxirane, it is also called dihydrooxirene; dimethylene oxide; 1,2- epoxyethane; oxacyclopropane; oxane; oxidoethane; and a, b-oxidoethane.¹ The Chemical Abstracts Service (CAS) registry number for ethylene oxide is 75-21-8.

Ethylene oxide is normally handled under pressure as a liquid, but at ambient conditions it is a gas with a pungent, irritating, ether-like odor. It condenses to a colorless liquid at 10°C (50°F). It is completely miscible with water and with organic solvents. Ethylene oxide possesses reactive and volatile properties which make it a highly flammable and potentially explosive chemical. It has a flash point of 8°C (0.4°F) and is flammable in air at concentrations ranging from 3 to 100 volume percent.¹ Having no upper explosive limit, special safety precautions must be taken when handling and storing EO. Additional physical and chemical properties of EO are summarized in Table 1.

Ethylene oxide is reactive in the environment. Its atmospheric residence time, the estimated time in days required for a given quantity to be reduced to 1/e (37 percent) of its original amount, is 5.8 days.² In water, EO reacts with anions such as chloride and carbonate; it has a fresh water (pH 7, 25°C) half-life of 2 weeks and a salt water half-life of 4 days.¹

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF ETHYLENE OXIDE^{1,3,4,5}

Property	Value
Molecular weight	44.053
Physical state, room temperature	gas
Melting point, °C	-112.44
Boiling point, °C	10.5
Density	0.8711
Vapor pressure, torr at 25°C	1305
Viscosity, centipoises at 4°C	0.31
Specific heat, cal/°C-g at 20°C	0.44
Heat of vaporization, cal/g at 1 atm	136.1
Flash point, tag open cup, °C	<-18
Autoignition temperature, °C in air at 1 atm	429
Flammability limits, vol percent	3-100
Heat of combustion, kJ/mol at 25°C	1306.04
Partition coefficient, log P	-0.3
Coefficient of cubical expansion, per °C at 20°C	0.00161
Critical pressure, MPa	7.19
Critical temperature, °C	195.8
Dielectric constant at °C	13.71
Dipole moment, C-m	6.34 x 10 ⁻³⁰
Heat of fusion, kJ/mol	5.17
Refractive index, n _D at 4°C	1.3614
Heat of solution, kJ/mol in pure water at 25°C and constant pressure	6.3
Ionization potential, J	
experimental	1.73 - 1.80 x 10 ⁻¹⁸
calculated	1.65 x 10 ⁻¹⁸
Solubility	Completely soluble in water, acetone, benzene, carbon tetrachloride, ether, methanol
Reactivity	Potentially explosive when heated or when in the presence of alkali metal hydroxides and highly active catalytic surfaces

OVERVIEW OF PRODUCTION AND USE

Ethylene oxide (EO) is produced by direct oxidation of ethylene over a silver catalyst. The oxygen source can be either air or oxygen. Though neither option has been proven to be more economical than the other, there appears to be a trend toward the use of oxygen in newer facilities.⁶ Both options are discussed in this document. An alternative EO production process, with a chlorohydrin intermediate, is no longer used in this country.⁷

About 60 to 77 percent of the ethylene consumed by the oxidation reaction is converted to ethylene oxide.⁵ A side reaction produces carbon dioxide, water, and small amounts of acetaldehyde and formaldehyde.

Twelve companies at 13 locations, most in the Gulf Coast area, produce EO in the United States. Total 1986 capacity is estimated to be 2944 Gg (6490 x 10⁶ lbs).⁸ Table 2 lists these producers, their locations, and their method of oxidation. Figure 1 illustrates the geographical locations of these facilities. In 1983, U.S. production constituted about 40 percent of global EO production.⁹

In the 1970's, the EO industry was operating at more than 80 percent of its production capacity, peaking in 1979 at 2570 Gg (5665 x 10⁶ lbs).¹⁰ Production in 1983 was about 2271 Gg (5003 x 10⁶ lb), which is up slightly from the 2212 Gg (4873 x 10⁶ lb) recorded for 1982.^{10,11,12} Average annual growth for the industry in the past few years has been about 4 percent.⁹

Ethylene oxide can form in the photochemical smog cycle by reaction of ethylene with an organic peroxide by the following mechanism:¹

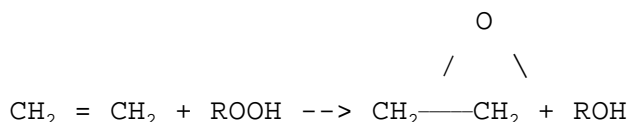
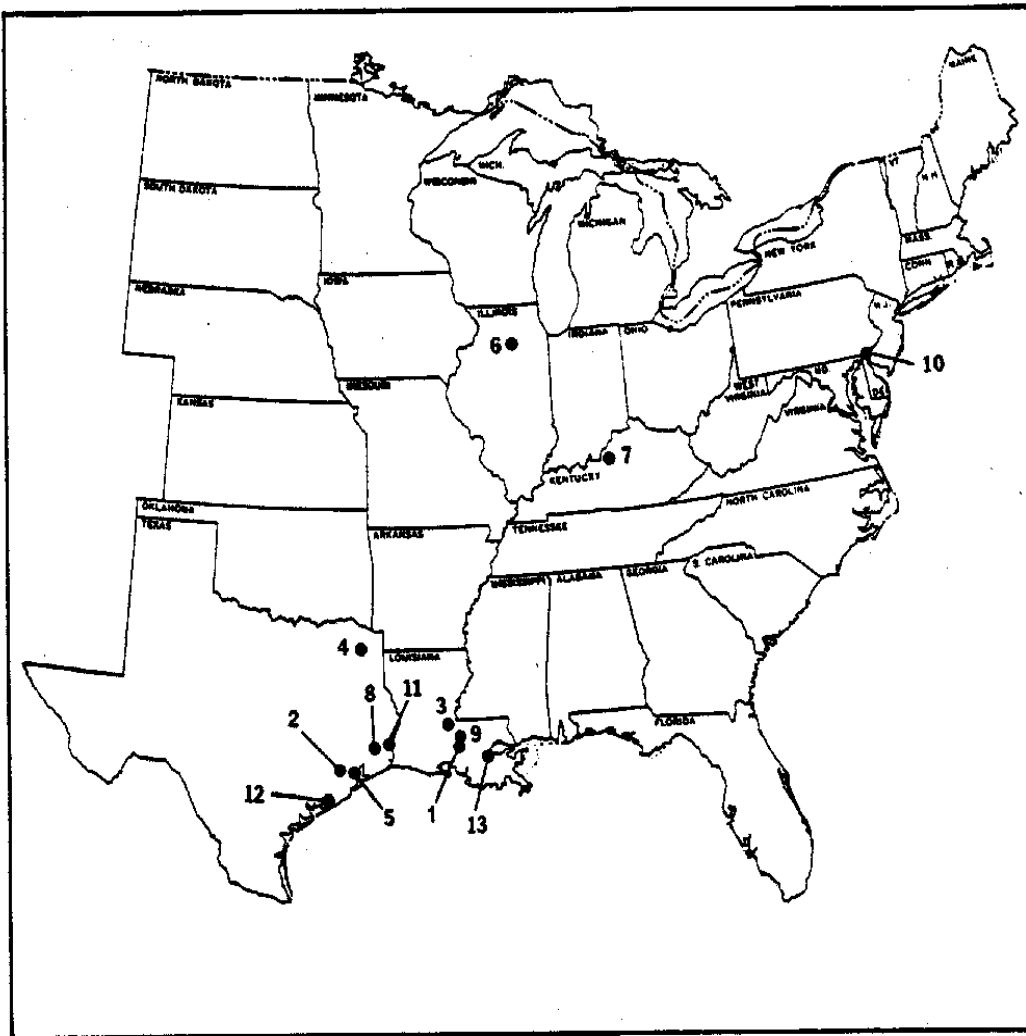


TABLE 2. PRODUCERS OF ETHYLENE OXIDE IN THE UNITED STATES IN 1986⁸

Producer	Location	Process Oxidant
BASF Wyandotte	Geismar, LA	oxygen
Celanese	Clear Lake, TX	oxygen
Dow Chemical	Plaquemine, LA	air
Texas Eastman	Longview, TX	oxygen
ICI Americas	Bayport, TX	oxygen
HNG/InterNorth, Inc.	Morris, IL	oxygen
Olin	Bradenburg, KY	oxygen
PD Glycol	Beaumont, TX	oxygen
Shell	Geismar, LA	oxygen
SunOlin	Claymont, DE	oxygen
Texaco	Port Neches, TX	air
Union Carbide	Seadrift, TX Taft, LA	air air

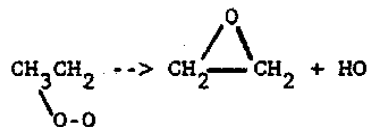
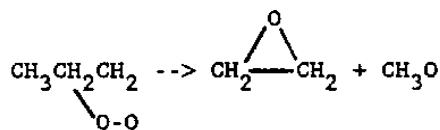
NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of ethylene oxide emissions from any given facility is a function of variables such as capacity, throughput, and control measures. It should be determined through direct contacts with plant personnel.



- | | |
|---|--|
| 1. BASF Wyandotte Corp., Geismar, LA | 8. PD Glycol, Beaumont, TX |
| 2. Celanese Chemical Co., Clear Lake City, TX | 9. Shell Chemical Co., Geismar, LA |
| 3. Dow Chemical Co., Plaquemine, LA | 10. SunOlin Chemical Co., Claymont, DE |
| 4. Eastman Kodak Co., Longview, TX | 11. Texaco, Port Neches, TX |
| 5. ICI Americas, Bayport, TX | 12. Union Carbide Corp., Seadrift, TX |
| 6. HNG/InterNorth, Inc., Morris, IL | 13. Union Carbide Corp., Taft, LA |
| 7. Olin Corp., Brandenburg, KY | |

Figure 1. Locations of plants which manufacture ethylene oxide.⁸

It can also form photochemically from the decomposition of alkyl peroxides:¹



One reference suggests that EO may be present in automobile and stationary source combustion exhaust.¹ However, no direct measurements of such emissions have been found to corroborate this claim.

More than 99 percent of all EO made is subsequently used as a chemical intermediate in the production of mono-, di-, and triethylene glycols, mono-, di-, and triethylene glycol ethers, ethanolamines, surface active agents, and other chemicals.¹ A large portion (about 80 to 90 percent) is used captively by its producers to produce these derivatives.¹³ One reason for immediate captive use is because EO has definite limitations as a transportable commodity due to safety considerations.

Figure 2 illustrates the end distribution of the EO produced in the United States.^{13,14} Major chemical users of EO and EO products are listed in Table 3. Users which are also producers are identified in the table.

Ethylene glycol (EG) is the predominant derivative of EO. Consumption of EO has, in the past, largely depended on the EG market. A major use of ethylene glycol is as automotive antifreeze. It is also used in the manufacture of polyethylene terephthalate (PET) resin plastic film and bottles and in the manufacture of polyester fibers. PET bottles are used in the soft drink industry and have been approved for use by the liquor bottle industry.

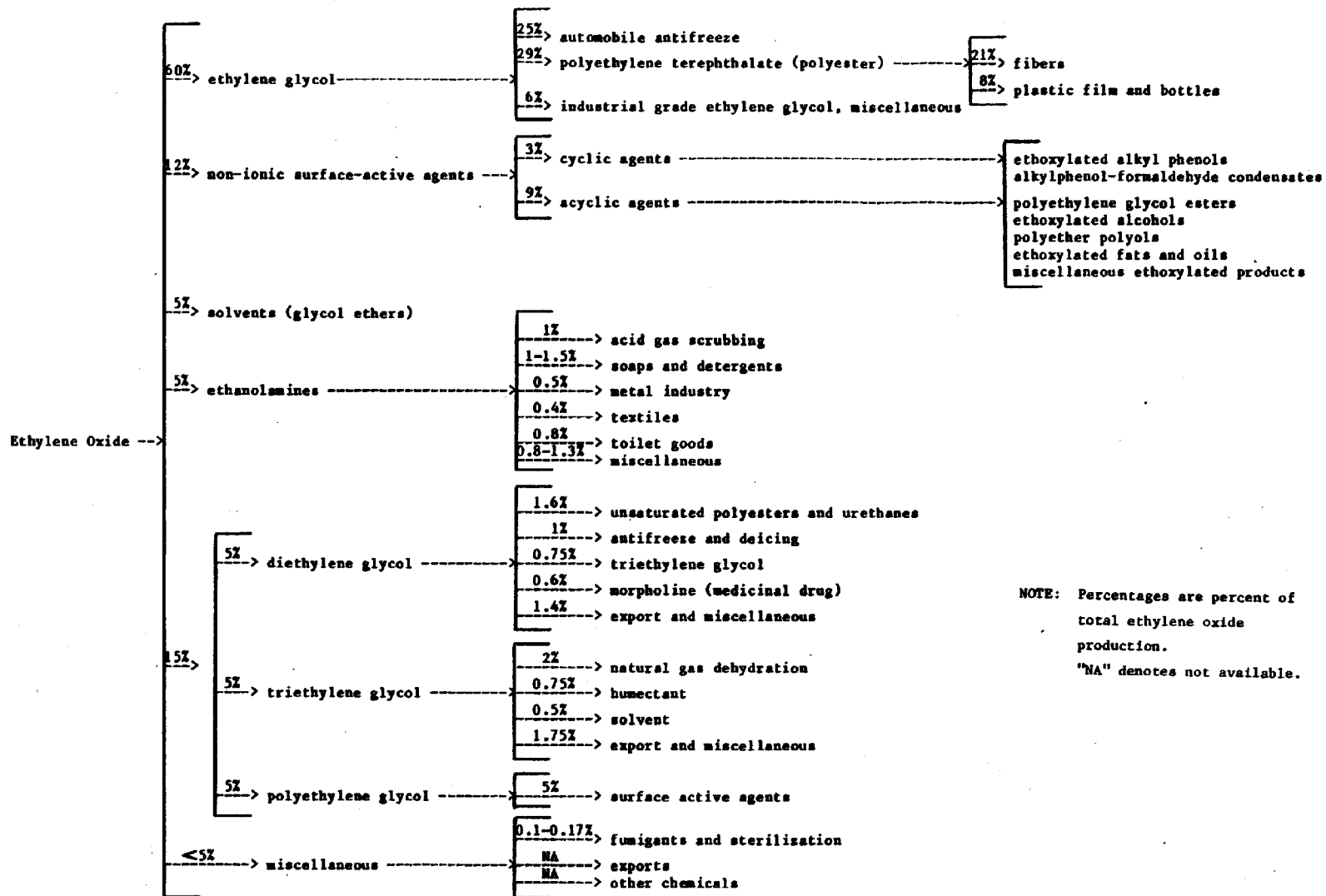


Figure 2. End use distribution of ethylene oxide.^{6,10,13,14}

Owner	Plant Location ^b	ethylene glycol	glycol ethers	Product ^a ethanol- amines	diethylene glycol	triethylene glycol	polyethylene glycol
ARCO Chemical Company	Channelview, TX		X ^c				
BASF Wyandotte	*Geismar, LAX Spartanburg, SC Washington, NJ	X			X		X X
Celanese	*Clear Lake, TX	X			X	X	
Dow	Freeport, TX *Plaquemine, LA Midland, MI	X	X X	X X	X	X X	X
ICI Americas	*Bayport, TX	X		X	X		
Hodag Chemical	Skokie, IL						X
National Distillers and Chemicals	Mauldin, SC						X
HNG/InterNorth, Inc.	*Morris, IL	X			X		
Olin	*Brandenburg, KY	X	X	X		X	X
PD Glycol	*Beaumont, TX	X			X	X	
Shell	*Geismar, TX	X	X		X	X	
Texaco	*Port Neches, TX	X		X	X	X	X
Texas Eastman	*Longview, TX	X	X		X	X	
Union Carbide	*Taft, LA *Seadrift, TX Texas City, TX	X X	X X	X	X X X		X
Total Product Capacity (Gg)		2629	483	327	276	68	NA

NA = Not available.

^a An "X" indicates that the facility uses EO to manufacture the indicated product.

^b An asterisk (*) by the plant location indicates that the facility also produces EO.

^c Only produces propylene glycol monoethers.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of ethylene oxide emissions from any given facility is a function of variables such as capacity, throughput, and control measures. It should be determined through direct contacts with plant personnel.

Ethylene oxide is also used as a fumigant, sterilant, and insecticide. It is particularly useful for sterilizing items which would be damaged by heat. For example, EO is used a fumigant/sterilant in the health products and medical fields; in libraries, museums, research laboratories; during beekeeping, dairy packaging, and cosmetics manufacturing; and for animal and plant quarantine at ports-of-entry. It is also used to fumigate spices and seasonings, nut meats, tobacco, transportation vehicles, clothing, furs and furniture.

Some potential exists for volatile substances, including EO, to be emitted from waste treatment, storage, and handling facilities. Reference 15 provides general theoretical models for estimating volatile substance emissions from a number of generic kinds of waste handling operations, including surface impoundments, landfills, landfarming (land treatment) operations, wastewater treatment systems, and drum storage/handling processes. If such a facility is known to handle EO, the potential for some air emissions should be considered.

The Occupational Safety and Health Administration (OSHA) has enacted a 1 ppm, 8 hour time-weighted average occupational exposure standard that may result in some control of EO emissions.¹⁶ OSHA states that the EO producers and ethoxylator industry sectors could use rupture disks for minimizing low-level leakage from pressure relief devices; closed sampling devices at process sampling locations, and vapor-tight unloading connections, magnetic level gauges, and nitrogen purge systems on tank car loading facilities. For operators of large industrial sterilizers, engineering and work practices include changer evacuation systems, liquid/gas separation units to prevent excessive EO emissions during chamber evacuation, local exhaust hoods installed over the sterilizer door, local ventilation of aeration chambers, and allowing the sterilizer contents to aerate for a short period of time after opening the sterilizer door. Hospital sterilizers are smaller than sterilizers used by medical product manufacturers, but the control of EO involves the same principles and types of control equipment and methodology used for industrial sterilizers.

Emission controls are discussed further in Sections 4 and 5 of this report.

REFERENCES FOR SECTION 3

1. Bogyo, D.A., et al. Investigation of Selected Potential Environmental Contaminants: Epoxides. Syracuse Research Corporation, Syracuse, New York. Prepared for the U.S. Environmental Protection Agency, Washington, D.C. March 1980. NTIS Publication No. PB80-183197.
2. Cupitt, L.T. Fate of Toxic and Hazardous Materials in the Air Environment. EPA-600/3-80-084. Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1980.
3. Assessments of Human Exposures to Atmospheric Concentrations of Selected Chemicals. SAI, Inc. Prepared for the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Prepared under EPA Contract No. 68-02-3066. 1981.
4. National Institute for Occupational Safety and Health. Current Intelligence Bulletin 35, 22 May 1981: Ethylene Oxide. DHHS Publication No. NIOSH81-130. Cincinnati, Ohio. 1981.
5. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 9, Ethylene Oxide. John Wiley and Sons. New York, New York. 1980. pp. 432-471.
6. Kuhn, W. What's Ahead for Propylene and Ethylene Oxide. Chemical Engineering Progress. January 1980. pp. 53-56.
7. Kalcevic, V. and J.F. Lawson. Ethylene Oxide. In: Organic Chemical Manufacturing, Volume 9. EPA-450/3-80-028d. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.
8. SRI International. 1986 Directory of Chemical Producers, United States of America. Menlo Park, California. 1986.

9. Ozero, B.J. and J.V. Procelli. Can Development Keep Ethylene Oxide Viable? Hydrocarbon Processing. March 1984. pp. 55-61.
10. Chemical Products Synopsis. Mansville Chemical Products. Cortland, New York. December 1982.
11. Telecon. Smith, C., Radian Corporation with Strasser, J., Chemical Marketing Reporter. May 1983. Ethylene oxide production.
12. Chemical Marketing Reporter. 223(13). 28 March 1983.
13. Markwordt, D.W. Sources of Ethylene Oxide Emissions. EPA-450/3-85-014. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1985.
14. SRI International. Chemical Economics Handbook. Stanford Research Institute, Menlo Park, California. 1980.
15. Farino, W. et al. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. EPA-450/3-84-020. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1984.
16. Federal Register. Volume 50, Number 1. January 2, 1985. pp. 64-77. U.S. Government Printing Office, Washington, D.C.

SECTION 4
EMISSIONS FROM ETHYLENE OXIDE PRODUCTION

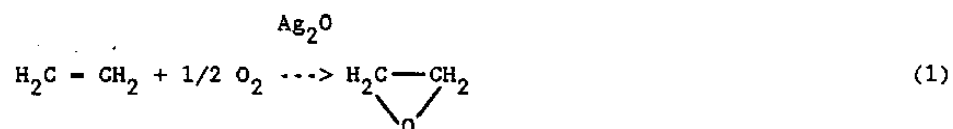
Ethylene oxide can be released to the atmosphere during its production, during its consumption as a raw material in other manufacturing processes, and during its use as a fumigant/sterilant. This section details the production of EO and the emission factors associated with that production. Manufacturing processes which use EO as a feedstock are also described in Section 3, as is the use of EO as a fumigant/sterilant.

ETHYLENE OXIDE PRODUCTION

Process Description ¹⁻³

Ethylene oxide is produced by continuous direct oxidation of ethylene over a silver catalyst. Either air or pure oxygen can be used as the oxidant for the process. Before 1957, ethylene oxide was produced from ethylene with an ethylene chlorohydrin intermediate. This chlorohydrin process for EO production was phased out in the U.S. because it could no longer compete economically with the direct oxidation process.⁴ Of the total amount of EO produced in the United States in 1983, 60 percent was produced at six locations by air oxidation of ethylene; the other 40 percent was produced at nine locations by oxygen oxidation. Neither process is clearly considered economically superior to the other at this time. However, there appears to be a trend toward the use of oxygen in newer facilities.⁵ Plant capacities in the U.S. range from about 50 to 600 Gg/yr of EO production.

In the direct ethylene oxidation process, reactions take place in the vapor phase. The two main reactions are:



The loss of 25 to 30 percent of the ethylene to carbon dioxide and water by Reaction 2 is a major drawback of the oxidation process. Reaction 2 also releases 13 times as much heat energy as does Reaction 1. Reaction 2 can be suppressed by replacing the catalyst regularly and by carefully controlling the temperature on the surface of the catalyst, thereby limiting the conversion of ethylene to CO₂ and H₂O on each catalyst pass to less than 30 percent. These reactions also produce small amounts of acetaldehyde (less than 1 percent of the EO product) and trace amounts of formaldehyde.⁶ For certain uses, EO is now produced with an aldehyde content of less than 10 ppm.⁷

In both the air and oxygen oxidation processes, the ethylene feed must be >98 mole percent pure. Air feed in the air oxidation process must be purified to minimize the presence of contaminants which may deactivate the catalyst or react to form unwanted by-products. Most EO plants include an associated glycol plant which is able to process aqueous and organic bleeds from the EO plant and recover the EO contents as glycol. By integrating the two plants, it is not always necessary to dry and purify the EO needed for fiber grade glycol production, yielding substantial capital cost and utilities savings.⁶

Specific characteristics of the air and oxygen oxidation processes for EO production are discussed below.

Air Oxidation--

Figure 3 illustrates the basic operations that may be found in the continuous air oxidation process. The process streams and vents shown in Figure 3 are described in Table 4. Ethylene and compressed air (Streams 1 and 2) combine with a recycle ethylene stream (Stream 3), then enter one of several primary reactors operated in parallel. The air-to-ethylene feed ratio is usually about 10:1 by weight. The reaction takes place over a silver catalyst packed in tubes; the heat from the reaction is dissipated by a jacket of heat transfer fluid. Reaction temperature and pressure are maintained at 220° to 280°C and 1 to 3 MPa (427° to 536°F; 10-20 atm). The activity of the catalyst can be enhanced by the addition of promoters such as alkali metals or alkali earth metals. Catalyst inhibitors such as halides may be added to suppress conversion of ethylene to carbon dioxide while not interfering with the primary reaction. In addition to the main by-product, carbon dioxide, small amounts of formaldehyde and acetaldehyde are also formed.

The effluent from the reactor (Stream 4) contains 1 to 2 mole percent ethylene oxide, 2 to 3 mole percent ethylene and about 7 mole percent carbon dioxide. It is cooled, compressed, and passed through the primary absorber. As it passes up the packed column absorber countercurrent to cold water, the ethylene oxide and some of the carbon dioxide, hydrocarbons, and aldehydes dissolve in the water.

Most of the unabsorbed gas that exits the top of the absorber is cooled and becomes the recycle ethylene stream (Stream 3). A smaller portion of the unabsorbed gas stream (Stream 5) is purged to prevent the accumulation of inert gases such as nitrogen and carbon dioxide in the system. To recover its ethylene content, the purged stream enters a secondary purge reactor. The effluent from the secondary purge reactor (Stream 6) enters a purge absorber which operates on the same principle as the primary absorber. The overhead gas from the purge absorber is recycled to the purge reactor (Stream 8) or, in

Note: The numbers in this figure refer to process streams as discussed in the text. Letters designate process vents. Heavy lines represent product flow through the process.

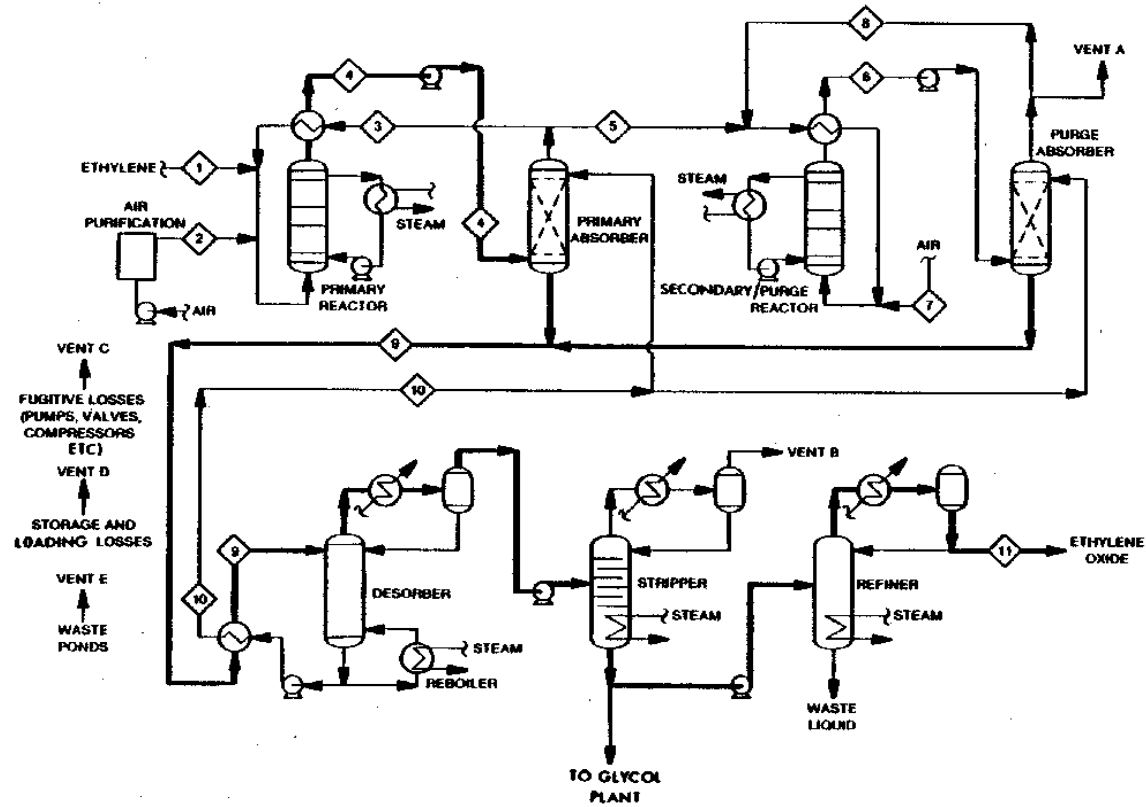


Figure 3. Basic operations that may be used in the production of ethylene oxide by air oxidation.^{1,2}

TABLE 4. DESCRIPTIONS OF STREAMS AND VENTS ILLUSTRATED IN FIGURE 3
FOR THE AIR OXIDATION OF ETHYLENE TO ETHYLENE OXIDE ^{2,3}

Code Number	Description
<u>Stream</u>	
1	Ethylene feed, >98 mole percent
2	Purified process air
3	Recycle to primary reactor
4	Primary reactor product gas, 1 to 2 percent EO
5	Purge reactor feed
6	Purge reactor effluent, 2 percent EO
7	Process air
8	Recycle from purge absorber
9	Absorber bottoms, minor EO levels
10	Recycle water to absorbers
11	Ethylene oxide product, 99.5 percent EO
<u>Vent</u>	
A	Main process vent (CO ₂ , nitrogen purge)
B	Stripper vent (light gas purge)
C	Fugitive losses (pumps, valves, compressors, etc.)
D	Storage and loading losses
E	Waste ponds

larger plants, sent to yet another purge reactor and absorber (not shown) to achieve an overall ethylene conversion well in excess of 95 percent of the total feed.⁶ A portion of the stream from the last absorber is vented (Vent A). The number of purge stages depends on the value of ethylene recovered versus the cost of additional purge stages.

The dilute aqueous solutions of EO, CO₂, and other volatile organic compounds (VOC) from the absorbers are combined (Stream 9) and fed to the desorber where the EO and dissolved inerts are distilled under reduced pressure. The desorber water, virtually free of EO, is recirculated to the absorbers (Stream 10). The crude EO from the desorber is then sent to a stripper for removal of CO₂ and inert gases and then sent to a final refining column. (Note that in some plants the EO from the absorbers [Stream 9 in Figure 3] may go first into a stripper and then into a light ends refractory column. The nomenclature is different but the basic operations are the same.) Light gases separated in the stripper are vented overhead (Vent B). The final product (Stream 11), 99.5 mole percent EO, is stored under a nitrogen atmosphere in pressurized tanks. In some plants, crude EO is sent directly to a glycol plant rather than undergoing complete refining.

Oxygen Oxidation--

Virtually all of the differences between the air oxidation and oxygen oxidation processes result from the difference in oxygen content of the oxidants (~20 mole percent versus 98 mole percent). Figure 4 illustrates a continuous oxygen oxidation process. The streams and vents shown in Figure 4 are described in Table 5.

In the oxygen oxidation process, ethylene and oxygen (Streams 1 and 2) enter the reactor, which is operated under conditions similar to that in the air oxidation process. The effluent from the reactor (Stream 4) passes through the absorber, in which the EO product and some of the carbon dioxide, hydrocarbons, and aldehydes dissolve in the water. Most of the unabsorbed gas that leaves the top of the absorber is cooled and becomes the recycle ethylene stream (Stream 3).

Note: The numbers in this figure refer to process streams as discussed in the text. Letters designate process vents. Heavy lines represent product flow through the process.

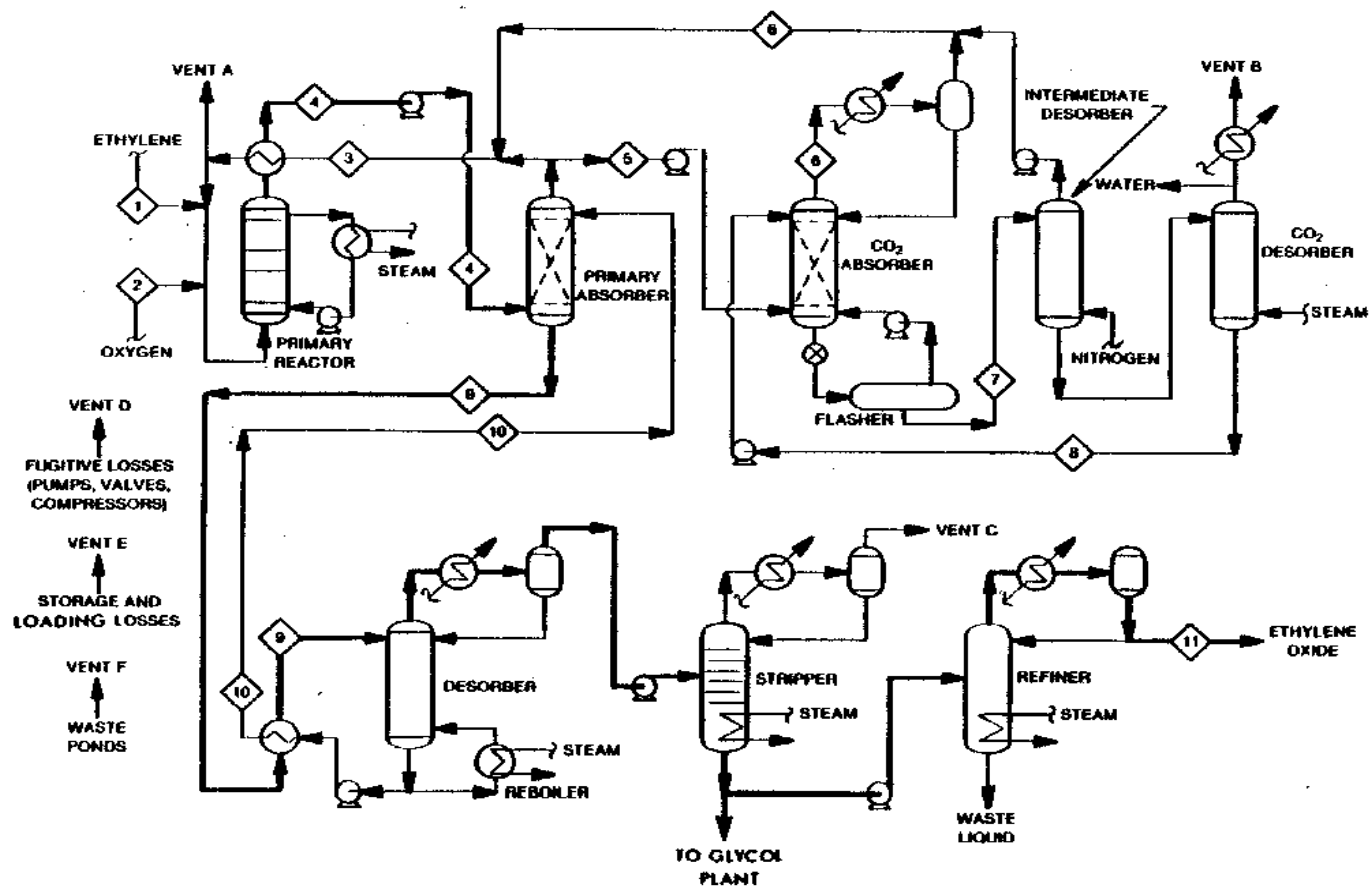


Figure 4. Basic operations that may be used in the production of ethylene oxide by oxygen oxidation.^{1,2}

TABLE 5. DESCRIPTIONS OF STREAMS AND VENTS ILLUSTRATED IN FIGURE 4 FOR
THE OXYGEN OXIDATION OF ETHYLENE TO ETHYLENE OXIDE ^{2,3}

Code Number	Description
<u>Stream</u>	
1	Ethylene feed, >98 mole percent
2	Oxygen feed, >97-99 mole percent
3	Recycle to primary reactor, 0.006 percent EO
4	Primary reactor product gas, 2 percent EO
5	CO ₂ purge stream
6	CO ₂ -free recycle to primary reactor
7	CO ₂ -rich CO ₂ absorbent (KHCO ₃)
8	Reactivated CO ₂ absorbent (KHCO ₃)
9	Absorber bottoms, minor EO levels
10	Recycle water to absorbers
11	Ethylene oxide product, 99.5 percent EO
<u>Vent</u>	
A	Main process vent (argon purge)
B	CO ₂ desorber vent (CO ₂ , nitrogen purge)
C	Stripper vent (light gas purge)
D	Fugitive losses (pumps, valves, compressors, etc.)
E	Storage and loading losses
F	Waste ponds

Gaseous impurities from the oxygen feed, such as argon, are purged from the recycle gas stream through the main process vent (Vent A). Because there are fewer impurities in the oxygen feed than in air feed, the purge stream can be much smaller and there is no need for a purge reactor system. There can be almost total recycling of unreacted ethylene.

There is still, however, a buildup of by-product CO₂ which could reduce catalytic selectivity to EO at high levels if not removed from the system. A portion of the overhead gas from the absorber (Stream 5) passes through a CO₂ absorber which uses potassium carbonate as an absorbent, then (as Stream 6) joins the recycle to the reactor. The spent CO₂ absorbent (Stream 7) is reactivated in the CO₂ desorber, then recycled to the CO₂ absorber (Stream 8). The CO₂ is vented from the CO₂ desorber (Vent B).

The desorption, stripping, and refining steps are basically the same as those in the air oxidation process. The stripper vent labeled Vent B in the air oxidation process corresponds to Vent C in the oxygen oxidation process. An alternative to stripping inerts from the EO stream is to vent these gases from the reabsorber towers where EO is reabsorbed in water. Inert gases can also be purged from the EO purification tower.

Process Emissions from Vents-- ^{1,2}

Air Oxidation - The main process vent (Vent A) is the larger of the two sources of EO process emissions in the air oxidation plant. The vented gases contain nitrogen and unreacted oxygen from the air feed, ethane and unreacted ethylene from the ethylene feed, product EO and by-product CO₂. The exact composition of the vent stream depends on the reactor conditions, absorber conditions, purity of the ethylene feed, and number of purge stages.

The air feed rate is kept consistent with the ethylene feed rate during start-up; therefore, the emission rate from the main process vent during start-up is about the same as that for normal operation. Process

upsets, however, can cause a sharp increase in emissions. When an upset occurs, the ethylene feed rate is reduced to lessen the amount of VOC in the vent stream.

Because EO is completely soluble in water, the purge absorber shown in Figure 3 can be 99.9+ percent effective for its removal.² The EO content of the main process vent stream (Vent A) is therefore quite low. The ethane and ethylene contents, however, are sufficient for combustion. This stream is now normally burned in a thermal or catalytic oxidizer,⁸ but in the past, was commonly vented to the air.² During upsets, the main process vent stream can be directed to an emergency flare.

The stripper vent (Vent B) of the air oxidation process releases the inert gases and ethylene which were absorbed into the main and purge absorber waters. The composition of the stream depends on the solubilities of the gases in the circulating water. The amount of emissions is affected by the water use rate, but not by process start-ups or shutdowns. Ethylene oxide is normally scrubbed from the stripper vent stream with water and returned to the process. The resulting vent stream is normally combusted in a boiler, effecting virtually 100 percent EO emissions control.⁸

Some plants route both vent streams (Vents A and B) to an absorber for recovery of EO, then to a boiler or flare.

Oxygen Oxidation -- The volume of the main process vent (Vent A) of the oxygen oxidation process is much less than that of the corresponding vent in the air oxidation process, but it contains about the same mole percent EO, ranging from about 0.005 to 0.01 percent. This vent stream also contains argon and nitrogen from the oxygen feed and the ethane from the ethylene feed. The composition and quantity of the stream depend directly on the purity of the feed materials and are not affected by process upsets or start-ups if the composition of the oxygen feed is established before start-up.

The ethylene content of the main process vent stream (Vent A) is sufficient to support combustion and is routinely vented to a boiler or incinerator.⁸ In some plants, methane is added to facilitate a higher safe oxygen concentration. The methane, inert in the oxidation reaction, also allows more flexibility in the feed rates to the reactor by narrowing the flammability limits of the incoming gas.

The CO₂ desorber vent (Vent B) is more than 99.7 percent CO₂ and water. No information is available on the EO content. The vent stream is sometimes processed or sold to recover CO₂. If the stream is sold, there is intermittent discharge during start-up, malfunction, and maintenance, estimated by one producer as 6 percent of the time.⁹ The stream can also be vented to the atmosphere; in this case, a carbonate flasher and vent condenser reduce emissions.⁸ One producer uses the stream in another process (not specified in reference). In this case, the VOC content is ultimately thermally oxidized or fed to an incinerator.

The stripper vent stream (Vent C) has sufficient ethylene content to support combustion in a boiler or flare. If methane is added to the reactor stream some will also be vented in this stream. In newer installations, the vent stream is compressed and recycled to the CO₂ absorber feed. No EO content is reported for this stream.

When inerts are purged from a reabsorption tower, the vent stream from the reabsorber can be incinerated. When inerts are also purged from the EO purification tower, this stream can be scrubbed, vented to an absorber, and recycled to a reabsorber.

Most modern EO producers employ closed cooling cycles to cool the oxygen oxidation process' recirculated effluent from the EO stripper column; however, cooling towers are sometimes used.¹⁰ With cooling towers, the cooling process is achieved by evaporation when the process cooling water and air are contacted. The emission rate is inversely proportional to the efficiency of the stripper column in EO removal.

Fugitive Emissions--

Fugitive EO emissions in either the air or oxygen oxidation process emanate from pump seals, compressors, valves, flanges, pressure relief devices and sample connections. Fugitive emission estimates can be made by applying emission factors to the number of pumps seals, valves, flanges, etc., in a typical EO production facility, and by adjusting these totals to reflect the EO content in each stream. An example of this type of analysis is shown in Reference 8, excerpts of which are included in Appendix A of this report. For a hypothetical model plant, this analysis yields fugitive EO emission estimates ranging from 148 to 188 kg/day in oxygen and air oxidation facilities, respectively. These estimates are for relatively uncontrolled facilities employing no measures for leak detection and repair and maintenance. These fugitive emission levels will be reduced considerably by inspection and maintenance (I/M) programs in which equipment is routinely monitored and leaks corrected. Depending on the stringency of the I/M measures, varying levels of control are possible, ranging from 38 percent reduction for the measures in EPA's Control Techniques Guideline (CTG)¹¹ to 65-78 percent if the I/M measures reflect EPA's New Source Performance Standards.¹²

Several EO producers indicate that because of process safety considerations, EO handling units have always been designed, built and maintained to tight standards because of flammability, explosion and health hazards inherent in the chemical. Measures taken for safety reasons also reduce EO emissions. These measures include:¹³

- S** Installation of EO and flammable gas detectors in strategic plant locations, with sample analyses performed regularly (e.g., every 20 minutes)
- S** Equipping EO pumps with double mechanical seals having liquid buffer zones and alarms or automatic pump shutoffs in case of seal failure
- Routine gasket replacement during planned maintenance turnarounds
- S** Using pressurized nitrogen in labyrinth shaft seals of centrifugal EO compressors

- S Use of all welded construction, where possible, to minimize the number of flange joints
- S Using leak detectors for critical flanges in EO piping
- S Use of closed loop sample systems
- S Providing extra maintenance for EO piping
- S Preventing relief valve leaks by use of upstream rupture disks
- S Analyses of rotating equipment for vibration characteristics to anticipate pending problems
- S Collecting, absorbing in water and discharging to sewer any EO leakage or drainage from sampling operations and pump vents
- S Daily inspection for leaks by plant personnel
- S Immediate leak repair

Note that not all of these measures are applied at any one plant.

Sources desiring not to use the fugitive emission factor development approach outlined in Appendix A for assessing EO fugitive emissions may instead use EPA's Reference Method 21 and the procedures specified in Reference 14.^{15,16} Method 21, "Determination of Volatile Organic Compound Leaks," is intended to be used as a screening tool for detecting, locating, and classifying leaks. It is not designed to be a direct measure of mass emissions from individual sources. Method 21 is used to produce a statistical leak/no leak frequency. Reference 14 describes the approach of how the leak/no leak frequency (or screening distribution), produced by Method 21 for a particular piece of equipment, can be statistically correlated with empirical data on chemical industry fugitive VOC emissions and extensive statistical analyses of leakers and non-leakers (for that equipment) to generate average fugitive VOC (or compound specific) emission factors for pumps, valves, flanges, compressors, and pressure relief devices.

Waste Ponds--

Emergency holding ponds may also be sources of EO emissions. One source uses a pond for emergency twentyfold dilution of EO to reduce the possibility of explosions during shutdowns. As much as 5,000 to 10,000

pounds of EO may have to be dumped at once. The company assumes that the EO converts to ethylene glycol, but is considering the addition of catalysts to speed this conversion.¹⁷ It is not known how much EO is lost to the atmosphere from such ponds, or how common this practice is in the industry.

Other Secondary Emissions--

Wastewater streams from various processes may contain some, albeit generally low levels of EO. These streams are commonly treated by bio-oxidation. Most producers report negligible or no EO emissions from this source.¹³ One producer reports one EO unit wastewater stream having an EO content of 280 ppm, of which 75 percent, or about 92 kg/day, is estimated to be stripped into the atmosphere.¹⁸

Storage and Loading Losses--

Because product EO is a gas at ambient temperatures, it is generally stored under nitrogen at approximately 10°C (50°F).⁸ Some plants may store EO at ambient temperatures and elevated pressures.¹ Losses from storage tanks are assumed to occur only because of displacement during filling operations.¹⁹ If not used captively, EO is normally shipped in 38,000 and 76,000 liter (10,000 and 20,000 gallon) railroad tank cars, which are normally loaded directly from plant storage tanks. The transfer generally occurs at about 50 psi nitrogen pressure.²⁰ At most facilities, displaced vapors from the filling of tank cars and storage tanks are either recycled to the process or scrubbed prior to incineration or flaring.⁸ When the vapors are scrubbed, the liquid effluent from the scrubber is routed to the desorber for EO recovery.¹ Emissions of EO from storage and loading are assumed to be nearly zero if either control approach is used. However, one producer reports 39 Mg/yr (86 x 10³ lb/yr) of EO emissions from storage and loading. No explanation was given for this emission rate; the producer uses a caustic scrubber for control of emissions.⁸

Emission Factors--

Table 6 and Table 7 give EO emission factors for air and oxygen oxidation plants, respectively. Because the production of EO and the production of EO derivatives are often closely related, the factors in Table 6 and Table 7 do not necessarily represent the isolated production of EO. For example, the fugitive emission source counts used for the calculation of fugitive emissions include components used in derivative production as well as EO production (albeit many fewer components in EO service will be present in derivative production processes). Similarly, the process vent emissions may reflect the recycle of certain vents in derivative plants back to the EO plant. The contribution to total EO emissions from vents, fugitive components, and storage in derivative production is not believed to be significant compared to overall emissions from EO production operations.

TABLE 6. EMISSION FACTORS FOR THE RELEASE OF ETHYLENE OXIDE FROM
AN AIR-OXIDATION ETHYLENE OXIDE PRODUCTION PLANT^{1,2,8}

Source	Uncontrolled Emission Factor g/kg ^b	Controlled		
		Control Device or Technique	Emission Reduction Percent	Emission Factor g/kg ^b
Vents ^a				
A (main process)	0.005 - 1	Catalytic oxidation	100	0
		Thermal oxidation	80 ^c	0.04
		Emergency flare ^d	100	0
B (stripper) ^e	≤0.7	Boiler	100	0
Storage and Loading	2.6 ^f	Recycle or scrubber with incineration or flaring	100	0
Fugitive ^g	158 kg/day	Detection and correction of major leaks	39-78	42-115 kg/day
Waste Ponds ^h	NA	Catalyst	NA	NA
Wastewater Streams	NA	Biooxidation or equilization pond	NA	0

NOTE: The source configuration, emission factors and level of control of any given plant may vary from those given here. The reader is encouraged to confirm the existence of emitting operations and control technologies at a particular plant before estimating emissions therefrom.

^a See Figure 3 for vent designations. In some plants these vents are directed to secondary absorbers recovery of EO, with the resulting vent stream routed to a boiler or plant flare.

^b Grams of ethylene oxide emitted per kilograms of ethylene oxide produced. Multiply by 2 to convert g/kg to lb/ton. These factors do not necessarily reflect the emissions from any one plant.

^c This reduction was reported for a plant having a very low inlet EO value. Normally, a reduction approaching 100 percent is possible for thermal oxidation.^{21,22}

^d For use during process upsets. Emissions from this vent are not affected by process startup.

^e The purpose of this vent is to discharge inerts (primarily N₂ and CO₂) that build up in the system. This venting may occur at other points in some processes, such as the light ends rejection column. Emissions from this vent are not affected by process startup or upset.

^f Assumes EO stored under nitrogen pad in pressure tanks and transferred at 16°C. Assumes 20 percent of EO production is shipped by tank car. Assumes day tanks vapor-balanced with storage tanks and that an equivalent amount of vapor saturated with EO at 10°C is displaced from the system for each volume of EO produced. Assumes the following tank sizes and turnover rates:

Tank Type	Number of Tanks	Tank Size (m ³)	Turnovers/year
Day	2	225	550
Storage	6	470	89

^g Per plant, for all pump seals, valves, flanges, compressors, pressure relief devices, sample connections and open ended lines (the latter used during maintenance operations). May include components in EO service in derivative production. See text and Appendix A for emission derivations.

^h EO may be discharged to waste ponds during shutdown. Emission factors for this practice are not available. A possible control measure is the addition of catalysts which enhance the conversion of ethylene oxide to ethylene glycol.

ⁱ One producer reports 92 kg/day of EO is air stripped from one EO Unit wastewater stream, or about 75 percent of the 280 ppm of EO in the stream.

TABLE 7. EMISSION FACTORS FOR THE RELEASE OF ETHYLENE OXIDE FROM AN OXYGEN-OXIDATION ETHYLENE OXIDE
PRODUCTION PLANT ^{1,2,8}

Source	Uncontrolled Emission Factor, g/kg ^b	Control Device or Reduction Technique	Controlled Emission Reduction Percent	Emission Factor, g/kg ^b
Vents ^a				
A (main process)	0.001-0.002	Boiler or incinerator	100	0
B (CO ₂ purge)	0.0006-0.75	Carbonate flasher/vent Condenser	92	0.06
		CO ₂ recovery or methanol unit	100	0
C (stripper) ^c	<0.1	(d)	85-100	<0.002
Storage and Loading	2.6 ^e	Aqueous scrubber	100	0
Fugitive Sources ^f	148	Detection/correction of major leaks	38-65	52-91
Cooling Towers	0.07	Increase stripper column effectiveness ^g	80	0.014
Waste Ponds ^h	Not available	Catalyst to promote EO to EG conversion	Not Available	Not Available
Wastewater Streams	Not available ⁱ	Biooxidation or equilization ponds	Not Available	0

NOTE: The source configuration, emissions and level of control of any plant may vary from those given here. The reader is encouraged to confirm the existence of emitting operations and control techniques at a particular facility before estimating emissions therefrom.

^a See Figure 4 for vent designations.

^b Grams of EO emitted per kilogram of ethylene oxide produced. Multiply by 2 to convert g/kg to lb/ton. These factors do not necessarily reflect the emissions from any one plant.

^c Various types of equipment can be used in the refining stages of EO production, including reabsorbers and purification towers in addition to strippers. The EO emission factors reported here generally apply to any such configuration (with the exception of one plant that reported uncontrolled emissions of 11.4 g EO per kg capacity; however, its outlet emissions after a vent absorber were reduced to 0.0004 g/kg, within the range given above).

^d Numerous control measures are employed to control this source, including reabsorbers, incinerators, water scrubbers and vent absorbers.

^e See assumptions listed in footnote f in Table 6.

^f Per plant, for all pump seals, valves, cospessors, pressure relief devices, sample connections and open ended lines (the latter used during maintenance operations). May include components in EO service in derivative production. See text and Appendix A for emission derivatives.

^g Stripper column effectiveness can be improved by utilizing high efficiency trays and packing intervals.

^h EO may be discharged to waste ponds during shutdown. A possible control measure is the addition of catalysts which enhance the conversion of ethylene oxide to ethylene glycol. ⁸

ⁱ One producer reports 92 kg/day of EO is air stripped from one EO unit wastewater stress, or about 75 percent of the 280 ppm of EO in the stream. ¹⁸

REFERENCES FOR SECTION 4

1. Kalcevic, V. and J.F. Lawson. Ethylene Oxide. In: Organic Chemical Manufacturing, Volume 9: Selected Processes. EPA-450/3-80-028d. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.
2. Field, D.D., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 6: Ethylene Oxide Manufacture by Direct Oxidation of Ethylene. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Prepared under EPA Contract No. 68-02-0255. June 1975.
3. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition, Volume 9. Ethylene Oxide. John Wiley and Sons. New York, New York. 1980. pp. 432-471.
4. Telecon. Smith, C., Radian Corporation with Arnold, S., Dow Chemical. May 1983. Ethylene oxide production processes.
5. Kuhn, W. What's Ahead for Propylene and Ethylene Oxide. Chemical Engineering Progress. January 1980. pp. 53-56.
6. Ozero, B.J. and J.V. Procelli. Can Development Keep Ethylene Oxide Viable? Hydrocarbon Processing. March 1984. pp. 55-61.
7. DeMaglie, B. Oxygen Best for EO. Hydrocarbon Processing. March 1976. pp. 78-80.
8. Markwordt, D.W. Sources of Ethylene Oxide Emissions. EPA-450/3-85-014. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1985.
9. Nonconfidential portions of a letter from R.K. Bernard, Northern Petrochemical Company to J.R. Farmer, U.S. Environmental Protection Agency. 4 January 1984. Ethylene oxide production information.
10. Letter from Macauley, D.C., Union Carbide to Lahre, T., U.S. Environmental Protection Agency. 10 April 1986. Comments on draft ethylene oxide emission factor document.
11. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment. EPA-450/3-83-006. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1984.

12. VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry - Background Information for Proposed Standards. EPA-450/3-80-033a. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. November 1980.
13. Nonconfidential portions of letters submitted to J. Farmer or D. Markwordt, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, by industrial producers and users of ethylene oxide. October 1983 to January 1984.
14. Stelling, J.H. Emission Factors for Equipment Leaks of VOC and HAP. EPA-450/3-86- 002. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. January 1986.
15. Federal Register, Volume 48, 18 August 1983. p. 37600. U.S. Government Printing Office, Washington, D.C.
16. Federal Register, Volume 48, 22 December 1983. p. 56581. U.S. Government Printing Office, Washington, D.C.
17. Telecon. Smith, C., Radian Corporation with Dorgant, G., Celanese Chemical Corporation. 9 September 1983. Emissions from ethylene oxide production.
18. Letter from Macauley, D.C., Union Carbide to Markwordt, D.W., U.S. Environmental Protection Agency. 23 April 1984. Emissions from ethylene oxide production.
19. Compilation of Air Pollutant Emission Factors, Third Edition. AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. August 1977, with supplemental updates.
20. Bogyo, D.A., et al. Investigation of Selected Potential Environmental Contaminants: Epoxides. Prepared for the U.S. Environmental Protection Agency, Washington, D.C. March 1980. NTIS Publication No. PB80-183197.
21. Memo from Mascone, D.C., U.S. Environmental Protection Agency to Farmer, J.R., U.S. Environmental Protection Agency. 11 June 1980. Thermal Incinerator Performance for NSPS.
22. Memo from Mascone, D.C., U.S. Environmental Protection Agency to Farmer, J.R., U.S. Environmental Protection Agency. 22 July 1980. Thermal Incinerator Performance for NSPS, Addendum.

SECTION 5
EMISSIONS FROM INDUSTRIES WHICH USE ETHYLENE OXIDE

This section describes several production processes which use EO as a feedstock. The processes included are for the production of ethylene glycol, di-, tri- and polyethylene glycols, glycol ethers, ethoxylates, and ethanolamines. No specific information is available on the use of EO in the production of surface active agents or other miscellaneous chemicals. Therefore, these production processes are not included in this section.

The use of EO as a fumigant, sterilant, and insecticide is included because, although only a small percentage of the total EO produced is used for these purposes, a large percentage of that used is released directly to the atmosphere.

Specific estimates of EO emissions are not available for processes using EO as a feedstock. Hence, the following discussions mainly describe the basic operations found in each process and identify the potential emitting points therein. Control devices, operating practices, etc., are also discussed that are known to reduce emissions.

In most cases, as shown in Table 3 in Section 3, EO derivatives are manufactured at the same plants that produce EO. This practice is especially common in glycol production since it is advantageous to integrate the oxide unit with the glycol unit to optimize energy utilization.

ETHYLENE GLYCOL AND ITS HOMOLOGS¹

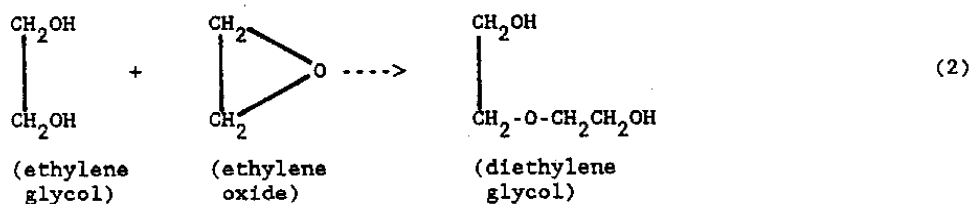
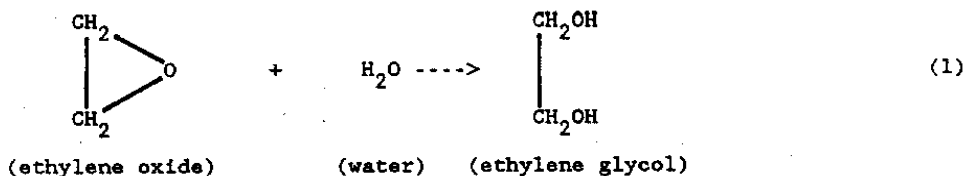
About 60 percent of the EO produced in the United States is used directly in the production of ethylene glycol (EG). Another 15 percent is reacted with the glycol produced to form the homologs

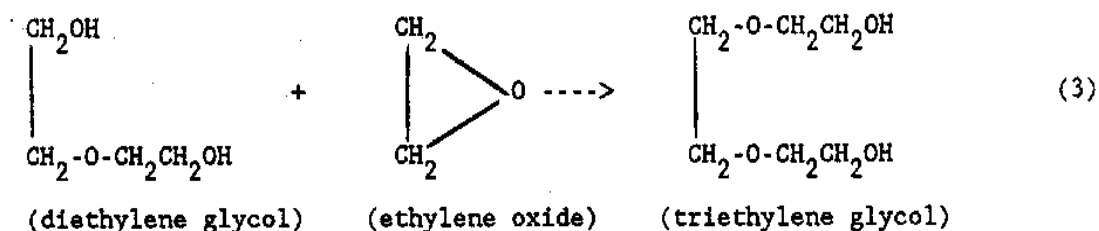
diethylene glycol (DEG), triethylene glycol (TEG), and higher polyethylene glycols. Some producers market all homologs higher than ethylene glycol as unspecified polyethylene glycol.

Most ethylene glycol (and its homologs) is produced commercially by noncatalyzed hydration of ethylene oxide. This is the only process discussed in detail in this section. Ethylene glycol and its homologs can also be produced from EO by contact with a 0.5 to 1.0 percent sulfuric acid catalyst solution maintained at 50 to 70°C (122 to 158°F). A major drawback to this method is an acid contaminant left in the product. No estimate is available of the amount of EG produced by this method. Other methods for the production of EG, some of which do not use EO as a feedstock, have been used in the past or are in various stages of development. One process nearing commercialization involves the synthesis of ethylene carbonate, from CO₂ and EO, which is then hydrolyzed to glycol.²

Process Description

In most cases, ethylene glycol and its homologs are produced by noncatalyzed hydration of ethylene oxide at a temperature of 200°C (392°F) and pressure of 1380 kPa (200 psia) according to the following equations:





Theoretically, yields of EG from Reaction 1 are 87 to 88.5 weight percent, while yields of DEG from Reaction 2 are 9.3 to 10.5 weight percent, and yields of TEG from Reaction 3 are 2.2 to 2.5 weight percent of the total product. However, because there is more demand for TEG, conversion of DEG to TEG (Reaction 3) is promoted by varying the feed ratio and/or other process variables.

Figure 5 shows a simplified process flow diagram for the production of EG and its homologs by the conventional noncatalyzed ethylene oxide hydration process. In some plants, refined liquid EO (Stream 1) and water (Stream 2) are fed to the hydrolyzer. In other plants, however, crude EO vapor from the EO desorber or stripper/light ends column (see Figure 3 and Figure 4) is fed directly to the EG plant. These two options are illustrated in Figure 6. In either case, the product stream (Stream 3) from the hydrolyzer is passed through a multiple-effect evaporation system for removal of water. The concentrated glycol solution (Stream 4) is further dried in a water removal column, then the individual glycols are distilled in vacuum distillation columns. Bottoms from the last distillation column (Stream 5) are disposed of or sold as by-products.

Emissions¹

Uncontrolled emissions from the hypothetical plant illustrated in Figure 5 originate from the evaporator calandria vents (Vent A), the water removal column steam-jet ejector (Vent B), the distillation column ejectors (Vent C), and the evaporator first-effect purge stream (Vent D). The plant shown in Figure 5 uses barometric condensers to condense and absorb the vapor from the evaporator purge and the steam-jet ejectors. The emissions from these sources then

Note: Dots indicate possible sources of ethylene oxide emissions. Heavy lines indicate product flow through the process.

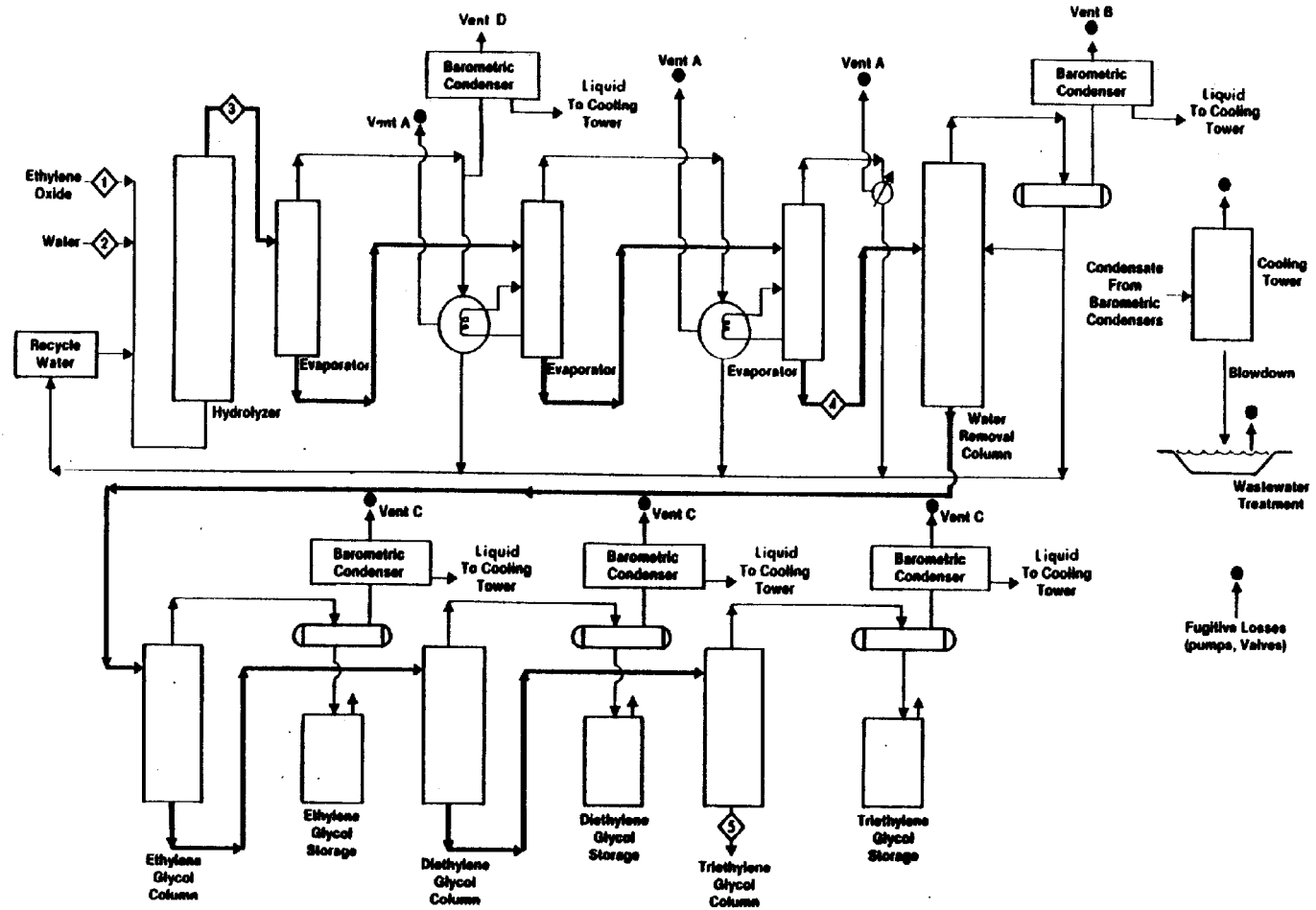


Figure 5. Basic operations that may be used in the production of ethylene glycol, diethylene glycol, and triethylene glycol by conventional noncatalyzed hydration of ethylene oxide.

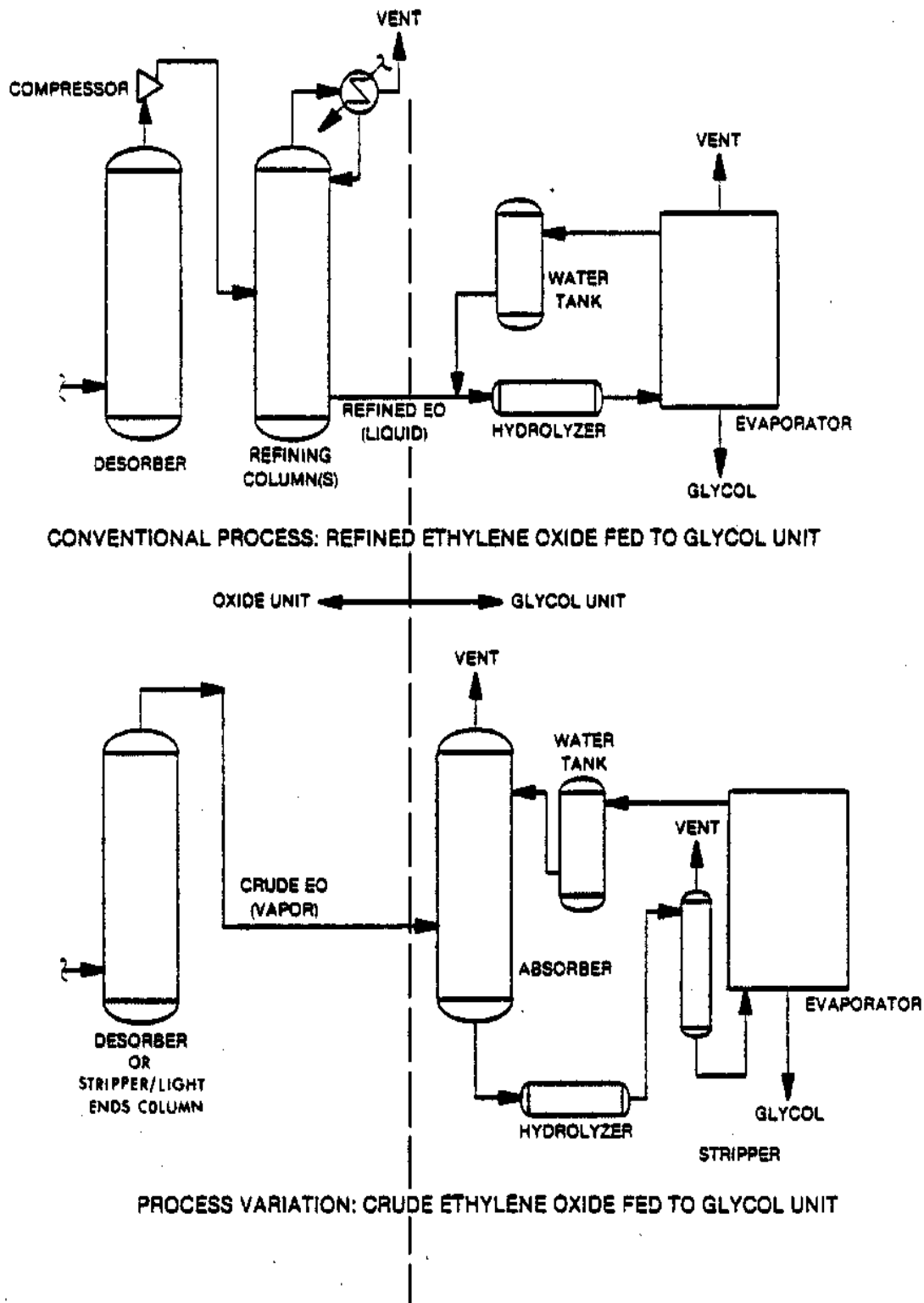


Figure 6. Process operations for transfer of ethylene oxide to the ethylene glycol plant.¹

circulate with the cooling water. Partial desorption occurs as the cooling water passes through the cooling water circuit and the cooling tower. The remainder of the contaminants end up in the cooling tower blowdown stream. The evaporator calandria emissions for the uncontrolled plant are vented directly to the atmosphere. One source reports that the EO content of the evaporator overheads and the water removal column overheads should be minimal.³

To prevent contamination of the cooling water, controlled plants commonly use surface condensers instead of barometric condensers. The condensate from the surface condensers is discharged to wastewater treatment. Uncondensed gases are vented to the atmosphere. A surface condenser may also be used to control emissions from the evaporator calandria vents in the controlled plant.

The installation of surface condensers to isolate the condensate from the cooling water eliminates fugitive emissions from the cooling tower, but increases emissions from wastewater treatment. Also, the uncondensed gases vented from the surface condensers contain some VOC. However, there is a net reduction in overall plant emissions when surface condensers are used because the emissions from condensers and wastewater treatment are small in comparison to those from cooling tower blowdown when barometric condensers are used.

The hypothetical plant in Figure 5 is estimated to have 7 pumps, 38 process valves, and 3 relief valves handling light organics in the feed and water removal sections. Only a small portion of the emissions from these sources can be assumed to be EO. The typical level of fugitive emission control is not known.

Emissions from storage and handling of EO depend on whether or not it is piped directly to the glycol production process. Presently, all EG is produced at sites where EO is also produced. Because the EO can be piped directly to the EG process, emissions of EO from storage and handling are negligible. Several companies do,

however, produce other glycols at locations where EO is not produced on-site (see Table 3). At these sites emissions do occur from storage and handling of EO.

Waste liquid streams (particularly cooling tower blowdown) may be treated by a primary clarifier followed by activated sludge treatment. No control system has been identified for the control of the secondary emissions from wastewater treatment.

Source Locations

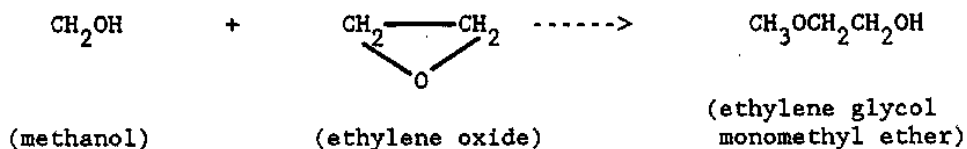
Table 3 lists the names and locations of companies which in 1986 produced EG, DEG, TEG, and polyethylene glycols from EO. Total production capacities for 1986 are 2629 Gg (5795 x 10⁶ lb) for EG, 276 Gg (609 x 10⁶ lb) for DEG, and 68 Gg (149 x 10⁶ lb) for TEG.⁴ Production rates for plants manufacturing glycols, especially DEG and TEG, fluctuate greatly with markets for the products. Diethylene glycol production capacity is sometimes reported simply as 10 percent of EG capacity.

GLYCOL ETHERS⁵

About 5 percent of the EO produced is used as a feedstock in the production of mono-, di-, tri-, and polyethylene glycol ethers. As in the production of glycols, additional EO reacts with the product glycol ether to simultaneously form higher glycol ethers.

Process Description

Ethylene oxide is reacted with anhydrous alcohols such as methyl, ethyl, or n-butyl alcohol to form the corresponding glycol ethers. Ethylene glycol monomethyl ether and its homologs are produced according to the following equations:



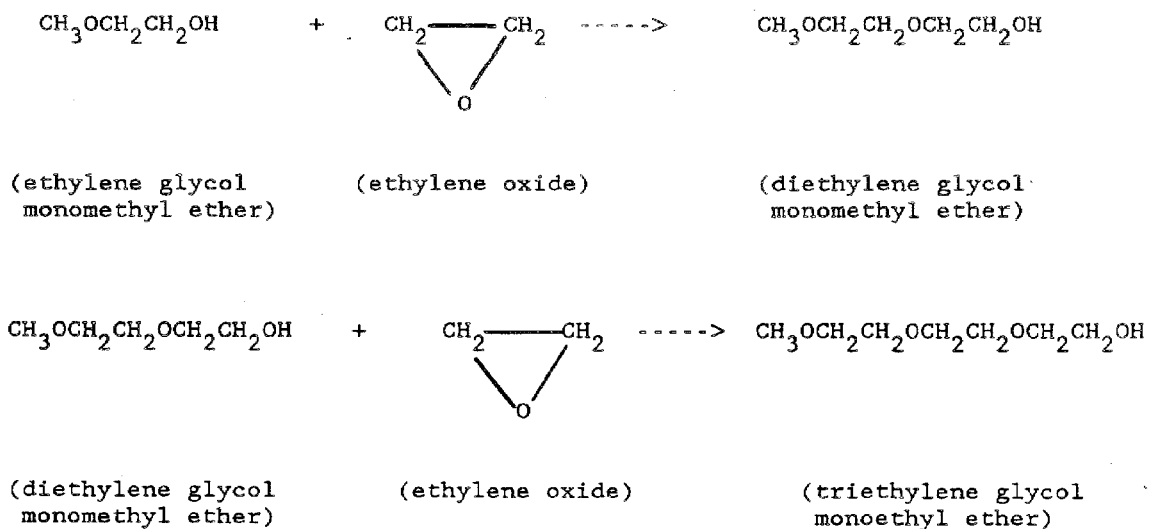


Figure 7 is a simplified process flow diagram for the production of glycol ethers from EO. An anhydrous primary alcohol and a sodium hydroxide or acid catalyst are blended in a mix tank, combined with EO and recycled alcohol, and sent to the glycol ether reactor. A mixture of mono-, di-, and triethylene glycol ethers is formed in the reactor. A high alcohol-to-EO ratio inhibits the formation of di- and triethylene glycol ethers.

Unreacted alcohol is separated from the product stream in a distillation column and recycled to the reactor. The distillation column is normally operated at atmospheric pressure, but is sometimes operated under a slight vacuum to accommodate the higher vapor pressures of ethyl or n-butyl alcohol. The product stream then passes through consecutive vacuum distillation columns where the various glycol ethers are separated. The vacuum system consists of a four stage steam-jet series with surface intercondensers. The bottoms from the last column are disposed of, probably by incineration or landfill.

● Denotes possible source of ethylene oxide emissions.

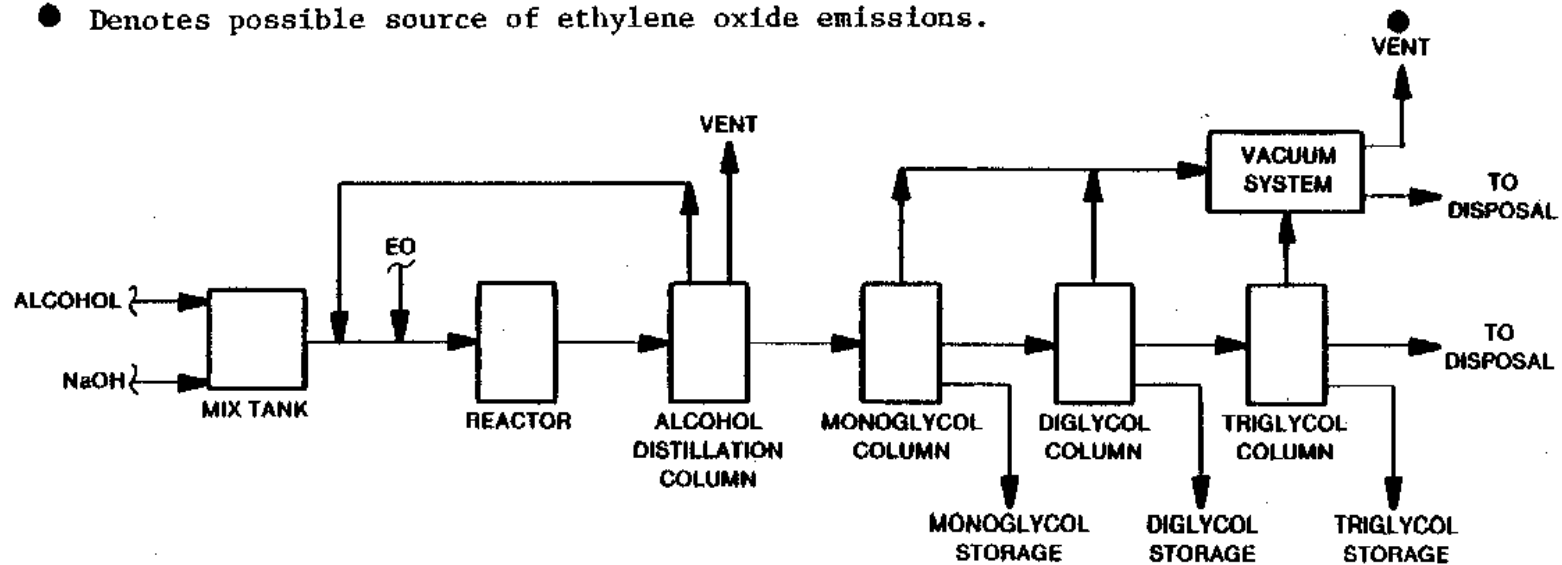


Figure 7. Basic operations that may be used in the production of glycol ethers from ethylene oxide.

Emissions

Emission factors for EO (as opposed to other VOC) are not available because the percentages of EO in the emission streams are not known. The vent from the vacuum system is the only process emission source for which there are VOC emissions, some portion of which could be EO. Volatile organic compound emissions from this vent are reported as 0.013 g per kg of product. No emission control devices are used by the industry for this vent. A vent from the alcohol distillation column releases alcohol and inert gases. Other process vents are in the alcohol section which contains no EO.

Emissions of EO from storage and handling depend on whether or not EO is piped directly to the process. It is normal practice to pipe EO directly from the EO production facility to the glycol ether production facility. In this case, emissions of EO from storage and handling are negligible. One company, however, produces glycol ethers at a location where EO is not produced on-site. At this site, emissions do occur from storage and handling of EO.

The hypothetical glycol ether production process in Figure 7 has approximately 34 pumps, 300 process valves, and 30 pressure relief valves handling VOC. The emission factor for fugitive VOC emissions from glycol ether production is reported as 0.28 g VOC per kg product. Only a small part of these emissions can be assumed to be EO. The level of fugitive emission control is not known.

Source Locations

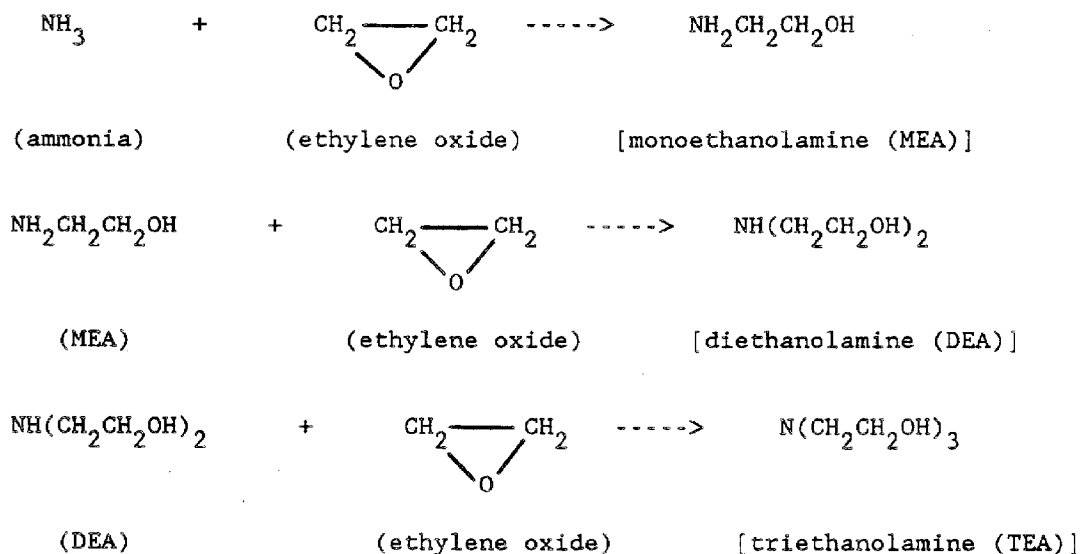
Table 3 lists the names and locations of companies which produce glycol ethers. Production rates for glycol ethers fluctuate according to the market for the products. Total 1986 capacity for the production of glycol ethers is 483 Gg (1065×10^6 lb).⁴ This production total may include some propylene oxide-based glycol ethers.

ETHANOLAMINES⁶

About 5 percent of the total EO produced in the United States is used as feedstock in the production of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). As in the production of glycols, additional EO reacts with the product ethanolamine to simultaneously form higher ethanolamine homologs.

Process Description

Ethylene oxide is reacted with aqueous ammonia in the liquid phase to form the ethanolamines. Monoethanolamine and its homologs are produced according to the following equations:



No catalysts are used in any of the above reactions. The product distribution depends on the ammonia-to-EO ratio. Excess ammonia favors a larger proportion of MEA in the product blend.

The continuous manufacture of ethanolamines is shown schematically in Figure 8.⁷ Ethylene oxide (Stream 1) and aqueous ammonia (Stream 2) are fed to a reactor. The reaction conditions usually are a temperature range of 50 to 100°C (122°-212°F), a pressure of 1 to 2 MPa (10-15 atm), and an excess of 28 to 50 percent aqueous ammonia. The reactor effluent (Stream 3) is stripped of unreacted ammonia and some water (Stream 4) in an ammonia stripper operated under pressure. This ammonia, together with fresh feed (Stream 5), is absorbed in recycled water in the ammonia absorber and fed back to the reactor (Stream 2). The noncondensable overhead gas (Stream 6) from the ammonia stripper is scrubbed of ammonia in an ammonia scrubber with recycle water (Stream 7) and is vented (Vent A). Inert gases enter the system with the ethylene oxide feed, which is stored under a nitrogen pressure pad.⁷

The ammonia stripper bottoms (Stream 9) are vacuum distilled in a series of distillation columns to sequentially remove overhead water (Stream 7), which is recycled, and MEA, DEA, and TEA (Streams 10, 11, 12), which are products. Noncondensables from the vacuum distillation columns are vented (Vent B) from the vacuum-jet discharges, and the vacuum-jet wastewaters are discarded to waste treatment. The bottoms residue (Stream 13) from the triethanolamine column is sent to waste treatment or is sold. The product storage tanks are ordinarily equipped with steam- heating coils to keep the products liquid and are padded with a dry inert gas, such as nitrogen, to prevent product discoloration.⁷

Emissions

Total VOC emissions from the production of ethanolamines are at most only a trace, therefore no emission controls are used for process sources. No sources of EO emissions from the process have been identified.

The potential for EO emissions from feed storage and handling during ethanolamine production is negligible if the EO is produced at the same facility and piped directly to the ethanolamine process. In 1983, all domestic producers of ethanolamine had captive EO production.

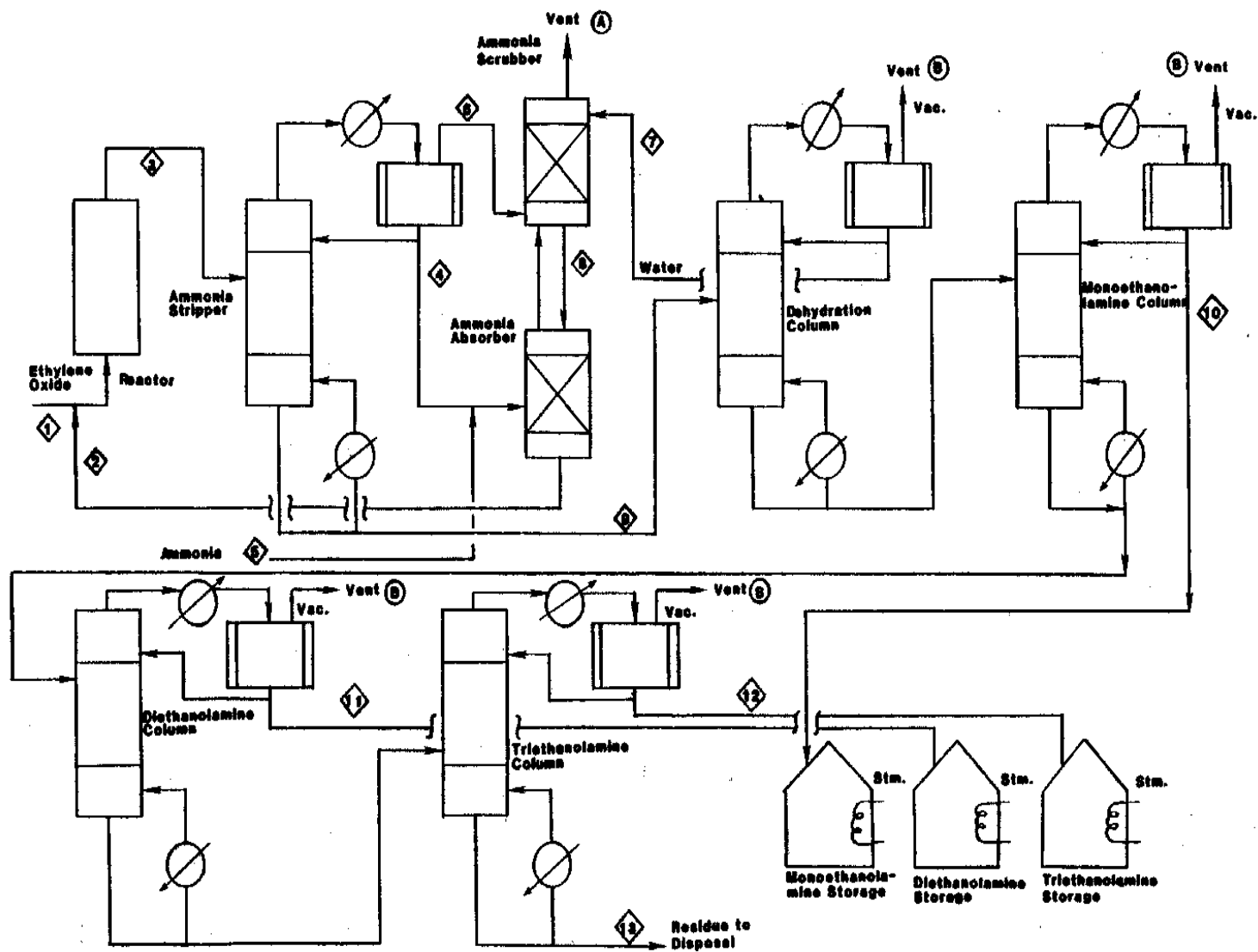


Figure 8. Production of ethanlamines by the oxide-ammonia process.⁷

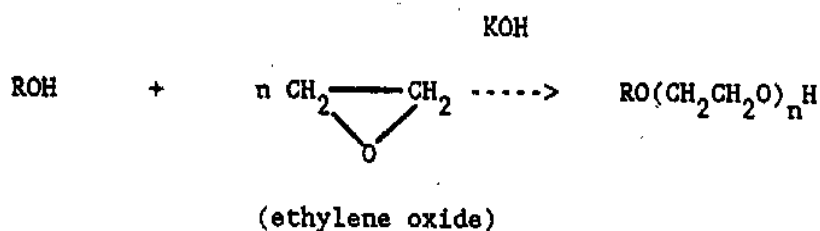
No information is available on fugitive emissions from valves and pumps.

Source Locations

The names and locations of companies which produce ethanolamines are given in Table 3. Total 1986 capacity is 327 Gg (722 x 10⁶ lb)/yr.⁴

ETHOXYLATION

Detergent alcohol ethoxylates are produced by reacting detergent linear alcohols with ethylene oxide in the presence of a base catalyst such as potassium hydroxide. The general reaction may be represented as follows:



The molar ratio of ethylene oxide to alcohol in the final product may vary from 2 to 40. Ethoxylates produced for subsequent conversion to alcohol ether sulfates usually contain 3 moles of ethylene oxide per mole of alcohol. Products made for direct use as nonionic surfactants usually contain 6 to 12 moles of ethylene oxide per mole of alcohol.⁷

The primary source of EO emissions is assumed to be fugitive leaks from equipment components, although minimal data have been collected. As a rough estimate, the number of components handling EO at ethoxylation facilities is approximately 10 percent of those at EO production facilities. Other emission sources at these facilities are assumed to be negligible.⁷

FUMIGATION/STERILIZATION

The use of ethylene oxide as a fumigant and sterilant is a potentially large source of atmospheric EO emissions. Although a very small amount of all EO produced is used as fumigants or sterilants, a large portion of the EO used for this purpose eventually reaches the atmosphere.

Types of Equipment⁸

The type of equipment used for EO fumigation/sterilization varies with the application as shown in Table 8. Each type of equipment is discussed in the following sections.

Vacuum Chambers--

Vacuum chambers are pressure vessels with a vacuum pump to remove air from the chamber before sterilization begins and to remove some of the EO/air mixture after sterilization. Though the units vary widely in size and design features, the operating procedure is essentially as follows:

1. Contaminated material is loaded into the chamber.
2. The chamber door is closed and hermetically sealed.
3. Air is vacuumed from the chamber.
4. The sterilant (100 percent EO, 12 percent EO/88 percent Freon, or 10 percent EO/90 percent carbon dioxide) is introduced into the chamber to a set pressure or concentration and for a specified time period. 100 percent EO is used with negative pressure; EO mixtures are used with positive pressure. Pressure, concentration of sterilant, and time period are adjusted for the individual situation.
5. An exhaust vacuum removes the EO or EO/gas mixture from the chamber. The EO or EO/gas mixture is vented through a vent line to the atmosphere or to a sewer drain.

TABLE 8. TYPES OF ETHYLENE OXIDE STERILIZATION/FUMIGATION EQUIPMENT USED AT DIFFERENT SITES⁸

Sites of Use	Vacuum Chamber	Atmospheric Chamber	Ampule/ Linear Bag	Sterijet System	Tent Fumigation	No Containment
Health care and health diagnosis and treatment facilities	x	x	x	x		
Medical products industry	x			x		
Libraries	x					
Museums	x	x				
Research laboratories	x					
Transportation sites						x
Beekeeping industry	x	x				
High containment research laboratories in agriculture	x					
Animal and plant service quarantine at ports of entry					x	
Spices, seasonings and black walnut meats industry	x					
Cosmetics industry	x					
Dairy packaging industry	x					

6. Fresh air is drawn into the chamber until atmospheric pressure is reached.
7. The door is opened and the treated material removed.
8. The treated material may be transferred to an aeration cabinet which circulates heated air around the material until residual EO has escaped. (Aeration cabinets are used almost exclusively in hospitals.)

Small countertop models with capacities less than 0.1 m³ (ft³) are most commonly used in health care and health diagnosis facilities. In hospitals they are used in areas such as operating rooms. One industrial use is in the manufacture of contact lenses. Ethylene oxide is supplied either in single-dose cartridges of 100 percent EO or in pressurized cylinders of 12 percent EO/88 percent Freon. Small chambers generally vent directly into the atmosphere through a length of tubing. Some models vent into a sponge kept damp in a bucket of water.

Intermediate-sized chambers of from 0.1 to 2.8 m³ (4-100 ft³) are used primarily in hospital central supply facilities. They are also used in research and industrial facilities, libraries, museums, and beehive fumigation facilities. An EO mixture is supplied in pressurized cylinders. Intermediate-sized chambers of this type may vent emissions to the atmosphere or the emissions may be mixed with water, then routed to a sewer drain.

Large chambers with capacities greater than 2.8 m³ (100 ft³) are used primarily for industrial sterilization of medical products, spices, and other products. They may be as large as 85 m³ (3000 ft³) in capacity and are custom-made. In such large capacity custom chambers, an EO mixture or 100 percent EO is fed from pressurized cylinders or from large tanks. Emissions from large chambers of this type are generally mixed with water, then routed to a sewer drain.

Atmospheric Chambers--

Atmospheric chambers are primarily used in health care and health diagnosis centers, in museums, and in the beekeeping industry. They do not evacuate air before treatment, therefore a longer exposure time is usually necessary. Some units introduce EO into the chamber under pressure, then after treatment, flush out the EO with pressurized air. Ethylene oxide is supplied as a gas mixture in cartridges. Some units have no venting mechanism and release all of the EO used directly into the workplace. Other units vent emissions by manual pumping through a charcoal adsorbent on the top of the unit.

Ampule/Liner Bag--

With this method, the article to be sterilized and a broken ampule of 100 percent EO are put into a plastic liner bag. The bag is closed with a twist-tie, put into a non-gasketed metal container and left undisturbed for 12 hours. The EO is intended to escape slowly into the atmosphere. The purpose of the metal container is to prevent inadvertent ignition of the EO/air mixture in the bag.

Sterijet System--

The Sterijet system is marketed to hospitals and the medical products industry. It is similar to the ampule/liner bag in that the EO used is intended to escape slowly from a confining enclosure. After the article to be sterilized is placed in a pouch, the pouch is attached to a gas delivery machine which closes the bag around a protruding nozzle, draws a slight vacuum on the pouch, injects a premeasured amount of EO mixture and heat-seals the pouch. The pouch is then placed in an aeration cabinet at 50°C (122°F) for 12 hours as most of the EO leaks out. After 12 hours, the package has a vacuum-tight appearance which remains until the package is opened either intentionally for use of the contents or accidentally. Because the vacuum-tight appearance is lost if the package is accidentally punctured, the appearance serves as a visible indicator of sterility. Some EO remains in the pouch for as long as 36 hours after sterilization.

Tent Fumigation--

Tent fumigation is used only at ports of entry to fumigate cargo infested with snails or certain plant disease organisms. Procedures are specified by the U.S. Department of Agriculture (USDA) and treatment is supervised by USDA inspectors.

The cargo to be fumigated is placed on a concrete or other impervious surface and is covered with a vinyl, rubber-coated nylon, or polyethylene tarpaulin which is sealed around the edges. A wooden frame built over the cargo supports the tarpaulin. A 10 percent EO/90 percent carbon dioxide mixture is used for fumigation. Air in the enclosure is circulated by fans. After the fumigation period is over, the EO is dispersed from the enclosure either by the circulation fans or by large exhaust fans.

No Containment--

In some instances, the article to be fumigated serves as the container for the EO fumigant. This method is used primarily for the fumigation of railroad cars, but may also be used for rooms or entire buildings. In the case of a railroad car, the car is isolated, all openings but one are sealed, and warning signs are posted. An operator places a cylinder of EO in the car, opens the valve, exits the car and seals the opening. After about 6 hours, the seals are removed and the car is aired out.

Emissions

An estimate of the amounts of EO used per year for various fumigation/sterilization purposes is given in Table 9. This estimate was prepared by EPA's Office of Pesticide Programs. It shows that a total of 2600 to 3900 Mg (5.7 to 8.6 x 10⁶ lb)/yr of EO is estimated to be used for these purposes. This amount is 0.1 to 0.17 percent of the total predicted 1983 EO production.⁹ About 0.024 percent of the total EO production (0.5 Gg, 1.1 x 10⁶ lb) is used for sterilization/fumigation in medical facilities.¹⁰

TABLE 9. MISCELLANEOUS USES AND USE RATES OF ETHYLENE OXIDE AS A FUMIGANT AND STERILANT ^{9, a}

Site	Ethylene Oxide Used, Mg/yr ^b
Manufacturing Facilities (production of sterile medical disposables)	1,500 to 2,600
Medical Facilities	
Hospitals	400 to 450 ^c
Medical clinics	50
Dental clinics	29.7
Doctors (private)	16.8
Dentists (private)	3.3
TOTAL	<u>500 to 550</u>
Veterinarians (private and clinics)	0.045
Museums	0.3
Libraries/archives	0.86
Research Laboratories	
Annual breeding	22.7
Drug/medical devices	250 to 410
Microbiological/cancer	2.3 to 11.4
TOTAL	<u>275 to 444</u>
Railroad Cars	1.0
Beehives (State, USDA)	0.68 to 0.9
USDA High Containment Research Labs	2.0
USDA APHIS Quarantine Port of Entry	0.3
Spices	340
Black Walnuts	1.5
Cosmetics	11
Dairy Packaging	14.5
TOTAL	<u>2,600 to 3,900</u>

^a Estimates prepared by Benefits and Use Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, 1983.

^b Multiply by 2,200 to convert to millions of pounds.

^c 1976 value.

Much of the EO used for sterilization/fumigation is released, either immediately or gradually, to the environment. In most sterilization facilities, EO emissions are released directly to the atmosphere. Some industrial sterilization facilities do, however, control EO emissions with add-on equipment such as incinerators, scrubbers, and chemical conversion vessels. Emissions from some vacuum sterilizers are vented to a sewer or to a damp sponge. In some installations, EO emissions are passed through an evacuation pump where process water strips out EO and the EO-containing wastewater is discharged to a municipal sewer or recycled.^{11,12} No estimate is available for the amount of EO emissions released to a sewer versus the amount released directly to the atmosphere. Although EO is completely soluble in water, it has been shown to revolatilize into air due to its having a vapor pressure greater than that of water.¹³ Estimates of the amount of dissolved EO that will volatilize into air from drainage water range from 60 to 95 percent; however, definitive data documenting the amount of EO volatilized are not available.

Some portion of the EO charged to sterilizers has also been shown to be retained in the treated materials and the containers used to hold the treated materials.^{12,14} In a test at a spice sterilizing operation, immediately after sterilization the spice materials were found to contain 23 percent of the total amount of EO originally used for sterilization. After 24 hours, the treated spices contained about 9 percent of the original EO charge and after 1 week, the retained amount was about 3 percent.¹⁴

Atmospheric EO emissions from sterilizers can be controlled by either chemical conversion, wet scrubbing, incineration, or reclamation. A description of each of these methods is given below.¹⁵

- Chemical conversion - In chemical conversion processes, a weak acid solution is used to convert EO gaseous emissions to ethylene glycol liquid. The ethylene glycol can be sold to reprocessors or disposed of. This method of EO emissions control is greater than 99 percent effective. One prominent

chemical conversion system for controlling sterilizer EO emissions is the DEOXX® system designed by Chemrox, Inc.⁷ In an application at a spice sterilizing operation, the DEOXX® system achieved an average EO emissions reduction of greater than 99.98 percent.¹⁴ DEOXX® EO emission control systems have been or are scheduled to be installed in New York, Maryland, Michigan, Utah, Hawaii, California, Florida, Connecticut, Texas, Rhode Island, Illinois, Pennsylvania, South Carolina, and Minnesota.⁷ Chemrox, Inc. has estimated that by the end of 1986, 35 to 40 percent of medical supply manufacturing sterilization facilities will have installed or committed to install DEOXX® systems.¹⁵

- Wet Scrubbing - In scrubbing devices, gaseous EO emissions are passed through water or a weak acid solution which absorbs EO and produces limited conversions of EO to ethylene glycol. Some sources have judged scrubbing to be minimally effective;¹⁵ however, one test of an industrial sterilizer controlled by scrubbing produced an EO reduction efficiency of 99.3 percent.¹⁶ The scrubber used at the sterilizer operation was a bubble plate with a 3 inch demister. The scrubbing medium was a weak sulfuric acid solution with a water to sulfuric acid ratio of 10:1.¹⁷
- Incineration - In this process, gaseous EO emissions are converted to constituent elements and compounds, such as carbon, hydrogen, oxygen, water, and carbon dioxide, by combusting the stream using common fuels like propane. Incineration processes are greater than 99 percent effective at reducing EO emissions.
- Reclamation - In this process, refrigeration is used to condense gaseous EO emissions to a liquid for recycle and reuse. Reclamation systems are specially designed for use in EO sterilization operations with a gas mixture of 12 percent EO and 88 percent Freon®. These systems are greater than 99 percent effective at collecting reusable EO. It has been reported that only one sterilization operation in the United States is using this reclamation procedure.¹⁸

The decision on which EO emissions control method is most appropriate for a particular sterilization operation is dependent on the size of the sterilizer units, the type of sterilization gas mixture used, frequency of use of the sterilizer, and the number of sterilization units that can be ducted to a single control system.¹⁵

It has been reported that one facility in the United States ducts potential atmospheric emissions from EO sterilization chambers to storage vessels for recycle and reuse.¹⁸ Because some air will be introduced into the EO/Freon sterilization mixture during sterilization, the EO concentration will be lower than at the start of the sterilization cycle. To compensate for the EO dilution effect, higher pressures are used on each additional sterilization pass. As the EO concentration systematically decreases, higher and higher pressures are required for the sterilization. At some point, the required pressures are too high for safe sterilization. When the EO concentration drops below some minimum level, it is discharged and the cycle starts over.^{12,18}

Source Locations¹⁰

In 1976 there were less than 50 very large [$>28.3 \text{ m}^3$ (1000 ft³)] industrial sterilizers and about the same number of smaller industrial units. These were primarily in facilities which manufacture sterile disposable medical supplies such as syringes, needles and microbiological laboratory supplies. Life-support items such as pacemakers, blood oxygenators and dialyzers are also sterilized with EO. These facilities are in SIC Group Number 384. The trade association, Health Industry Manufacturers Association (HIMA), in Washington, D.C., would be a good source of information on the number and distribution of medical supplies sterilizers.

Most hospitals have at least one and perhaps more EO sterilizers. These units are also used in smaller medical, dental and veterinary clinics. In 1977 there were an estimated 1,000 to

2,000 intermediate to large sterilizers used in hospitals and more than 10,000 units in all used in hospitals and other medical facilities.

No detailed survey is available of the locations of these sterilizers, or of other fumigating equipment which uses EO.

REFERENCES FOR SECTION 5

1. Lovell, Ralph. Ethylene Glycol. In: Organic Chemical Manufacturing, Volume 9: Selected Processes. EPA-450/3-80-028d. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.
2. Ozero, B.J. and J.V. Procelli. Can Development Keep Ethylene Oxide Viable? Hydrocarbon Processing. March 1984. pp. 55-61.
3. Letter from Macauley, D.C., Union Carbide to Lahre, T., U.S. Environmental Protection Agency. 10 April 1986. Comments on draft ethylene oxide report.
4. SRI International. 1986 Directory of Chemical Producers, United States of America. Menlo Park, California. 1986.
5. Schomer, T.L. Glycol Ethers: In: Organic Chemical Manufacturing, Volume 9: Selected Processes. EPA-450/3-80-028d. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.
6. Schomer, T.L. Ethanolamines. In: Organic Chemical Manufacturing, Volume 9: Selected Processes. EPA-450/3-80-028d. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. December 1980.
7. Markwordt, D.W. Sources of Ethylene Oxide Emissions. EPA-450/3-85-014. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1985.
8. Goldgraben, R., et al. Mitigation of Worker Exposure to Ethylene Oxide. Mitre Corporation. McLean, Virginia. March 1981.
9. Memo from Reinhart, J., U.S. Environmental Protection Agency to Smith, C., Radian Corporation. 26 May 1983. Ethylene oxide used in fumigation.
10. Glaser, Zorach. Special Occupational Hazard Review with Control Recommendations for the Use of Ethylene Oxide as a Sterilant in Medical Facilities. National Institute for Occupational Safety and Health (NIOSH). Rockville, Maryland. August 1977.
11. California Air Resources Board. Performance Evaluation Test Report - Supplement to Number C-83-049. Ethylene Oxide Emissions from a Sterilization Chamber at McCormick and Company, Inc. (Schilling), Salinas, California. December 1983.
12. Desai, P.R. and A.J. Buonicore. Toxic Air Pollutant Emission Measurement Techniques for Non-Steady-State Processes: A Case Study with Ethylene Oxide Sterilizers. Paper presented at the 1986 EPA/APCA Symposium on the Measurement of Toxic Air Pollutants, April 27-30, 1986, Raleigh, North Carolina.

13. Letter from Macauley, D.C., Union Carbide to Lahre, T., U.S. Environmental Protection Agency. 10 April 1986. Comments on draft ethylene oxide emission factor document.
14. Letter and attachments from Thoits, F., Monterey Bay Unified Air Pollution Control District to Honrath, R., Radian Corporation. 4 April 1986. Test report on the DEOXXR ethylene oxide detoxification system.
15. Letter from Jorkasky, J.F., Health Industry Manufacturers Association to Lahre, T.F., U.S. Environmental Protection Agency. 30 January 1986. Comments on draft ethylene oxide emission factor report.
16. Letter from Myers, R., New Jersey Department of Environmental Protection to Lahre, T.F., U.S. Environmental Protection Agency. 3 March 1986. Comments on draft ethylene oxide emission factor report.
17. Telecon. Brooks, G.W., Radian Corporation with Myers, R., New Jersey Department of Environmental Protection. 17 April 1986. Description of the scrubbing system used to control ethylene oxide emissions.
18. Telecon. Brooks, G.W., Radian Corporation with Desai, P.R., Chemrox, Inc. 14 July 1986. Description of ethylene oxide reclamation and recycle/reuse systems.

SECTION 6
SOURCE TEST PROCEDURES

The U.S. EPA Office of Research and Development (ORD) is currently investigating viable source sampling and analytical procedures for EO air emissions, but has not yet published or recommended any particular method. The sampling and analysis methods presented in this chapter represent a collection of EO emission detection and quantification techniques that have been published in the literature as viable methods. These methods are adaptable both for grab sampling with subsequent laboratory analysis of the sample and for continuous monitoring with direct readout of the EO concentration. The presentation of these published methods in this report does not constitute endorsement or recommendation, nor does it signify that the contents necessarily reflect the views and policies of the U.S. EPA.

SAMPLING AND ANALYSIS

The various sampling and analysis methods found in the literature are listed in Table 10 along with a brief description of the advantages and disadvantages of each. Sampling and analysis techniques are discussed in general terms below.

Sampling Methods

Most sampling methods for EO are oriented to personnel monitoring or, more generally, to ambient air monitoring. The most widely reported of these employ solid adsorbent tubes of charcoal or Tenax-GC. The EO is desorbed from the tube either with carbon disulfide or by thermal desorption. The breakthrough volumes of both charcoal and Tenax-GC are adversely affected by high humidity. Since EO control processes use water absorption, it might be expected that these sampling procedures would not perform well in source sampling. The National Institute for Occupational Safety and Health (NIOSH)

TABLE 10. SELECTED PROCEDURES FOR ETHYLENE OXIDE MONITORING¹

Sample Collection Method	Analytical Method	Comments
<p>Sorbent Tube with Activated Charcoal</p> <ul style="list-style-type: none"> - NIOSH Method (2 tubes in series; adsorbing tube device. Contains 400 mg charcoal and back up tube contains 200 mg charcoal). - OSHA Method (2 tubes in series; each contains 150 mg charcoal). - Qazi-Hetcham Method (1 tube; front section charcoal and back up section contains 390 mg charcoal). 	<ul style="list-style-type: none"> - Desorption with carbon disulfide and gas chromatographic determination. <li style="text-align: center;">or - Thermal desorption and gas chromatographic determination. 	<p>Advantages:</p> <ul style="list-style-type: none"> - Small, portable sampling - Minimal interferences. <p>Disadvantages:</p> <ul style="list-style-type: none"> - Breakthrough can occur. - In areas with greater than 60 percent relative humidity, 10 contains to 40 percent EO loss found with sample volume 10 liters. - Not suitable for extremely short sampling periods (15 minutes) - Requires cold transportation and storage conditions.
<p>Impinger (gas bubble tube containing liquid medium)</p> <ul style="list-style-type: none"> - Romano Method (EO converted to EO in a 0.1N sulfuric acid solution). - Bolton Method (EO converted to EG in 20 percent sulfuric acid solution). 	<ul style="list-style-type: none"> - Neutralization of absorbing acid solution with 50 percent potassium hydroxide and gas chromatographic determination. - Oxidation to formaldehyde and colorimetric determination based on reaction with sodium chromotrope. 	<p>Advantages:</p> <ul style="list-style-type: none"> - Absorption efficiency not subject to ambient air temperature or relative humidity. <p>Disadvantages:</p> <ul style="list-style-type: none"> - Cumbersome sample apparatus. - wet method analysis (Bolton Method). during - Possible spillage during sampling and transfer. - Requires correction for evaporation.
<p>Sample Bag (Tedlar)</p>	<ul style="list-style-type: none"> - Gas chromatographic determination 	<p>Advantages:</p> <ul style="list-style-type: none"> - Suitable for 8-hour or short term (5 minutes or less) samples. - No sample loss at 50 ppm EO during 5 day storage period. - No need to transport under cold conditions. <p>Disadvantages</p> <ul style="list-style-type: none"> - Bulky sample apparatus. - Possible penetration by sharp object. - Bags may not be reusable due to EO adsorption on walls.

sampling tube assembly consists of two separate large tubes, the first containing 400 mg and the second (a backup) containing 200 mg of activated coconut charcoal.

Impingers, when used, are filled with a dilute sulfuric acid solution which converts the captured EO to ethyl glycol. Before analysis, the solution is neutralized with 50 percent potassium hydroxide.^{2,3}

For stack gases, particularly those from incineration, a known volume of gas is collected in an evacuated 2-liter gas bulb. The bulb should be coupled directly to a separate sampling line from the stack and not coupled with any other sampling train.⁴

Tedlar bags, though bulky, may be used to capture a known volume of ambient air.¹ This sampling procedure should also be adaptable to source sampling.

When attempting to establish a material balance for EO charged to and released from sterilizer facilities, all possible paths for EO releases need to be assessed. In addition to atmospheric discharges, some EO may also be absorbed in evacuation pump water, retained in the treated product, and bled off and recycled for reuse. Desai and Buonicoire have recently presented procedures for use in testing EO sterilizers that assess all these pathways for EO emissions.⁵

Analytical Methods

Gas chromatography (GC) coupled with flame ionization detection (FID)¹ is currently the method of choice for EO analysis and is the basis for the NIOSH method for determination of EO. For the NIOSH method, the column is filled with Porapak QS. The NIOSH method is considered specific for EO as long as there is no other compound present with the same retention time. A change in the separation conditions, such as column packing or temperature, will usually circumvent interference problems. The method is accurate over a wide

concentration range. It was validated at EO concentrations of 41 to 176 mg/m³. At the OSHA standard of 90 mg/m³ (50 ppm), the total sampling and analytical method has a standard deviation of 9.3 mg per cubic meter.³

Other available analytical methods include: 1) hydration to EG (in an impinger), oxidation to formaldehyde, then colorimetric determination of the formaldehyde by its reaction with sodium chromotrope; 2) spectrophotometry; 3) volumetric methods; and 4) conversion to ethylene chlorohydrin, then analysis of the chlorohydrin by mass spectrometry or gas chromatography.

DIRECT INSTRUMENTATION METHODS

A variety of direct-reading instruments are available for determination of EO concentrations in air. These instruments, which may be portable or fixed continuous monitors, are primarily intended for area monitoring situations. Available instruments for direct monitoring of EO concentrations are described in Table 11.

The most commonly used instrument for direct reading of EO concentrations is the infrared gas analyzer. It may be a portable unit or part of a fixed, multi-point continuous monitoring system. Two wavelengths are used for EO monitoring--11.8 μm and 3.3 μm . Freon, a common nonflammable carrier in EO/gas mixtures, interferes at the 11.8 μm wavelength. Alcohols interfere at 3.3 μm .¹

GC-FID, the most commonly used method for grab sample analysis, is also used in portable instruments. One such unit features a selective absorbent filter in the input line to the FID to eliminate interference from Freon.¹

TABLE 11. SELECTED ETHYLENE OXIDE DIRECT MONITORING METHODS¹

Method (Manufacturer)	Detection Range, ppm	Specificity	Remarks
Infrared Spectrophotometry (Beckman) (Foxboro/Vilks) (Mine Safety Appliances)	<50 1-10,000 1-12,000	Interference from Freon at 11 m, alcohol at 3.3 μ m	Limited accuracy below 10 ppm.
Flame Ionization Gas Chromatography (Century)	0.5-1,000 (TOC)	Detects total organics if GC not used. With GC, specific to EO except for compounds with similar retention times. Selective filter can eliminate Freon interference	Meter readout, audible alarm and strip chart recorder available.
Photoionization (HNU Systems)	0.1-2,000	Interference by any compound which ionizes below 0.5 electronvolts	Requires daily calibration.
Colorimetry (National Draeger) (SKC)	25-500	Interference by propylene oxide, Ethylene, ketones, aldehydes, esters	Accurate within 15 percent. Grab samples only.
Combustible Gas Detection (Bacharach) (Enmet) (Rexnord) (Surgicot) (Gas Tech)	1-10,000 1-100 3,000-30,000 >50 20-1,000	Detects any combustible gas	Some may be used for remote monitoring.
Solid State Sensor (International Sensor Technology)	1-150	Interference by CO ₂ , H ₂ , NH ₃	Non-linear scale, slow clearance to zero when operated continuously.

REFERENCES FOR SECTION 6

1. Goldgraben, R., et al. Mitigation of Worker Exposure to Ethylene Oxide. Mitre Corporation. McLean, Virginia. March 1981.
2. Bogyo, D.A., et al. Investigation of Selected Potential Environmental Contaminants: Epoxides. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1980. NTIS Publication No. PB80-183197.
3. National Institute for Occupational Safety and Health (NIOSH). NIOSH Manual of Analytical Methods, Second Edition. Part II: Standards Completion Program Validated Methods, Volume 3. U.S. Department of Health, Education, and Welfare. Cincinnati, Ohio. April 1977.
4. Harris, Judith C. Sampling and Analysis Methods for Hazardous Waste Incineration, First Edition. Arthur D. Little, Cambridge, Massachusetts. February 1982.
5. Desai, P.R. and A.J. Buonicore. Toxic Air Pollutant Emission Measurement Techniques for Non-Steady-State Processes: A Case Study with Ethylene Oxide Sterilizers. Paper presented at the 1986 EPA/APCA Symposium on the Measurement of Toxic Air Pollutants, April 27-30, 1986, Raleigh, North Carolina.

APPENDIX A
DERIVATION OF EMISSION ESTIMATES FOR FUGITIVE
EQUIPMENT LEAKS BASED ON EPA EMISSION FACTORS

The material in this appendix supports the emission estimates for fugitive equipment leaks presented in Table 6 and Table 7 of the main text. These derivations assume "model" air oxidation and oxygen oxidation plants, having a specified number of valves, pump seals, compressors, etc. As such, the estimates will not necessarily apply to a particular facility. Incorporated in these estimates are EPA's emission factors for fugitive leaks and EPA's estimates of control efficiencies that would result from application of Reasonably Available Control Technology (RACT), as defined in the Control Techniques Guideline (CTG), and the New Source Performance Standards (NSPS).

TABLE A-1. FUGITIVE EQUIPMENT LEAK PARAMETERS - AIR OXIDATION MODEL ETHYLENE OXIDE PRODUCTION PLANT^A

Emission Source	Number of Sources	Emission Factor (kg/day/source) ^b	Control	Controlled EO Efficiency (%) ^c		Emissions (kg/day)	
			Uncontrolled EO Emissions (kg/day)	CTG	NSPS	CTG	NSPS
Pump Seals							
Light liquid	27	1.19	15.9	33	61	10.7	6.2
Heavy liquid	-	-	-	-	-	-	-
Valves							
Gas	200	0.13	13.2	64	73	4.8	3.6
Light Liquid	581	0.17	49.3	44	59	26.7	20.2
Heavy Liquid	-	-	-	-	-	-	-
Safety/Relief Valves							
Gas	60	2.5	75	44	100	40.5	0
Open Ended Lines	192	0.04	(d)	100	100	0	0
Compressors	6	5.47	16.2	33	100	6.6	0
Sampling Connections	145	0.36	12.0	0	0	12.0	12.0
Flanges	1,214	0.02	<u>12.0</u>	0	0	<u>12.0</u>	<u>12.0</u>
TOTAL			188.2			112.2	42.0

^a From material in Tables 3-4, 4-2 and 5-3b in Reference 1. The equipment counts also include integrated EO derivative plants.

^b These are total VOC emissions. On average, each component sees 50 percent EO service, so a factor of 0.5 is introduced when calculating EO emissions. Actual EO service will vary from <5 to >99 percent in individual components.

^c See Table A-3 for a brief description of assumed control techniques.

^d All open ended lines (in model unit) are assumed to be controlled, therefore, there are no associated emissions.

^e 75 percent of sampling connections are assumed to be controlled; therefore, the emissions are based on 36 of 145 sampling connections.

TABLE A-2. FUGITIVE EQUIPMENT LEAK PARAMETERS - OXYGEN OXIDATION MODEL ETHYLENE OXIDE PRODUCTION PLANT^A

Emission Source	Number of Sources	Emission Factor (kg/day/source) ^b	Control	Controlled EO		Emissions (kg/day)	
			Uncontrolled EO Emissions (kg/day)	Efficiency (%) ^c		CTG	NSPS
Pump Seals							
Light liquid	30	1.19	17.8	33	61	11.9	6.9
Heavy liquid	-	-	-	-	-	-	-
Valves							
Gas	177	0.13	11.52	64	73	4.1	3.1
Light Liquid	693	0.17	58.9	44	59	33.0	24.12
Heavy Liquid	-	-	-	-	-	-	-
Safety/Relief Valves							
Gas	26	2.5	32.3	44	100	18.1	0
Open Ended Lines	160	0.04	(d)	100	100	0	0
Compressors	3	5.47	7.9	33	100	5.3	0
Sampling Connections	40	0.36	1.6 ^e	0	100	1.6	0
Flanges	1,738	0.02	<u>17.5</u>	0	0	<u>17.5</u>	<u>17.5</u>
TOTAL			147.5			91.5	51.6

^a From material in Tables 3-4, 4-2 and 5-3a in Reference 1.

^b These are total VOC emissions. On average, each component sees 50 percent EO service, so a factor of 0.5 is introduced when calculating EO emissions. Actual EO service will vary from <5 to >99 percent in individual components.

^c See Table A-3 for a brief description of assumed control techniques.

^d All open ended lines (in model unit) are assumed to be controlled, therefore, there are no associated emissions.

^e 75 percent of sampling connections are assumed to be controlled; therefore, the emissions are based on 5 of 40 sampling connections.

TABLE A-3. FUGITIVE EQUIPMENT LEAKS CONTROL TECHNIQUES¹

Emission Source	Control Technique ^a	
	CTG	NSPS
Pump seals (light liquid)	LDAR ^b (quarterly monitoring)	LDAR (monthly monitoring)
Valves (gas or light liquid)	LDAR (quarterly monitoring)	LDAR (monthly monitoring)
Safety/relief valves (gas)	LDAR (quarterly monitoring)	Performance standards+ ^c
Open-ended lines	Caps	Caps
Compressors	LDAR (quarterly monitoring)	Seal system
Sampling connections	None	Closed purge system

^a References 2 and 3, respectively, discuss control measures that constitute those corresponding to the CTG (Control Techniques Guideline) and NSPS (New Source Performance Standard).

^b LDAR - Leak Detection and Repair.

^c Except during pressure releases, relief valves must be operated with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background. After a pressure release episode, a relief valve must be returned to a condition of no detectable emissions as indicated by an instrument reading of less than 500 ppm above background, as soon as practicable, but no later than five calendar days after the release. See 40 CFR, Subpart VV, 60.482-4 for more information on relief valve requirements.

REFERENCE FOR APPENDIX A

1. Markwordt, D.W. Sources of Ethylene Oxide Emissions. EPA-450/3-85-014. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. April 1985.

2. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment. EPA-450/3-83-006. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. March 1984.

3. VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry - Background Information for Proposed Standards. EPA-450/3-80-033a. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. November 1980.