ETHYLENE OXIDE

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1.0 SCOPE

This document provides recommendations to prevent or minimize losses from fires and explosions involving ethylene oxide storage and handling.

The recommended safeguards are designed to limit losses in normally expected accidents. Impaired fire protection systems, inoperative control or safety devices, and improper procedures can lead to more extensive losses.

1.1 Changes

April 2013. Minor editorial revisions were made.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 General

2.1.1 Construction and Location

2.1.1.1 Design storage tanks and other vessels in accordance with the pressure vessel codes of the American Society of Mechanical Engineers (ASME) (Sections I, III, and VIII most applicable), for the minimum design working pressure consistent with process requirements and with the blanket gas pressure needed to maintain a nonexplosive vapor space.

Ambient temperature operations will normally require design pressures of 75 psi (515 kPa), with blanket gas pressure of 50 to 70 psi (345 to 485 kPa). In refrigerated operations, design pressures in the order of 15 psi (103 kPa) and blanket gas pressure of 10 psi (69 kPa) may be applicable.

Blanket gas and refrigeration systems are vital to maintain safe storage conditions. Ensure these systems are extremely reliable and well maintained. Evaluate the effects of a release from a relief vent for all types of storage systems and provide appropriate safeguards, if needed. (See Recommendation No. 2.1.4.1.) To reduce the potential for ethylene oxide releases due to loss of refrigeration, store ethylene oxide at ambient temperature and 75 psi (515 kPa).

2.1.1.2 Ensure tanks, reactors, sterilizers, piping, temperature and pressure sensing devices, and other equipment is constructed of steel (carbon, alloy or stainless). Metals such as copper, silver, mercury, and their alloys are potential explosion catalysts with ethylene oxide in the presence of acetylene, and should not be used unless the ethylene oxide and diluent are continuously proven to be acetylene-free.

Exception: Copper and copper alloys may be used with low-concentration mixes (20% of ethylene oxide or less) under those conditions that have been proven to be safe by past experience or tests. However, do not use copper and copper alloys if a process upset could result in ethylene oxide concentrations greater than 20%.

2.1.1.3 Ensure any building or enclosed area where ethylene oxide is processed is provided with damage-limiting construction in accordance with Data Sheet 1-44, *Damage-Limiting Construction*.

Exception: Damage-limiting construction may be omitted in areas where the maximum ethylene oxide concentration is 20% or less. See Section 3.1.6, *Sterilization Processes,* for guidance if 100% ethylene oxide is used to replenish consumed ethylene oxide in nonflammable mixes.

2.1.2 Occupancy

2.1.2.1 Do not make any deviations from standard procedures without careful study in laboratory and pilot plant stages, and consultation with fire protection engineers.

2.1.2.2 Ensure any building or enclosed area using ethylene oxide is well ventilated. Provide fixed mechanical ventilation at the rate of 1 cfm/ft^2 of floor area (0.3 m^3/min/m^2) where a leak potential exists. Examples include areas with pumps, valves, flanges, vaporizers, or where equipment is opened periodically as part of the operating cycle.

2.1.2.3 Ensure diluent gases remain dry and free from impurities, especially those such as oxygen, ammonia, acetylene, hydrogen sulfide, dirt, and grease. It may be necessary to continually monitor the inert gas to confirm the absence of impurities.

2.1.3 Protection

2.1.3.1 Have automatic water spray systems designed and installed in accordance with Data Sheet 4-1N, *Water Spray Fixed Systems* (NFPA).

2.1.4 Equipment and Processes

2.1.4.1 Refer to Data Sheet 7-49, *Emergency Venting of Vessels,* for guidance on pressure relief devices for reactors, storage tanks, and other vessels. Rupture disks may be used to provide part of the required venting capacity. On reactors where plugging may occur, protect pressure relief valves with rupture disks.Ensure discharge lines from relief devices and equipment vents terminate at a safe location.

2.1.5 Operation and Maintenance

2.1.5.1 Have controls, fire protection systems, and safety devices inspected at least monthly and ensure they are maintained in proper operating condition. Have all processes carefully logged, and ensure log books are checked frequently by supervisory personnel for abnormal operations or procedures.

2.1.5.2 Have equipment and piping system thoroughly cleaned, purged with inert gas, and tested for inertness before maintenance and before introducing ethylene oxide into the system.

2.1.6 Ignition Source Control

2.1.6.1 Electrically bond and ground all tanks and piping.

2.1.6.2 Provide appropriate hazardous-location electrical equipment for Class I, Group B locations in areas where ethylene oxide is used. Refer to Data Sheet 5-1, *Electrical Equipment in Hazardous Locations,* and NFPA 497A, *Classification of Class I Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas,* for guidance in determining areas requiring Division 1 or 2 equipment.

2.2 Storage

For storage of small containers (less than 7 oz [200 g] capacity), see Section 2.9, *Portable Sterilizers.*

2.2.1 Tank Storage of Ethylene Oxide

2.2.1.1 Construction and Location

2.2.1.1.1 Separate ethylene oxide tanks from important buildings, structures, utilities, and other outside storage in accordance with Figure 1. Note the following when using Figure 1:

a) The quantity used to determine spacing is the maximum total capacity of a tank or tanks that can be exposed to simultaneous flame impingement.

b) Prevent simultaneous flame impingement on tanks within a group by:

  i) separating tanks by at least 20 ft (6 m) or erecting barriers of two-hour fire resistance between tanks. Refer to Data Sheet 1-21, *Fire Resistance of Building Assemblies,* for details regarding barrier construction;

  ii) providing diking and drainage systems to prevent leakage at one tank from flowing under another; and

  iii) locating manifolded headers at least 10 ft (3 m) horizontally from tanks.

c) All distances in Figure 1 may be reduced 50% where the storage tanks have automatic water spray protection or where they are buried or mounded.

d) In chemical plants, where essentially open structures are using or producing ethylene oxide and both structures and tanks have automatic water spray or are buried, ethylene oxide tanks may be located with a minimum of 25 ft (7.6 m) separation. Provide temperature monitoring and ethylene oxide removal systems. Manually actuated ethylene oxide removal systems are acceptable if the plant is constantly attended by personnel well-trained in emergency procedures.

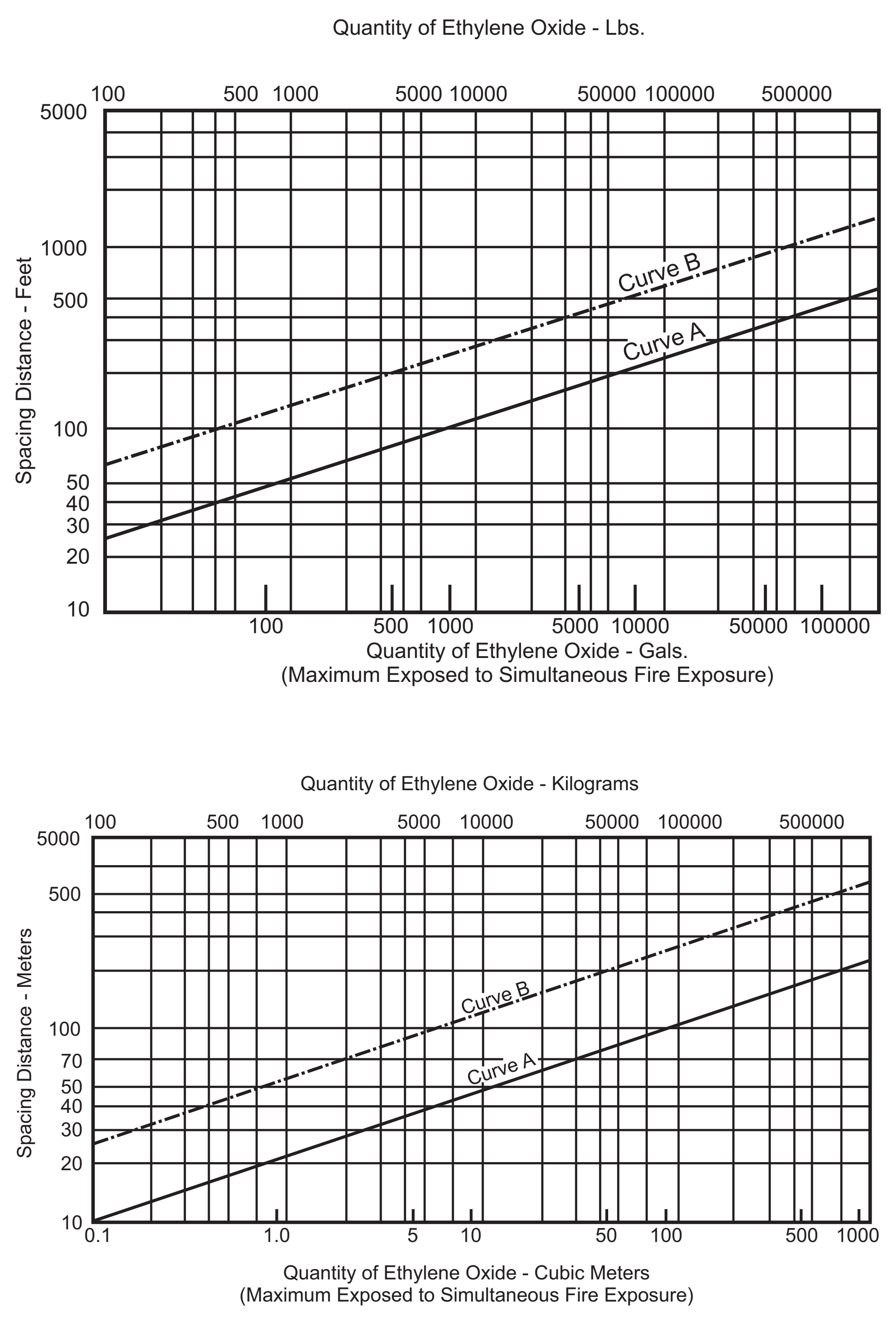


Fig. 1. Minimum distance requirements for storage of ethylene oxide. Use Curve A for distances from storage to major buildings and structures, and vital utilities of explosion-damage-limiting construction, including ignitable liquid and flammable gas tanks. Use Curve B for distances to major buildings of loadbearing wall construction.

2.2.1.1.2 Where spacing as indicated in Figure 1 is not available, provide automatic water spray protection, burying or mounding, and continuous monitoring of tank liquid temperature arranged to sound an alarm and to remove tank contents automatically to a safe location. Table 1 is a guide for alarm and removal temperature setting.

Table 1. Alarm and Dump Temperature and Pressure Relief Valve Settings for Concentrated Ethylene Oxide Storage Tanks Using Nitrogen as the Blanket Gas

a. English Units

Normal Vapor Space Pressure, psi at 85°F	*Settings Temperature, °F*		*Pressure Relief Valve Settings, psi*
	Alarm	*Dump (if provided)*	
50	95	105	65
55	100	100	72
60	100	115	80
70	100	120	100

b. Metric Units

Normal Vapor Space Pressure, kPa at 29.4°C	*Settings Temperature, °C*		*Pressure Relief Valve Settings, kPa*
	Alarm	*Dump (if provided)*	
345	35	40	450
380	38	43	500
414	38	46	550
483	38	49	690

2.2.1.1.3 Size ethylene oxide removal systems, if provided, to empty the full tank in no more than one hour. Provide a liquid trap near the end of the removal line. Ensure the removal system terminates at a safe and acceptable location. Have proposed locations reviewed by fire protection engineers as well as other interested parties, such as environmental engineers.

Previously used removal systems have included systems that terminate at bodies of water capable of diluting the ethylene oxide below the flammable concentration, and at burning pits with automatic water spray interlocked with the automatic controls to control burning.

2.2.1.1.4 Do not store ethylene oxide in the same containment area with other ignitable liquid storage tanks.

2.2.1.2 Protection

2.2.1.2.1 Provide automatic water spray on tank groups exceeding 60,000 gal (225 m^3) in capacity. Tanks separated by distances less than 25% of Curve A on Figure 1 are in the same tank group.

2.2.1.2.2 Isolate tank groups from each other and from important property by natural drainage, diversion dikes, and/or trenches to prevent leakage at one group from exposing property or another tank group.

2.2.1.2.3 Provide dedicated drains and dikes for ethylene oxide to prevent storage area spills from approaching buildings and other storage. Do not provide connections that may allow other materials to enter the drainage system and contaminate ethylene oxide.

2.2.1.2.4 Maintain the stable gas pressure automatically to keep the tank vapor space nonexplosive within the normal range of atmospheric temperature. Typically, the stable gas pressure is not less than 50 psi (345 kPa) (Figs. 2 and 3). An inert gas, such as nitrogen, is preferable to a flammable gas, such as methane.

2.2.1.2.5 Provide cooling for aboveground tanks if ambient temperatures can heat the liquid contents above 85°F (30°C). External heat exchangers or water spray systems (separate from fire protection water spray systems) provide a reliable method of cooling. Do not use ignitable refrigerants.

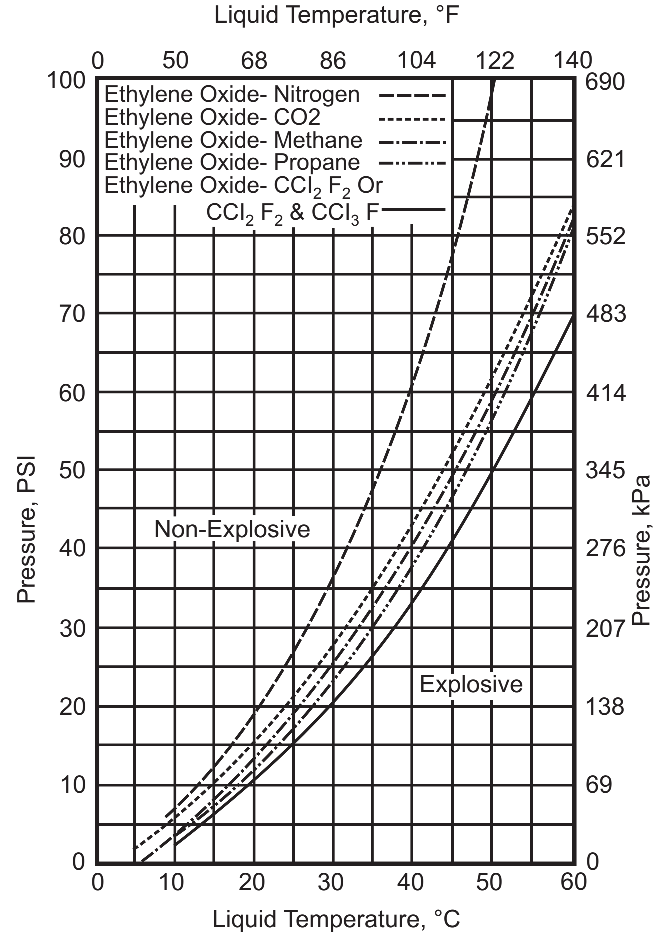


Fig. 2. Safe operating pressures for mixtures of ethylene oxide vapor and diluents over ethylene oxide liquid at various temperatures.

2.2.2 Drum and Cylinder Storage of Flammable Mixtures

2.2.2.1 Construction and Location

2.2.2.1.1 Store drums or cylinders of flammable mixtures in accordance with Curve A of Figure 1 up to 100 ft (30 m) maximum from important buildings and structures. Use the actual weight of the ethylene oxide. Up to 500 lb (225 kg) aggregate cylinder capacity may be stored outdoors against noncombustible walls if kept at least 10 ft (3 m) from building openings. (See Section 3.1.3, *Ethylene Oxide/Air/Diluent Mixtures,* for definition of flammable and nonflammable mixtures.)

2.2.2.1.2 Use noncombustible weather hoods or light noncombustible shelters for storage. Provide automatic sprinkler protection if the aggregate cylinder capacity exceeds 20,000 lb (9,070 kg) or drum storage exceeds 5,000 gal (19 m^3). Design sprinkler systems to provide at least 0.25 gpm/ft^2 (10 mm/min) over 3,000 ft^2 (280 m^2).

2.2.2.1.3 Store no more than two 180 lb (71 kg) U.S. Department of Transportation (USDOT) (or equivalent in non-U.S. locations), store cylinders indoors. If cylinders are stored indoors, provide protection as outlined in Data Sheet 7-50, *Compressed Gases in Portable Cylinders and Bulk Storage.*

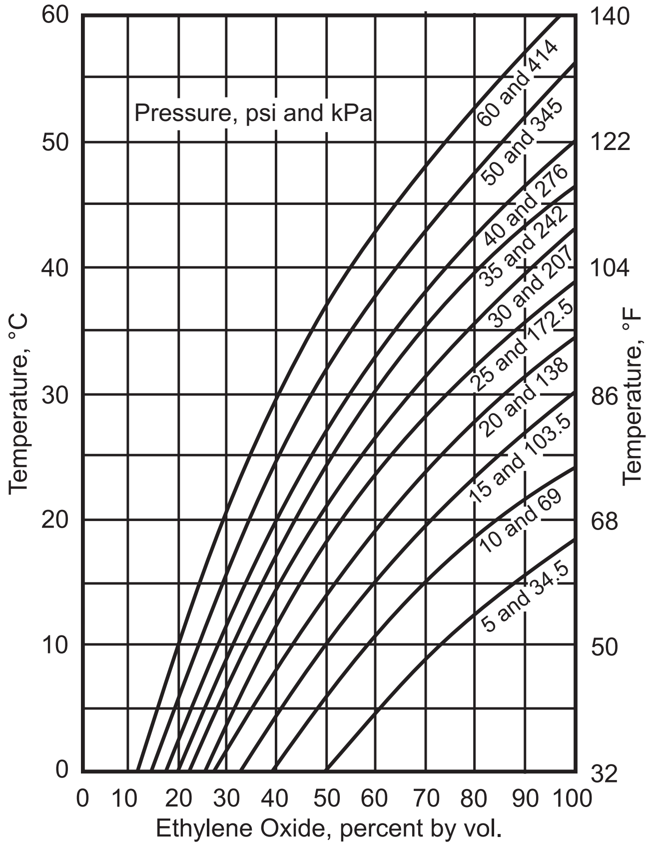


Fig. 3. Concentration of ethylene oxide vapor in mixtures with any inert gas in equilibrium with liquid at various temperatures and pressures

2.2.3 Storage of Nonflammable Mixtures

2.2.3.1 Construction and Location

2.2.3.1.1 Separate outdoor cylinder storage at least 20 ft (6 m) from combustibles.

2.2.3.1.2 Cylinders may be stored indoors where (a) buildings are well ventilated, (b) there are no combustibles within 10 ft (3 m), and (c) sprinkler protection is provided if construction or occupancy is combustible.

2.2.3.1.3 Two spare cylinders may be located at sterilizers in addition to those connected to the equipment.

2.3 Vaporizers

2.3.1 Construction and Location

2.3.1.1 Locate ethylene oxide vaporizers at least 50 ft (15 m) from storage tanks, buildings, and utilities.

Explosion-resistant barriers between vaporizers and other process equipment is an acceptable alternative to spacing. Vaporizers may be located near the point of ethylene oxide use in chemical process buildings of damage-limiting construction in accordance with Data Sheet 1-44, *Damage-Limiting Construction.*

2.3.2 Occupancy

2.3.2.1 Use hot water or low-pressure (less than 15 psi [105 kPa]) steam as a preferred heat source for vaporizers. Electric heat may be used for nonflammable mixtures.

2.3.2.2 Provide automatic shutdown of heat and feed to vaporizers in case of vaporizer temperature increase greater than 20°F (11°C) or pressure increase greater than 10% above normal operating conditions.

2.3.2.3 If the process permits, introduce sufficient stable gas directly downstream of vaporizers to prevent explosive mixtures in downstream piping and equipment.

2.3.3 Protection

2.3.3.1 Provide automatic sprinkler protection in vaporizer rooms or buildings. Design sprinkler systems to provide at least 0.25 gpm/ft^2 (10 mm/min) over a minimum area of 3,000 ft^2 (280 m^2).

2.4 Loading and Unloading Stations

2.4.1 Construction and Location

2.4.1.1 Locate loading-unloading stations for tank cars or trucks at least 50 ft (15 m) from storage tanks, important buildings, structures, and other yard storage, and provide automatic sprinklers or water spray. ***Clearly identify the stations to help prevent introducing any other material into the ethylene oxide system, or vice versa.***

2.4.1.2 Locate tanker cars awaiting unloading as far away from other exposures as possible, and minimize the storage time.

2.5 Piping

2.5.1 Occupancy

2.5.1.1 Design piping systems in accordance with ANSI Standard B31.3, *Chemical Plant & Petroleum Refinery Piping,* or equivalent international standard.

2.5.1.2 Use stainless steel, spiral-wound, polyfluoroethylene gaskets on all flanged fittings.

2.5.1.3 Provide check valves on fill and return lines at storage tanks and equipment. Provide excess flow valves and remotely operated fail-safe control valves on outlet lines on storage tanks or cylinders.

2.5.1.4 Arrange for emergency shutoff of ethylene oxide supply in case of leakage or process upset inside the building in accordance with good practices for ignitable liquid and flammable gas piping. Refer to Data Sheet 7-32, *Ignitable Liquid Operations,* and Data Sheet 7-54, *Natural Gas and Gas Piping,* for additional details.

2.5.1.5 Where ethylene oxide piping is directly interconnected with equipment or pipe lines containing other materials, arrange piping systems with appropriate devices, such as automatic valves controlled by pressure switches and flow meters, to prevent backflow of one material into the supply of another. Check valves alone are not reliable for this service.

2.5.1.6 Design transfer systems to withdraw liquid rather than vapor from the storage containers, unless specially designed flash arresters are provided in vapor lines. (Ordinary wire mesh-type flame arresters are not suitable.) With gas pressure transfer systems, do not apply heat to increase pressure. Terminate liquid inlet lines near the bottom of tanks and process equipment to minimize generation of static electricity.

2.6 Ethylene Oxide Pumping

2.6.1 Construction and Location

2.6.1.1 Locate pumps a minimum of 50 ft (15 m) from storage tanks and other vessels that contain ethylene oxide.

2.6.2 Occupancy

2.6.2.1 Provide high-temperature and low-flow alarms and interlocks on ethylene oxide pumps.

2.6.2.2 Provide remotely operated isolation valves on ethylene oxide pumps.

2.6.3 Protection

2.6.3.1 Protect pumping stations with water spray or deluge systems.

2.7 Insulation

2.7.1 Occupancy

2.7.1.1 Evaluate insulation used on ethylene oxide storage tanks, process vessels, or piping to verify the insulation minimizes the potential for catalyzing an ethylene oxide reaction and spontaneously igniting the insulation if an ethylene oxide leak occurs beneath the insulation.

2.7.1.2 Coat ethylene oxide vessels or piping with rust-preventive paint before applying insulation.

2.8 Fixed Sterilizers

2.8.1 Construction and Location

2.8.1.1 If a room explosion hazard exists, locate fixed sterilizers in noncombustible buildings of damage-limiting construction. (See Section 3.1.6, *Sterilization Process,* for explanation of equipment and room explosion hazard potentials.)

2.8.1.2 Separate the sterilizer area from major buildings and utilities by a minimum of 25 ft (7.5 m) in accordance with Figure 1, using 1 lb of ethylene oxide per 10 ft^3 (1.6 kg/m^3) of the volume of the largest sterilizer in the area. The sterilizer area may be connected to a main building by an enclosed passageway with self-closing doors at each end.

2.8.1.3 Locate sterilizers operating with low flammability ethylene oxide mixtures (20% ethylene oxide or less) in areas having a minimum ventilation of 0.25 $ft^3/min/ft^2$ of floor area (75 $L/min/m^2$). Ensure gas supply manifolds and piping are in accordance with Data Sheet 7-54, *Natural Gas and Gas Piping.*

2.8.1.4 Design sterilizers in accordance with applicable ASME codes for the maximum expected positive and negative pressures.

2.8.2 Occupancy

2.8.2.1 Design sterilization processes to avoid operation with flammable gas compositions. These compositions may be avoided by careful design as discussed in Section 3.1.4, Avoiding Flammable Mixtures of Ethylene Oxide/Air/Diluent.

2.8.2.2 Use hot water or low pressure steam supplied from a remote source for heating sterilizers. Electrical heating is acceptable for sterilizers that use nonflammable mixtures.

2.8.3 Protection

2.8.3.1 Provide automatic sprinkler protection in sterilization areas where explosive or flammable gas mixtures are used or other combustibles are present. Design automatic sprinkler systems to provide at least 0.25 gpm/ft^2 (10 mm/min) over the most remote 3,000 ft^2 (280 m^2).

2.8.4 Equipment and Processes

2.8.4.1 Provide pressure relief valves sized in accordance with LP-gas practice for vaporizers, sterilizers and piping where liquid can be trapped.

2.8.4.2 Provide automatic timing cycles and pressure switches interlocked to prevent the opening of the sterilizer chamber doors while charged with a flammable ethylene oxide mixture. Arrange the timing cycles and pressure switches to help ensure proper purging and filling operations.

2.8.4.3 Provide limit switches to automatically actuate an alarm, exhaust ethylene oxide vapors, flood with inert gas, and shut off the heat supply and ethylene oxide feed if unsafe temperatures or pressures develop in sterilizers.

2.8.4.4 Arrange relief and vent lines on sterilizers operating with explosive or highly flammable mixtures to terminate out-of-doors at a safe location, even if water scrubbers or chemical converters are used. Vents on sterilizers using nonflammable mixtures may terminate indoors if water scrubbers or chemical converters can effectively remove all ethylene oxide at the maximum discharge rate.

2.8.5 Operation and Maintenance

2.8.5.1 Keep vacuum pumps well maintained to ensure proper operation of the sterilization cycle.

2.9 Portable Sterilizers

The following safeguards pertain to the use of portable sterilizers using flammable mixtures (in most cases, 100% concentration) of ethylene oxide in small ‘‘single-charge’’ cartridges. Sterilization units with a maximum working volume of 8 ft^3 (0.3 m^3) that use single-charge cartridges containing approximately 7 oz (200 g) or less of ethylene oxide are considered portable sterilizers for the purposes of this data sheet. Protect larger sterilizers in accordance with Section 2.8, Fixed Sterilizers.

2.9.1 Construction and Location

2.9.1.1 Use the sterilizer in well-ventilated areas, at least 6 ft (1.8 m) from open flames and electrical ignition sources.

2.9.2 Occupancy

2.9.2.1 Design sterilization processes to avoid operation with flammable gas compositions. These compositions may be avoided by careful design as discussed in Section 3.1.4, Avoiding Flammable Mixtures of Ethylene Oxide/Air/Diluent.

2.9.2.2 Limit ethylene oxide cartridge storage near each sterilizer to a 1-day supply. Store these cartridges on open shelving under automatic sprinkler protection or in FM Approved ignitable liquid storage cabinets. Store additional cartridges in an area safeguarded in accordance with Data Sheet 7-31, *Storage of Aerosol Products.*

2.9.3 Equipment and Processes

2.9.3.1 Vent the sterilizer and associated aerator (if provided) directly to a safe location. Terminate vent lines at least 5 ft (1.5 m) from building openings.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 General Information

3.1.1 Hazards

Ethylene oxide, also known as ‘‘epoxyethane’’ and ‘‘oxirane,’’ is a flammable, highly reactive, low-boiling-point material used principally as an intermediate compound in chemical manufacturing and as a sterilizing or fumigating agent.

Ethylene oxide vapors are unstable and subject to explosive decomposition. Fire and explosion hazards associated with ethylene oxide manufacture, use, and storage include the following:

1. Fires involving flammable ethylene oxide liquid or vapor

2. Deflagrations involving confined combustion of ethylene oxide vapor

3. Runaway reactions involving ethylene oxide that result in excessive heat and pressure generation that may over-pressurize containment

4. Decomposition of ethylene oxide vapor (or liquid under extreme temperature and pressure)

5. An outdoor vapor cloud explosion involving large amounts of released ethylene oxide

3.1.1.1 Flammability

The lower flammable limit of ethylene oxide vapor in air is 3% and the upper flammable limit is approximately 80%. Concentrations of ethylene oxide in air above 80% may decompose exothermally. (See discussion below.) Therefore, ethylene oxide concentrations of 3% to 100% in air may deflagrate under appropriate conditions. The flammable range and decomposition potential may be altered by diluent gases such as nitrogen, carbon dioxide, steam, and methane. (See Section 3.1.3.)

Ethylene oxide is soluble in water. Fire in liquid ethylene oxide can be extinguished by diluting with 22 volumes of water to one volume of ethylene oxide.

Both concentrated and diluted mixtures of ethylene oxide are used commercially. The diluted mixtures can be classified as flammable or nonflammable depending on their composition.

Some mixtures containing as little as 65% ethylene oxide by weight can have explosive vapor in equilibrium with the liquid in closed containers. These mixtures have the same hazard as pure ethylene oxide and the same safeguards should be provided.

3.1.1.2 Stability

Ethylene oxide may decompose exothermally according to the following:

$$C_2H_4O \rightarrow aCH_4 + CO + 2(1 - a)H_2 + (1 - a)C$$

($0<a<1$, "a" will vary depending upon temperature and pressure)

This reaction will occur without catalysis at temperatures exceeding 930°F (500°C). Impurities, such as rust or trace quantities of contaminant chemicals significantly reduce the required temperature for the decomposition reaction. Literature indicates the decomposition reaction in the liquid phase is possible when the temperature exceeds 176°F (80°C) and pressures between 200 and 1500 psig (15 and 104 barg). With pressures between 1500 and 3000 psig (104 and 208 barg), the decomposition reaction can occur with temperatures exceeding 72°F (22°C).

Impurities may also catalyze a polymerization reaction. This may result in excessive heat and pressure generation and a runaway reaction.

3.1.2 Storage

Storage containers of ethylene oxide expose property to fire and explosion hazards. They should be arranged, located and protected to limit damage to important buildings, structures, utilities, and other storage in the event of an accident.

Separation provides a basic safeguard. Temperature and pressure monitoring, automatic water spray protection, and ethylene oxide removal capability or burying or mounding of tanks reduces the recommended separation. Minimize liquid hold-up in process areas to reduce exposure to process equipment.

Where large quantities of ethylene oxide are stored, tanks should be divided into groups and protected with automatic water spray systems to prevent the loss of the entire storage capacity.

Separation of storage tanks of concentrated ethylene oxide from important property is based on the maximum quantity in one or more tanks that can be exposed to sustained simultaneous flame impingement from leaks at tanks or nearby piping, and therefore, subject to simultaneous rupture. Careful arrangement of tanks, piping, and drainage systems and the use of fire resistive barriers can reduce the possibility of simultaneous flame impingement.

3.1.3 Ethylene Oxide/Air/Diluent Mixtures

3.1.3.1 Gaseous Mixtures

Figure 4 shows the flammability limits for ethylene oxide vapor, various diluent gases and air for mixtures below 100°F (38°C) and below 15 psig (1 barg). Higher temperatures and pressures will increase the area of explosive mixtures. Likewise, lower temperatures and pressures will decrease the area of explosive mixtures.

3.1.3.1.1 Example Using Figure 4

If a mixture that initially contains 20% ethylene oxide and 80% diluent mixes freely with air, the composition of the mixture will follow a straight line from 20% ethylene oxide - 80% diluent - 0% air (point A) to 100% air - 0% ethylene oxide - 0% diluent (point C), indicated by a dashed line on Figure 4.

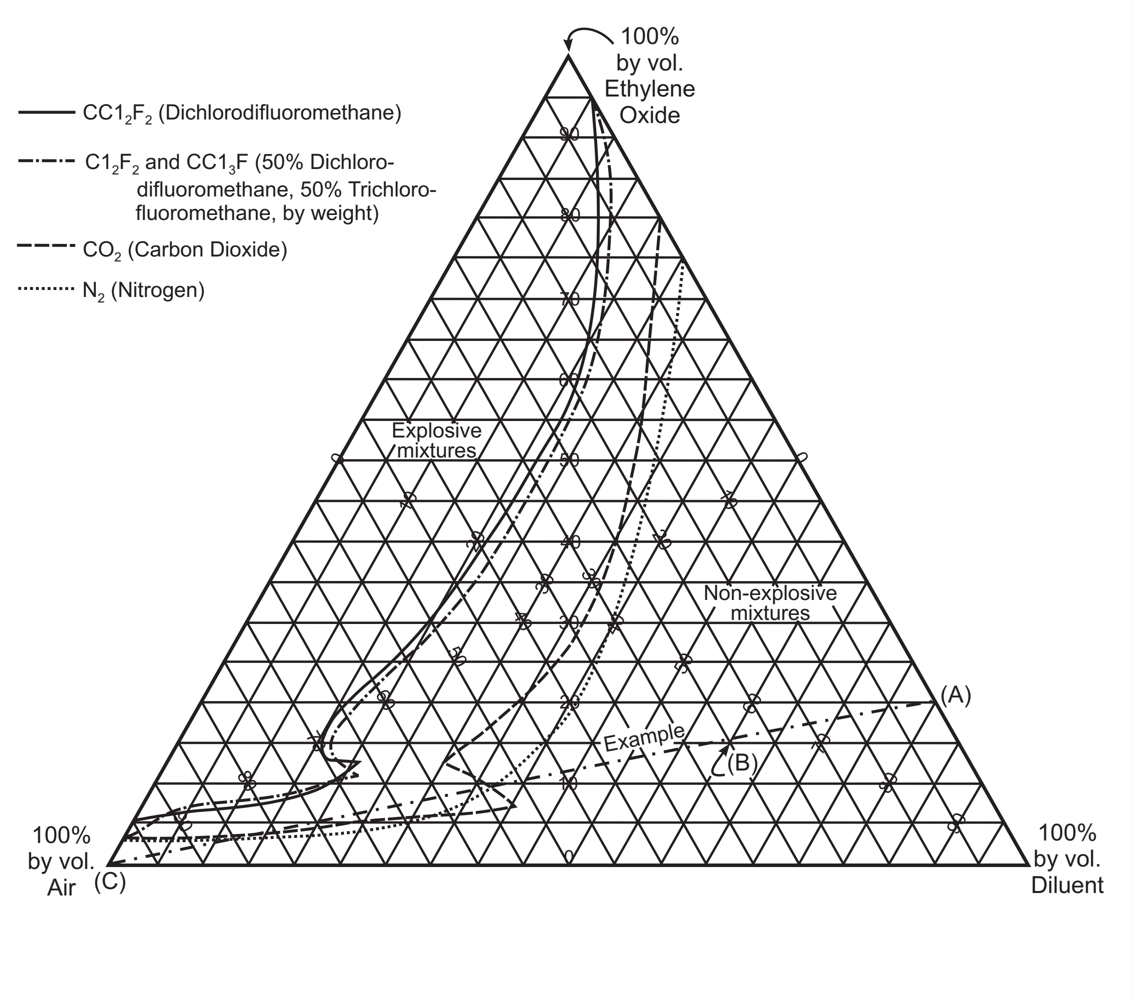


Fig. 4. Explosive mixtures of ethylene oxide vapor in typical diluents. This chart is suitable only for mixtures below 100°F (38°C) and below 15 psig (100 kPa). Higher temperatures and pressures will increase the area of explosive mixtures.

At point B, the composition of the mixture is 15% ethylene oxide, 60% diluent, and 25% air. It is still a nonexplosive mixture. As more air is added, the mixture passes through the explosive range if the diluent is nitrogen or carbon dioxide, but will stay in the nonexplosive ranges of the dichlorodifluoromethane-trichlorofluoromethane mixtures.

3.1.3.2 Nonflammable Mixtures

Several nonflammable pressurized mixtures of ethylene oxide are available (Table 2). These mixtures contain 12% or less by weight of ethylene oxide with inert materials. They are nonexplosive in themselves and cannot form explosive mixtures with air.

3.1.3.3 Flammable Mixtures

Pressurized liquid mixtures containing higher concentrations (usually up to 80% by weight) of ethylene oxide or using flammable diluents are also available. Although nonexplosive in themselves, they can form explosive mixtures with air.

Mixtures containing 20% or less by weight of ethylene oxide in inert diluents are considered to have low flammability hazard because the possible mixtures with air will have narrow limits of flammability and be capable of only low flame speed and low pressure development. The more concentrated ethylene oxide mixtures are considered to have high flammability hazard.

Table 2. Nonflammable Ethylene Oxide Diluent Mixtures

EtO (by wt)	*Diluent (by wt)*	*Gas Composition, Complete Vaporization (by Vol)*	
		EtO	*Diluent*
11%	35% CCl_3F*	26.6%	26.6% CCl_3F*
	54% CCl_2F_2**		47.0% CCl_2F_2**
	79% CCl_3F*	28.0%	63.0% CCl_3F*
	10 CCl_2F_2**		9.0% CCl_2F_2**
12%	88% CCl_2F_2**	27.4%	72.6% CCl_2F_2**
10%	90% CO_2	10%	90% CO_2

* Trichlorofluoromethane (Halon 113) ($CC1_3F$)
**Dichlorodifluoromethane (Halon 122) ($CC1_2F_2$)

3.1.4 Avoiding Flammable Mixtures of Ethylene Oxide/Air/Diluent

Equipment operating at high ethylene oxide vapor concentrations can avoid passage through the explosive range when charging and discharging by careful evacuation and purging. For example, a sterilizer may be evacuated to reduce the air concentration to a very low value. Inert gas is then introduced, followed by the introduction of ethylene oxide vapor to attain the desired concentration. Conversely, ethylene oxide in equipment may be safely exhausted by evacuating the equipment and then purging with inert gas before allowing air to enter. This procedure is frequently carried out by several repetitive steps of evacuation and introduction of inert gas.

A stable gas blanket over the vapor space above the ethylene oxide liquid eliminates the explosion hazard. The curves in Figure 3 show the relationship between temperature and concentration of ethylene oxide in the vapor phase above the liquid at various pressures when there is a stable gas present in the system. The pressures required for safe mixtures of ethylene oxide vapor and several diluents over the liquid at various temperatures are shown in Figure 2. Figures 2 and 3 assume that ethylene oxide and diluents follow the perfect gas laws, and a slight safety factor is included.

Flammable gases such as methane, butane, and propane can make nonexplosive mixtures with ethylene oxide. However, if allowed to mix freely with air, these mixtures will pass through the explosive range of ethylene oxide and the diluent gas, or if the ethylene oxide content is low, through the range of the diluent gas.

3.1.5 Vapor Cloud Explosion

Ethylene oxide at a chemical processing facility may represent an outdoor vapor cloud explosion hazard. Mitigation should be considered if a vapor cloud explosion is a credible event. Vapor cloud explosions and mitigation are beyond the scope of this document. For additional information, see Appendix E.

3.1.6 Sterilization Processes

Sterilizers that use 100% ethylene oxide control the sterilizer gas composition with a series of evacuations and inert gas purges before a predetermined amount of 100% ethylene oxide is added to the sterilizer. If the process is not properly designed or if the process control system fails to operate correctly, the sterilizer gas mixture may be flammable at some point in the process.

If 100% ethylene oxide is used in a sterilizer, the sterilizer should be considered an equipment explosion hazard and the room should be considered a room-explosion hazard.

Sterilizers using ‘‘low flammability’’ (<20% ethylene oxide) or nonflammable (<12% ethylene oxide) are not considered explosion hazards.

Some sterilizers recycle the sterilization gas and use 100% ethylene oxide to replenish consumed ethylene oxide. This may result in 100% ethylene oxide being pumped into a vessel normally containing 12% ethylene oxide (nonflammable). When this is the practice, a judgement must be made to determine if the worst credible event could increase the sterilizer ethylene oxide concentration above 20%. If this can occur, the sterilizer should be considered an equipment explosion hazard.

If equipment that is considered an equipment explosion hazard occupies more than 10% of a room volume, a room explosion hazard exists and damage-limiting construction should be provided.

For example, a cylinder of 100% ethylene oxide is used to replenish a sterilizer of relatively small volume and the flow is controlled by a flow valve. If the flow control valve fails to operate properly, the entire contents of the cylinder could be emptied into the sterilizer. If the volume of the sterilizer is sufficiently small, the ethylene oxide concentration could easily exceed 20% and the sterilizer should be considered an equipment explosion hazard.

Likewise, if the sterilizer was large enough that the entire contents of the cylinder would not increase the ethylene oxide concentration above 20%, then the sterilizer should not be considered an explosion hazard.

Current environmental conditions are encouraging sterilizer manufacturers to develop processes that minimize ethylene oxide and chlorofluorocarbon (CFC) emissions. This has resulted in processes that recycle ethylene oxide. Future modifications may include increased use of 100% ethylene oxide. This will reduce the use of CFCs, but may increase the hazards associated with sterilizer operations. New and modified sterilizer operations should be reviewed carefully to ensure that the operations are adequately protected.

3.1.7 Vaporizers

Vaporizers for concentrated and flammable mixtures of ethylene oxide are normally heated with hot water or low-pressure steam. Fuel-fired or electrically heated vaporizers are not recommended because they are ignition sources and along with high-pressure steam, present problems of localized overheating. Electrically heated vaporizers may be used with nonflammable mixtures and on portable sterilizers.

3.1.8 Pumps

Ethylene oxide pump fires may result in an exposure fire to adjacent piping or equipment. Additionally, the excess temperatures during a pump fire may result in a liquid phase decomposition of any exposed ethylene oxide liquid. Pumping against a closed discharge valve may cause excessive temperatures and a possible liquid phase decomposition.

3.1.9 Insulation Fires

Many types of insulation may catalyze an ethylene oxide reaction if ethylene oxide leaks beneath the insulation. This reaction may generate sufficient heat to spontaneously ignite the insulation. A fire may generate sufficient heat to exposed piping or vessels that enclosed ethylene oxide could violently decompose.

An ethylene oxide supplier should be able to determine if a particular type and size of insulation is suitable for the intended ethylene oxide service.

3.2 Loss History

An FM loss study indicates there were seven fires or explosions that involved ethylene oxide during a 20 year period.

Kletz (see Appendix E) reports 18 ethylene oxide fires and explosions, 17 ethylene oxide decomposition incidents, 4 fires and explosions involving flammable reactor coolant, and 9 miscellaneous incidents at ethylene oxide plants between 1955 and 1981. This list includes incidents reported in various forms. The financial impact of these losses is not included in his report.

Common deficiencies include process control failure, contamination of ethylene oxide, loss of inert gas blanket, pumping ethylene oxide against closed valves, and operator errors.

4.0 REFERENCES

4.1 FM

Data Sheet 1-21, *Fire Resistance of Building Assemblies*
Data Sheet 1-44, *Damage-Limiting Construction*
Data Sheet 4-1N, *Water Spray Fixed Systems*
Data Sheet 5-1, *Electrical Equipment in Hazardous Locations*
Data Sheet 7-31, *Storage of Aerosol Products*
Data Sheet 7-32, *Ignitable Liquid Operations*

Data Sheet 7-49, *Emergency Venting of Vessels*
Data Sheet 7-50, *Compressed Gases in Portable Cylinders and Bulk Storage*
Data Sheet 7-54, *Natural Gas and Gas Piping*

4.2 Others

ANSI Standard B31.3, *Chemical Plant & Petroleum Refinery Piping.*

NFPA 497A, *Classification of Class I Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas.*
NFPA 560, *Standard for the Storage, Handling and Use of Ethylene Oxide for Sterilization and Fumigation.*

APPENDIX A GLOSSARY OF TERMS

FM Approved: References to ″FM Approved″ in this data sheet mean a product or service has satisfied the criteria for FM Approval. Refer to the Approval Guide, an online resource of FM Approvals, for a complete listing of products and services that are FM Approved.

Ignitable Liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

APPENDIX B DOCUMENT REVISION HISTORY

April 2013. Minor editorial revisions were made.

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

May 2007. Made minor editorial changes.

May 2000. This revision of the document has been reorganized to provide a consistent format.

September 1999. Minor document update and reformatting.

May 1998. Minor document update and reformatting.

April 1992. Updating for technology changes and additional hazard data.

June 1974. Updating and significant additional information.

March 1968. Original document.

APPENDIX C MANUFACTURING HAZARD INFORMATION

C.1 Properties

Ethylene oxide, C_2H_4O, has an atmospheric boiling point of 50.8°F (10.4°C) and is often handled as a liquefied gas. Ethylene oxide's properties are summarized in Table 3.

C.2 Manufacturing

The air-based or oxygen-based direct oxidation processes are the predominant processes used to manufacture ethylene oxide. Both processes use a catalyst, typically silver, to adsorb oxygen and react ethylene, C_2H_4, with the adsorbed oxygen. Both processes are fundamentally similar. The reaction is as follows:

$$C_2H_4 + O^{-}_{2(\text{adsorbed})} \leftrightarrow C_2H_4O + O^{2-}_{(\text{adsorbed})}$$

A side reaction is:

$$C_2H_4 + 6\ O^{2-}_{(\text{adsorbed})} \leftrightarrow 2\ CO_2 + 2\ H_2O$$

The overall reaction is:

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

Process schematics based upon general public information are shown in Figure 5 and Figure 6. The processes consist of three major stages: the reaction system, oxide recovery, and oxide purification.

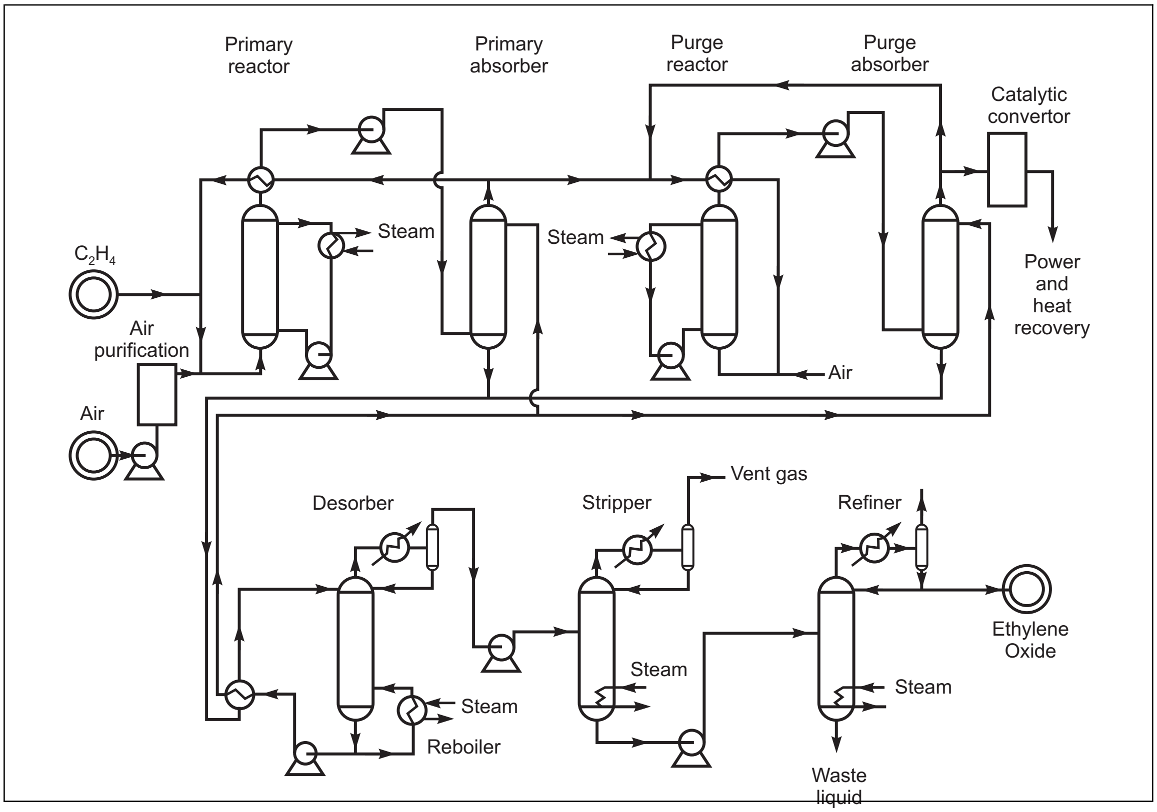
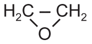


Fig. 5. Air-based direct oxidation process (Kirk-Othmer)

Table 3. Properties of Ethylene Oxide

Chemical Formula		*Solubility of Liquid in Water*	Infinite
Molecular Weight	44.05	*Heat of Vaporization* (at 1 atm [101 kPa])	245 Btu/lb 569 kJ/kg
Freezing Point (at 1 atm [101 kPa])	-170°F -112.2°C	*Flash and Fire Point*	<-20°F <-29°C
Boiling Point (at 1 atm [101 kPa])	50.8°F 10.4°C		
Specific Gravity of Liquid (at 68/68°F [20/20°C])	0.871	*Explosion Limits* (Vol. in Air) 80-100°F and at 1-2 atm (at 27-38°C and at 100-200 kPa)	3.0-100
Liquid Density (at 68°F [20°C])	7.26 lb/gal 54.4 lb/ft^3 871 kg/m^3	*Autoignition Temperature* (at 1 atm [101 kPa])	804°F 429°C
Vapor Pressure (at 68°F [20°C])	21.2 psia 146 kPa	*Heat of Combustion*	12,650 Btu/lb 29,400 kJ/kg
Specific Gravity of Vapor (Air = 1 at 104°F [40°C])	1.49	*Auto Decomposition Temperature* (at 1 atm [101 kPa])	1060°F 571°C
Vapor Density (at 104/104°F [40/40°C])	0.1049 lb/ft^3 1.68 kg/m^3	*Heat of Decomposition* (vapor)	694 Btu/lb 161 kJ/kg
Specific Volume *at 104°F and 1 atm* (40°C and 101 kPa)	9.53 ft^3/lb 0.595 m^3/kg	*Critical Temperature*	384.4°F 198.8°C
		Critical Pressure	1043 psia 7190 kpa

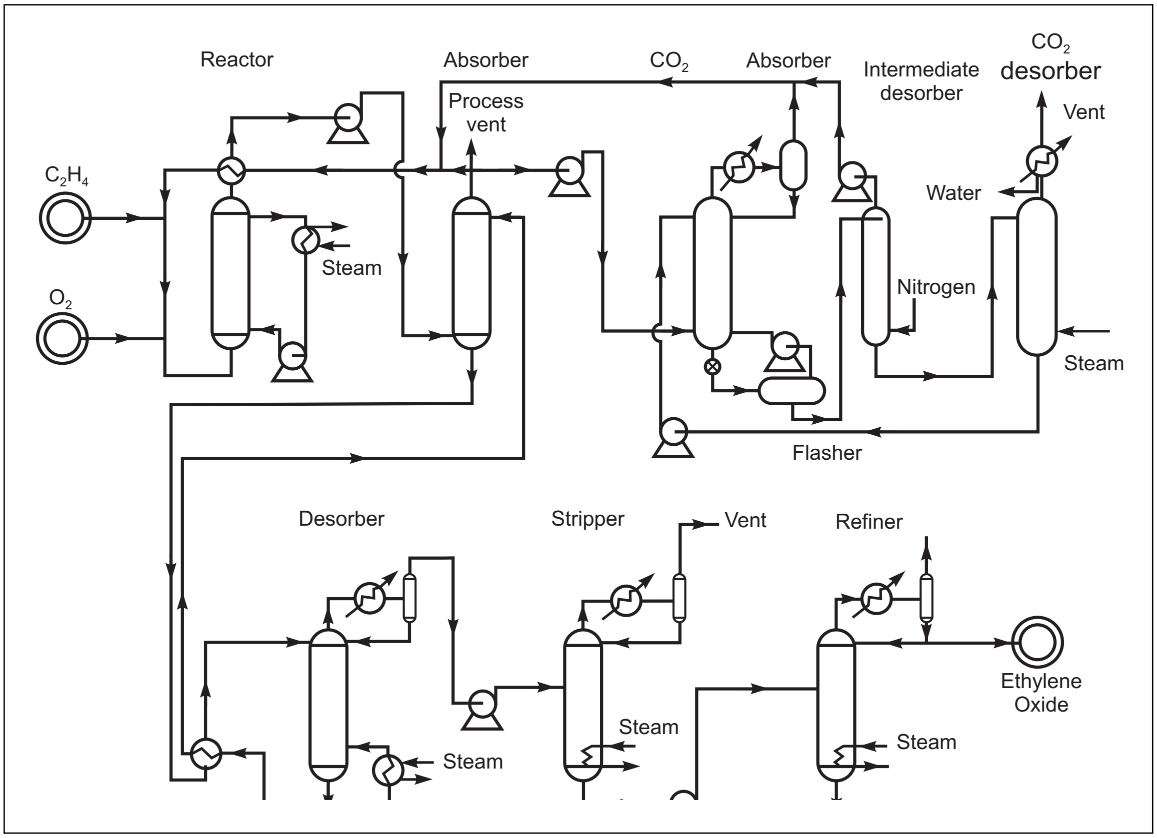


Fig. 6. Oxygen-based direct oxidation process (Kirk-Othmer)

Ethylene and air (or oxygen) are oxidized to ethylene oxide, carbon dioxide, and water in the packed-bed, multi-tubular reactors. Typical operating conditions are 400 to 600°F (200 to 300°C) and 150 to 450 psia (1 to 3 MPa). Organic heat transfer fluids typically provide reactor cooling. Vapor-phase oxidation inhibitors may be used to reduce carbon dioxide and water formation. Ethylene oxide is then recovered by absorption and purified by distillation.

C.3 Uses

Ethylene oxide is extremely reactive because of the weak -C-O-C- bonds and is used to manufacture many compounds. These compounds include poly (ethylene oxide), ethylene glycol, glycol ethers, polyesters, and rocket motor propellants. The polymerization reaction to form poly (ethylene oxide) is catalyzed by many materials, including organometallic compounds and alkaline earth compounds. The reaction may inadvertently be catalyzed by rust or other impurities.

Ethylene oxide is also widely used as a sterilizing or fumigating agent.

C.4 Handling

Unloading from tank car or truck to storage tank, and from storage tank or insulated drum to process equipment, is usually liquid transfer by gas pressure or pump. Transfer from cylinders to process equipment is normally liquid withdrawal by cylinder pressure, or preferably, by inert gas pressure.

Transportation of diluted mixtures, both flammable and nonflammable, in the United States is in USDOT cylinders. Transfer from cylinders to process equipment is the same as with undiluted ethylene oxide.

APPENDIX D COMPARISON WITH NFPA STANDARD

NFPA 560, *Standard for the Storage, Handling and Use of Ethylene Oxide for Sterilization and Fumigation*, is limited to portable cylinders. NFPA's recommendations for storage of cylinders outdoors are less restrictive than FM's. The NFPA plot for flammability of EO/Air/N_2 mixtures creates a somewhat larger envelope of flammable mixtures than is created by our Figure 4 (the NFPA more conservative). There appear to be no other significant discrepancies between NFPA 560 and this data sheet.

APPENDIX E BIBLIOGRAPHY

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Pesetsky, B. et al., *Liquid Phase Decomposition of Ethylene Oxide,* AlChE Loss Prevention, Vol. 13, (1980).