ETHYLENE

Product Stewardship Guidance Manual

December 2004

American Chemistry Council Good Chemistry Makes It Possible

CHEMSTAR

Legal Notice

The Ethylene Product Stewardship Manual was prepared by the American Chemistry Council's Olefins Panel Ethylene Product Stewardship Task Group (Task Group). It is intended to provide general information to persons who may handle or store ethylene. It is not intended to serve as a substitute for in-depth training or specific handling or storage requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons involved in handling and storing ethylene have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. The manual is necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions, and economic and technological feasibility.

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For more information on material presented in this manual, please contact your supplier.

To the Reader

The members and affiliated companies of the American Chemistry Council support efforts to improve the industry's responsible management of chemicals. To assist in this effort, the American Chemistry Council's CHEMSTAR® Olefins Panel chartered the Ethylene Product Stewardship Task Group to create and publish this manual to provide the reader with a better understanding of how ethylene is manufactured and used to produce products that play an important role in our lives. The Task Group is made up of representatives of the following American Chemistry Council member and affiliated companies:

BP Amoco Chemicals Company	Huntsman Corporation
The Dow Chemical Company	Nova Chemicals Inc.
Equistar Chemicals LP	Shell Chemical LP
ExxonMobil Chemical Company	Sunoco Inc.

Information and support of this effort was also provided by Eastman Chemical Company, Air Products and Chemicals, Inc., and Texas Petrochemicals LP.

This manual has been developed for use by producers and industrial users of ethylene. In it the health, safety, and environmental aspects associated with manufacturing, distributing, using, and disposing of ethylene are discussed. The bulk of the material emphasizes aspects of handling, storage, transport, and use. References to applicable regulations and industry practices are made in tables and text. A Glossary of terms is in the Appendix.

The American Chemistry Council encourages comments on the content of this document and a more in-depth dialogue concerning the issues presented. Contact your supplier to obtain the most current version of this manual or if you have questions about its content.

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

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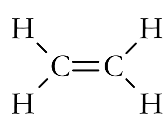
PART I - PRODUCT IDENTIFICATION

Product Name	Ethylene
IUPAC Name	Ethylene
Chemical Abstract Registry Name	Ethene
Chemical Name	Ethylene
Chemical Family	1-Alkenes
Chemical Abstract Registry Service Number	74-85-1
Chemical Formula	C_2H_4
Synonyms	Acetene Elayl Olefiant Gas Refrigerant 150 Ethene UN1038 UN1962 Athylen [German] Bicarburretted hydrogen Caswell No. 436 EINECS 200-815-3 EPA Pesticide Chemical Code 041901 Etileno HSDB 168



General Description: Ethylene is a volatile, colorless gas at room temperature with a faint, sweet odor. The primary hazard associated with ethylene is its flammability.

Ethylene Manufacturing Process Information

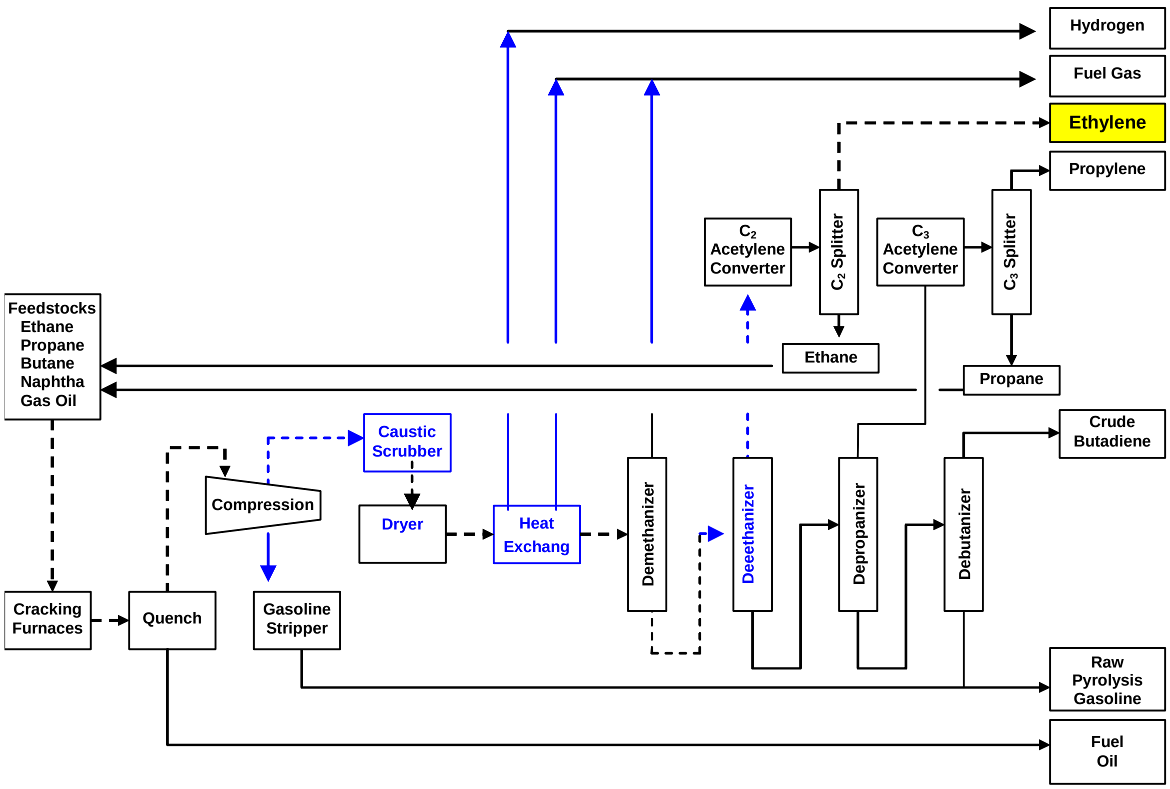
Ethylene is produced commercially primarily by two processes:

- Steam Cracking of Paraffinic Hydrocarbons
- Separation from Refinery Gas

Ethylene Production Via Steam Cracking Of Paraffinic Hydrocarbons

The steam cracking process is the predominant process used to produce ethylene. Figure 1.1 depicts a flow chart for a typical olefins plant. While this does not represent any particular plant, and there are many variations among olefins plants, this representation will provide the reader with a general understanding of the process.

Figure 1.1: Typical Olefins Plant*



*** Flow path for Ethylene noted by dashed line**

The indicated feedstocks (ethane, propane, butane, naphtha and gas oil) are fed to a pyrolysis (steam cracking) furnace, where they are combined with steam and heated to temperatures between approximately 1450 - 1600° F (790 - 870° C). Within this temperature range, the feedstock molecules "crack" to produce ethylene as well as methane, hydrogen, ethylene, propylene, butadiene, benzene, toluene and other co-products. After the pyrolysis reaction is quenched, the rest of the plant separates the desired products into streams that meet the various product specifications. Process steps include distillation, compression, process gas drying, hydrogenation (of acetylenes), and heat transfer.

While some olefins plant designs will accommodate any of the listed feedstocks, many olefins plants process only Natural Gas Liquids (NGLs) such as ethane, propane and sometimes butane. The mix of feedstocks, the conditions at which the feedstocks are cracked, and the physical plant design ultimately determine the amount of each product produced, and for some of the streams, the chemical composition of the stream.

Typical product streams obtained from cracking various ethylene feedstocks are detailed in Table 1.1.

Table 1.1: Typical Product Streams Obtained from Cracking Various Ethylene Plant Feedstocks [1]

(millions of pounds)

Feedstock	Ethane	Propane[2]	n-Butane[3]	Naphthas[4]	Atmospheric Gas Oil	Vacuum Gas Oil
Cracking Severity Products	High	Medium to High	High	Medium to High	Medium to High	Medium
Hydrogen-Rich Gas	73	38-46	30	25-31	27-58	38-57
Methane-Rich Gas	87	580-654	551	438-490	404-432	387-427
Ethylene	1,000	1,000	1,000	1,000	1,000	1,000
Propylene[5]	24	366-647	409	400-573	535-623	575
Butadiene	22	39-71	87	123-169	167-180	175
Butylenes/Butanes	10	28-48	166	131-282	168-195	185
Pyrolysis Gasoline	20	104-156	176	404-1,089	649-755	660
Benzene	10	38-58	65	113-186	212-240	240
Toluene	1	11-22	28	43-158	113-120	125
C_8 Aromatics	0	0	11	58-95	44-95	295
Other	9	55-86	72	190-650	280-300	
Fuel Oil	0	10-22	42	65-112	637-830	1,200-1,335
Total	1,256	2,165-2,644	2,637	2,586-3,746	3,587-4,073	4,220-4,414
Ethylene Yield (Weight Percent)	80.5%	39-42.6%	40.4%	27-37%	24-28%	24%

1 The data are representative of relative material balances from an ethylene plant with a capacity of one billion pounds per year when feeding one feedstock at the assumed severity conditions. Ethane and propane recycle to extinction is assumed for all feedstock categories.

2 The data are generally based on propane recycle as well as ethane recycle.

3 Generally, isobutane is not used as a feedstock for the production of ethylene. Some studies, however, have developed material balances for iso/normal mixtures of butane. The major differences when isobutane is present in the feedstock are a higher feedstock requirement and major increases in the production of propylene, butylenes, benzene and methane-rich gas.

4 The ranges for this category are wide because naphtha is not uniformly defined; the boiling-point range, and thus the average carbon chain length of the contained hydrocarbons, may vary significantly, and cracking severity (temperature, residence time) of heavy-liquid feedstocks has a large effect on the final product balance. There is a tendency in the industry to use light naphthas such as field condensates and to use lower-severity conditions to increase the yield of propylene.

5 Polymer-grade propylene production is assumed.

Source: Process Economics Program, SRI Consulting.

Ethylene Production Via Separation from Refinery Gas

Ethylene is also produced by separation from refinery gas streams, such as from the light ends product of a catalytic cracking process or from coker offgas. This separation process is similar to that used in steam crackers, and in some cases both refinery gas streams and steam cracking furnace effluent are combined and processed in a single finishing section. These refinery gas streams differ from cracked gas from a steam cracker in that they typically include only the hydrogen through C_3 hydrocarbon fraction, their olefin content is much lower, and the level of contaminants such as arsine and nitrogen oxides is higher. Thus, the finishing of these refinery gas streams yields primarily ethylene and ethane, and/or propylene and propane.

Chemical and Physical Properties of Ethylene

Ethylene is a colorless, non-corrosive, flammable gas with a faint, sweet odor at ambient temperature and pressure. Data pertaining to its chemical and physical properties are presented in Table 1.2. Additional data concerning the physical properties of ethylene and its temperature dependent properties can be found in Figures 1.2 - 1.11, (Source: Design Institute for Physical Property Data (DIPPR) Database unless otherwise indicated.)

Table 1.2: Chemical and Physical Properties of Ethylene [1]

Property	Value
Physical State	Gas, Liquid Under Pressure
Color	Colorless
Odor	Faint, sweet
Molecular Formula	C_2H_4
Molecular Weight	28.0538
Normal Boiling Point (at 1 atmosphere)	-154.7°F
Melting Point	-272°F
Critical Temperature	48.54°F
Critical Pressure	731.14 psia
Critical Volume	0.07480 ft^3/lb
Critical Compressibility Factor	0.281
Density (liquid), @Critical Temperature, 48.54°F	13.36 lb/ft^3 (1.786 lb/gal)
Relative Vapor Density @ 32°F (gas; air = 1)[2]	0.975
Liquid Heat Capacity @Critical Temperature, 48.54°F	1.236 BTU/lb °F
Ideal Gas Heat Capacity, @70°F	0.3626 BTU/lb*°F
Refractive Index, nD, @77°F	1.3632
Solubility in Water, @68°F	131 mg/l
Partition Coefficient n-Octanol/Water[3]	Log Pow 1.13
Viscosity (liquid), @Critical Temperature, 48.54°F	3.06E-05 lb/ft * s
Viscosity (vapor), @70°F	6.77E-06 lb/ft * s
Ideal Gas Heat of Formation @77°F	805.25 BTU/lb
Autoignition Temperature	842°F
Explosive Limits in Air, Vol. % @77°F, 1 atm	
Lower	2.3
Upper	32.3
Odor Threshold in Air	
Detection[4]	270 - 600 ppm
Recognition[4]	418 ppm

[1] Daubert, T.E., Danner, R.P., Sibul, H.M., and Stebbins, C.C., DIPPR® Data Compilation of Pure Compound Properties, Project 801 Sponsor Release, January,1994, Design Institute for Physical Property Data, AIChE, New York, N.Y. Note: Semiannual updates released in January and July, except as noted otherwise.
[2] Hawley, G.G., "The Condensed Chemical Dictionary", 8th ed., .New York, NY, Van Nostrand Reinhold Co., 1971, p. 362.
[3] Hansch, C., Leo, A., "Substituent Constants for Correlation Analysis in Chemistry and Biology," New York, N.Y., John Wiley and Sons, 1979, p.175.
[4] Odor Thresholds for Chemicals with Established Occupational Health Standards. AIHA, 1989. pp. 19, 58.

Figure 1.2: Liquid Density

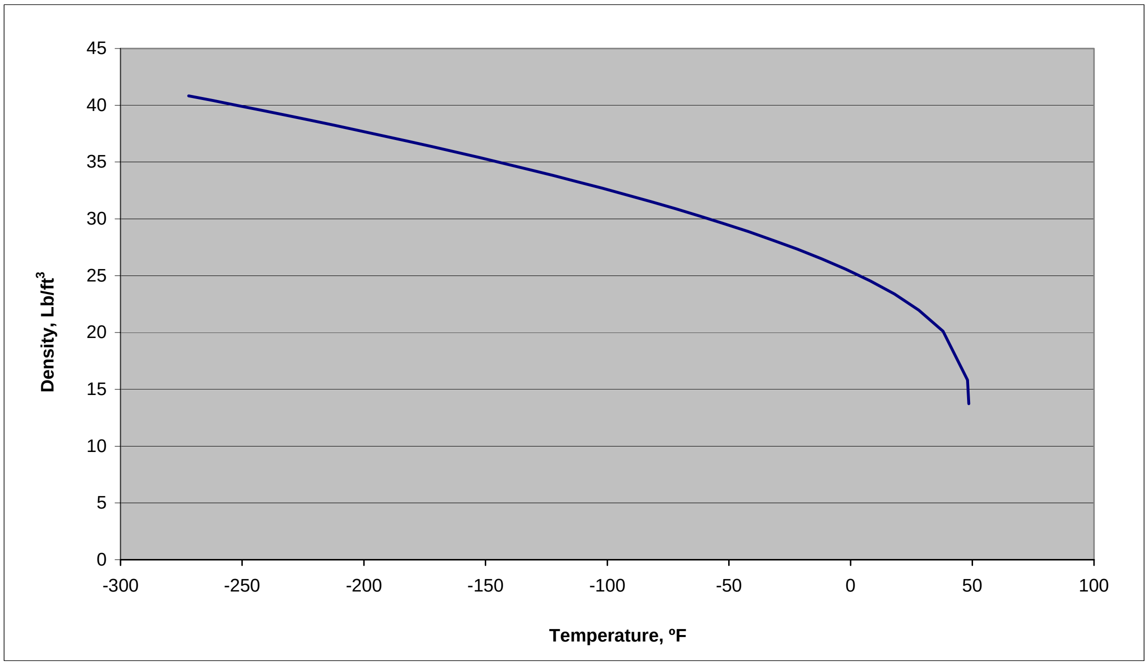


Figure 1.3: Vapor Pressure

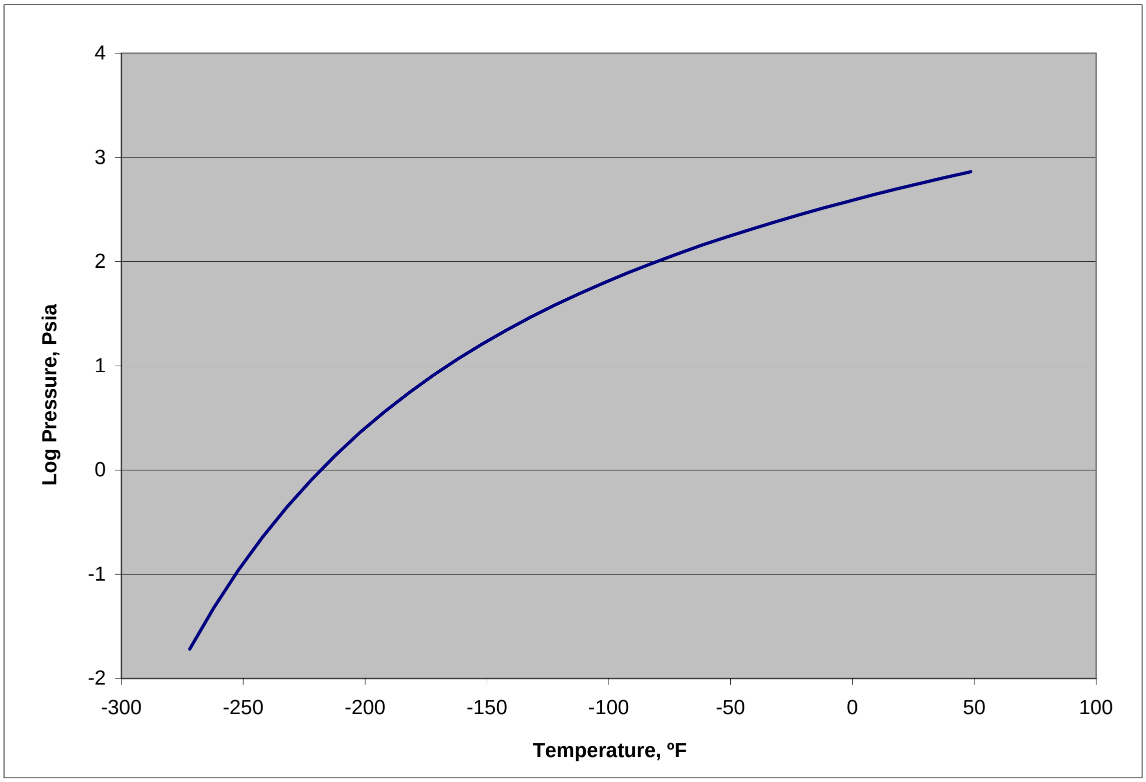


Figure 1.4: Heat of Vaporization

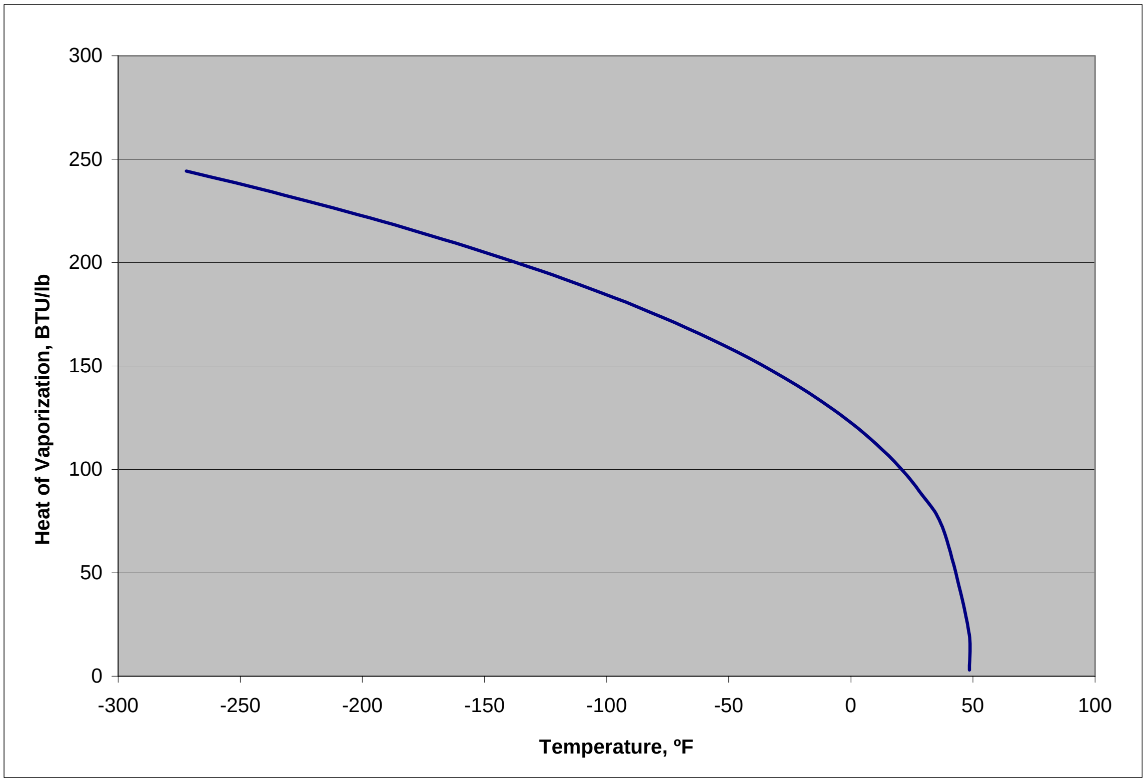


Figure 1.5: Liquid Heat Capacity

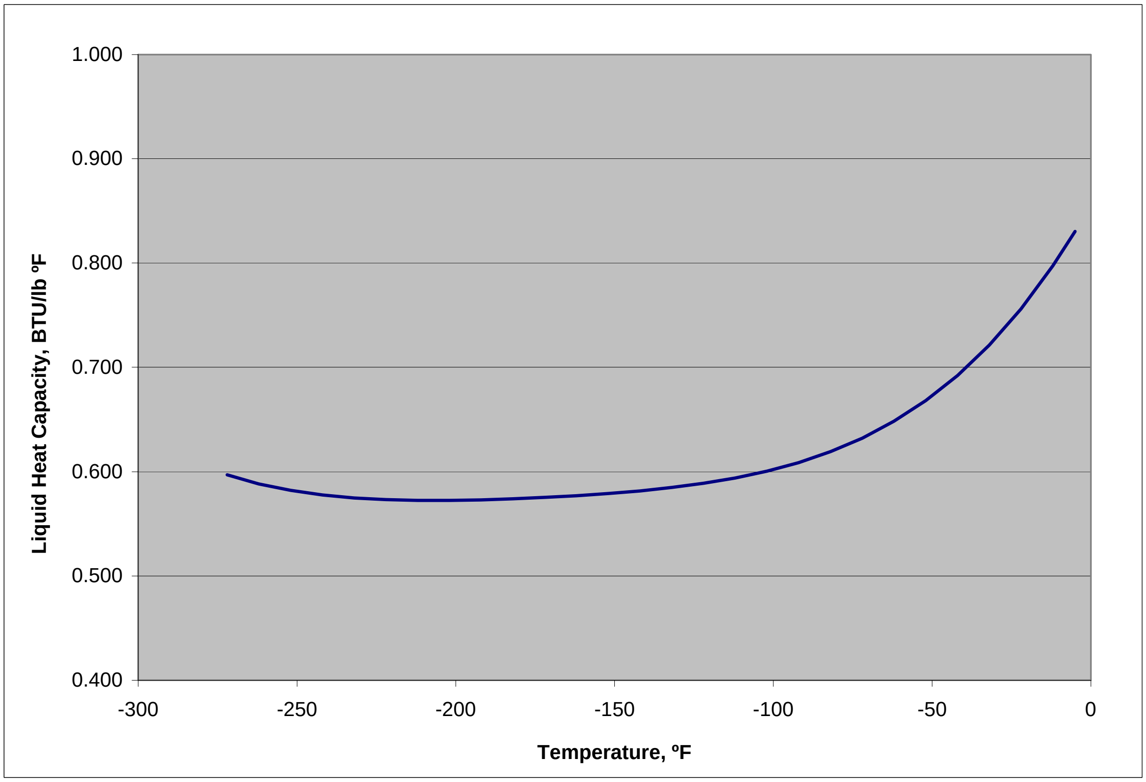


Figure 1.6: Ideal Gas Heat Capacity

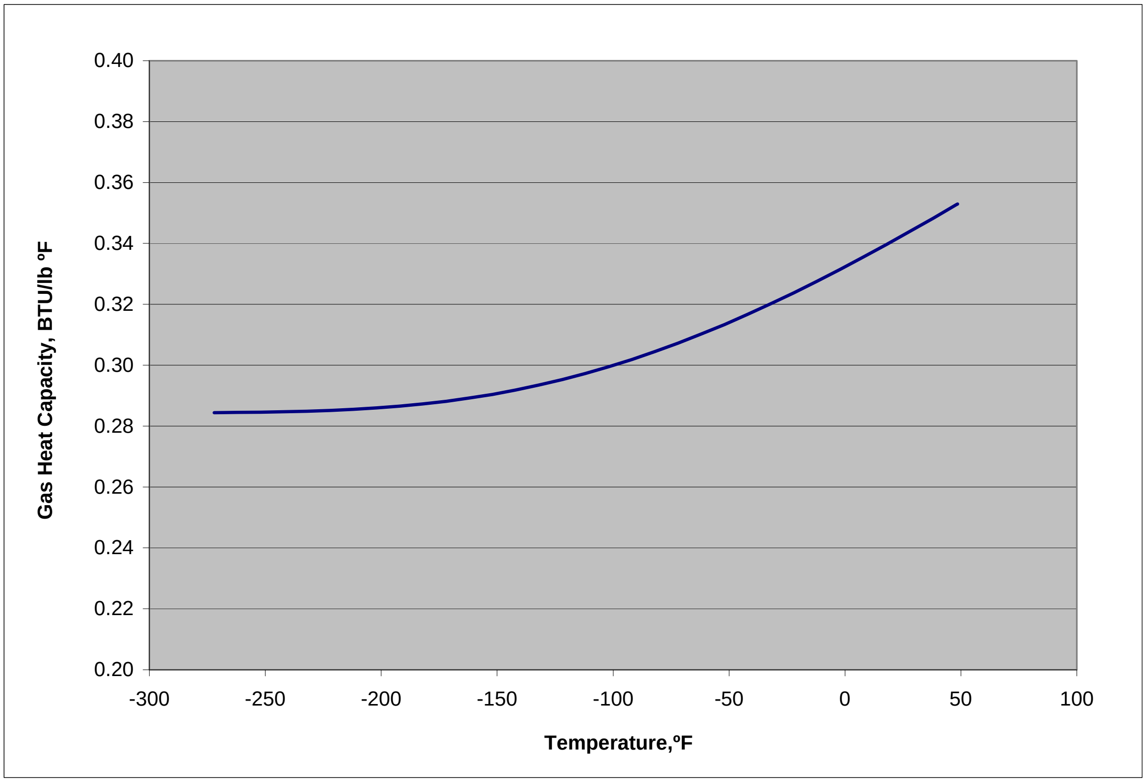


Figure 1.7: Liquid Viscosity

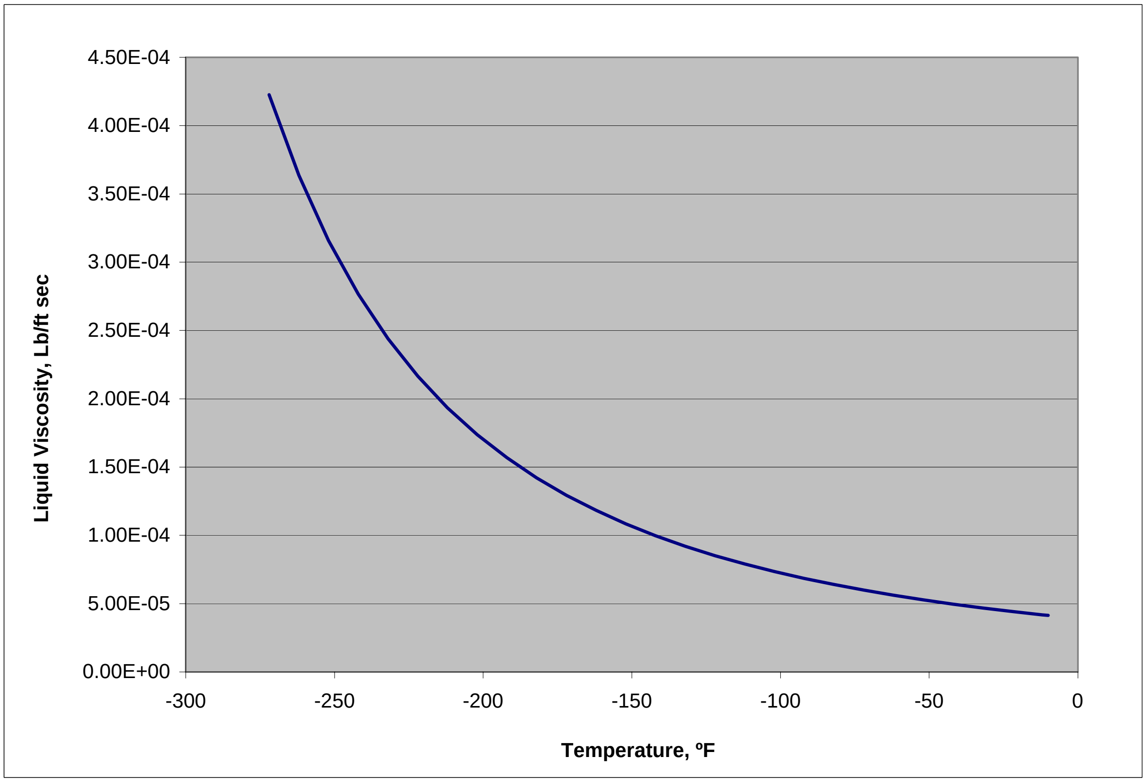


Figure 1.8: Vapor Viscosity

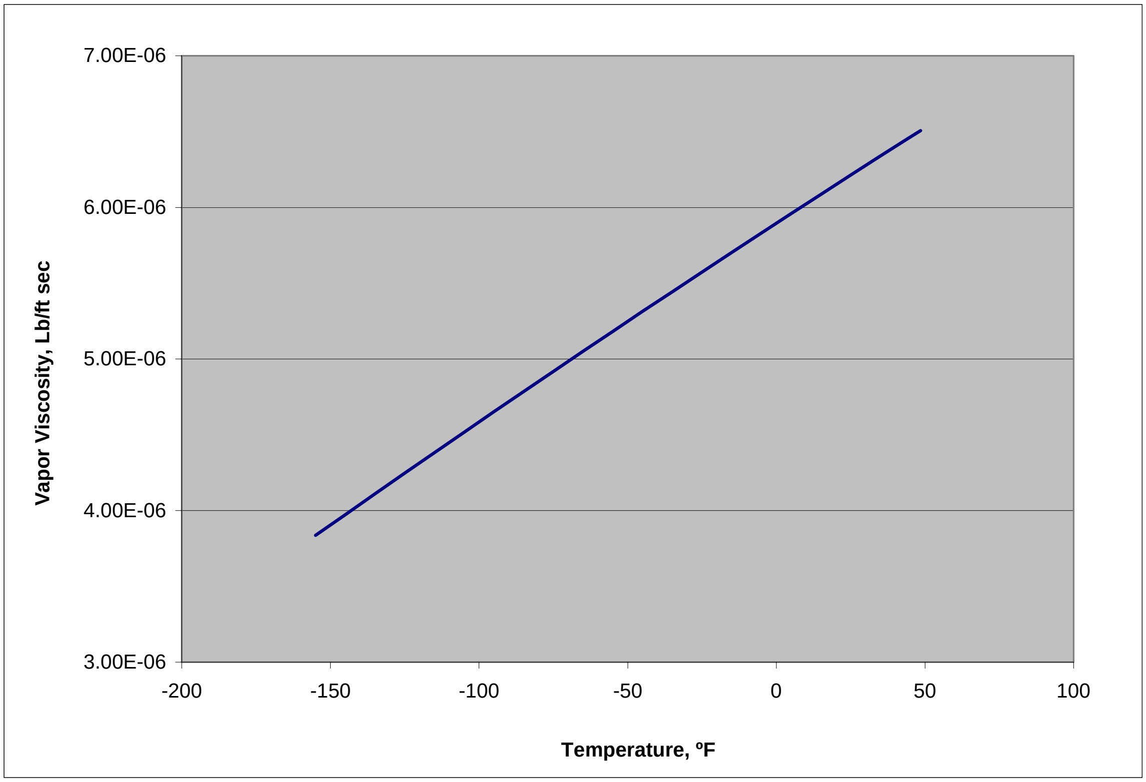


Figure 1.9: Liquid Thermal Conductivity

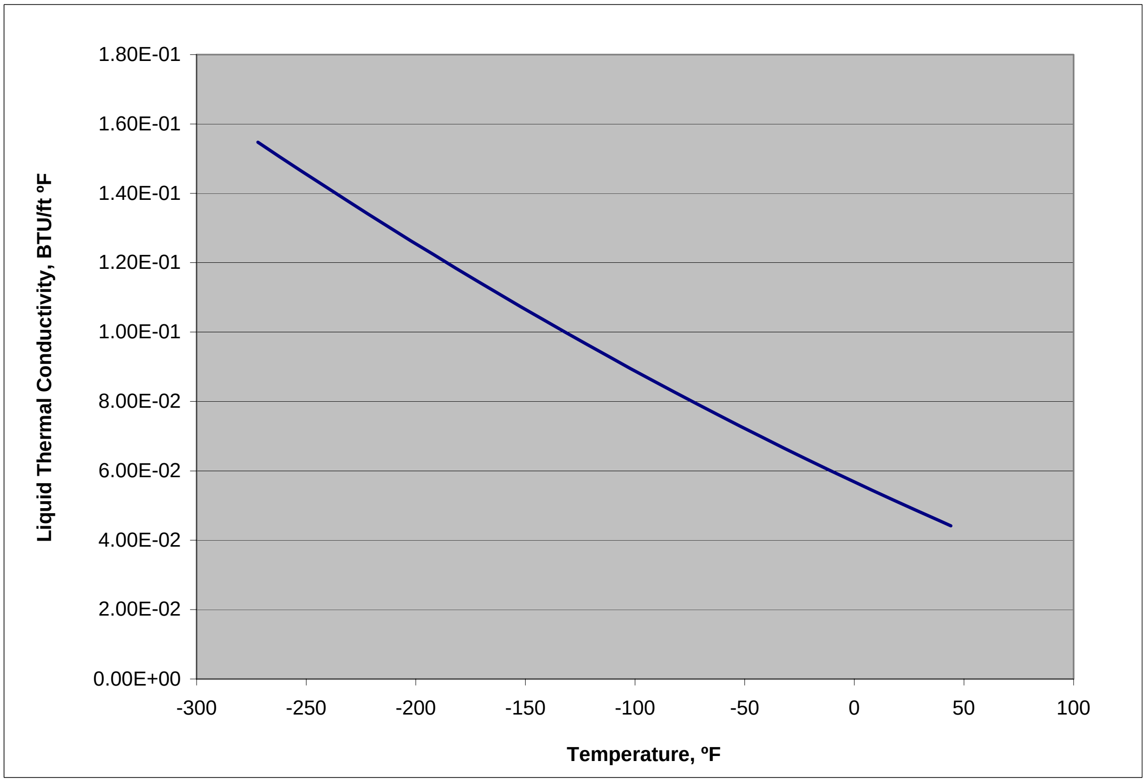


Figure 1.10: Gas Thermal Conductivity

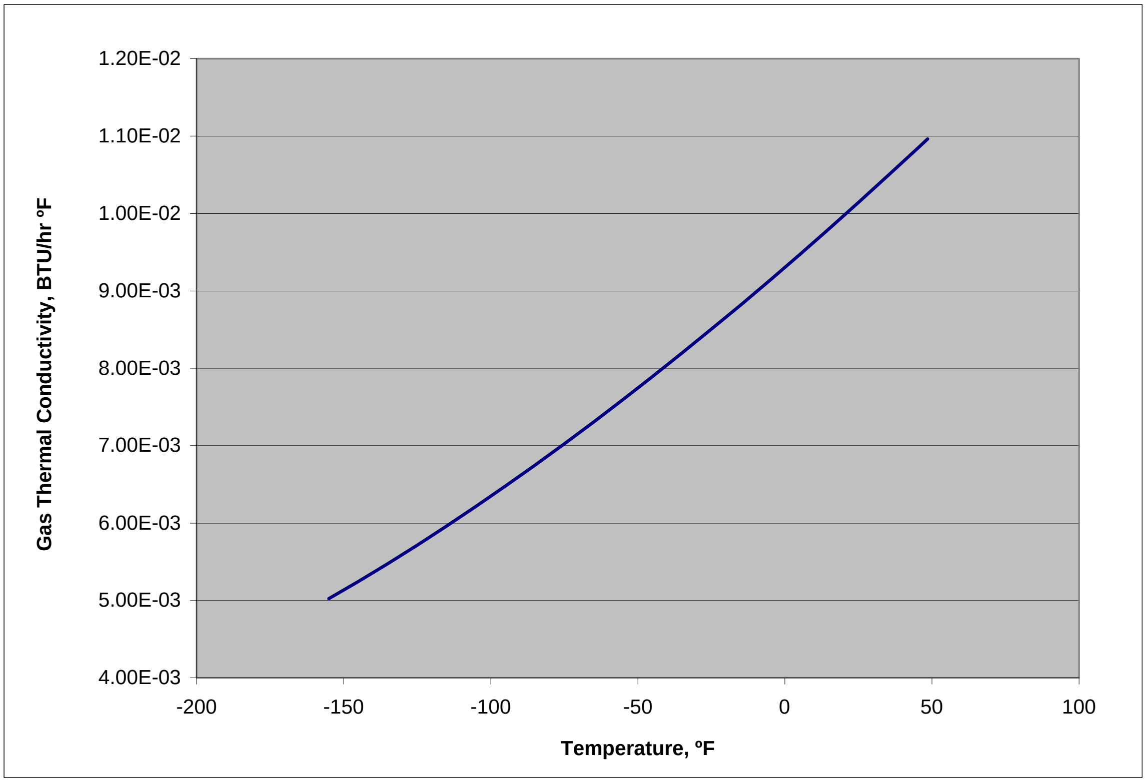
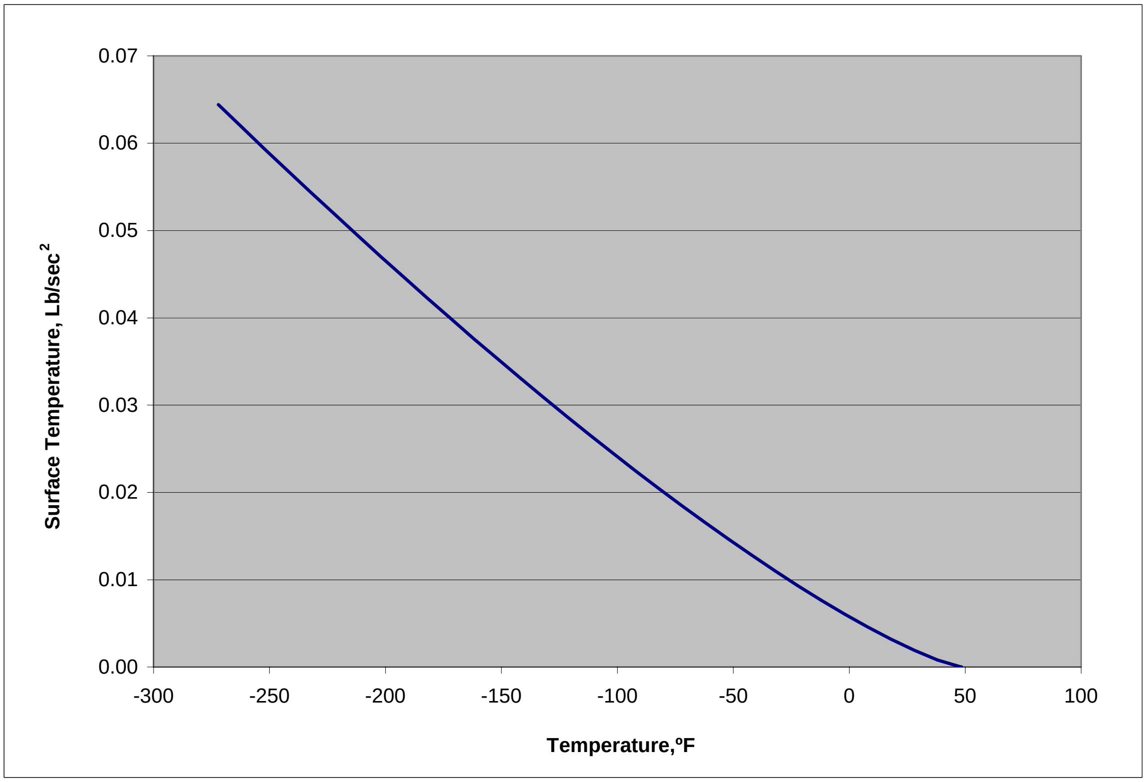


Figure 1.11: Surface Tension



Uses of Ethylene

Ethylene is a major product of the petrochemical industry. It is one of the highest volume chemicals produced globally. Estimated world consumption was 200 billion pounds in 2000. In the United States alone, approximately 55 billion pounds of ethylene were produced in 2000. (Chemical & Engineering News, June 25, 2001). Ethylene is primarily used as an intermediate for the production of other chemical raw materials that are subsequently used to manufacture a large variety of substances and products. The table below lists some of the main applications of ethylene and its derivatives.

Table 1.3: Ethylene Applications

Product Application	% of total use	Application Description
Polyethylene • High Density Polyethylene (HDPE) • Low Density Polyethylene (LDPE) • Linear Low Density Polyethylene (LLDPE)	 25 19 13	Common processing options for HDPE, LDPE, LLDPE resins are blow molding, extrusion and injection molding. The range of potential end products is quite diverse and includes: • Bins, pails and crates • Bottles • Piping • Food packaging films • Caps • Trash liners, sacks and carrier bags • Wire and cable sheathing • Insulation • Surface coating for paper and cardboard
Ethylene Dichloride/Vinyl Chloride/Polyvinyl Chloride	14	Ethylene is used in the production of ethylene dichloride, which is used to make vinyl chloride monomer (VCM). VCM is polymerized to produce polyvinyl chloride (PVC). PVC applications include: • Building and construction (pipe, tile, and flooring) • Packaging (film and bottles)
Ethylene Oxide (EO)	12	EO is used to produce many derivative products including: • Ethylene glycol (intermediate in production of terephthalate polyester resins for fibers, films, and bottles; used in automotive antifreeze) • Glycol ethers (solvents and intermediates in a variety of applications) • Non-ionic surfactants (detergents) • Ethanolamines EO is also used directly in the gaseous form as a fumigant and sterilizing agent.
Ethylbenzene/Styrene	7	Styrene is produced using ethylbenzene. Derivatives of styrene monomer are styrene-based polymers used in the manufacture of plastics and rubber products such as toys, construction pipe, foam, boats, latex paints, tires, luggage, food-grade film, and furniture. These polymers include: • Polystyrene and Expandable Polystyrene • Styrene-Butadiene rubber • Acrylonitrile-Butadiene-Styrene • Styrene-Acrylonitrile • Unsaturated polyester resins • Styrene-butadiene latices
Linear Olefins	3	• Used as base materials for the manufacture of detergents, plasticizers, synthetic lubricants, and additives • Comonomers in the production of polyethylenes
Others	7	Other chemical manufacturing processes using ethylene include: • Ethanol • Ethylene dibromide • Acetaldehyde • Vinyl acetate • Propionaldehyde • Ethyl chloride • Ethylene-propylene elastomers Ethylene is also used in the controlled ripening of fruit, vegetables, and flowers.

PART II - REGULATORY OVERVIEW

This section provides an overview of selected state, federal, and international health, safety, and environmental regulations that apply to ethylene as of the date of publication of this manual. Please note that this overview is NOT an exhaustive summary of all health, safety, and environmental regulations applicable to ethylene. For additional information, contact your supplier, consult your supplier's Material Safety Data Sheet (MSDS), or consult with the appropriate regulatory agencies or your legal counsel.

Occupational Exposure Limits

Table 2.1: Selected Occupational Exposure Limits for Ethylene

OSHA PEL[1]	Simple Asphyxiant[2]
ACGIH TLV®	Simple Asphyxiant (however, note proposed TLV of 100 ppm, 2003, pending at time of publication of this Manual)[3] Appendix 4 - Not Classifiable as a Human Carcinogen
NIOSH REL	None
AFS 2000 (Sweden)	Level Limit Value of 250 ppm Short Term Limit (KTV) of 1000 ppm
DFG (German) MAK	None

[1] Refer to the glossary in the Appendix for an explanation of the acronyms and terms used in this table.

[2] See 29 CFR § 1915.1000 (air contaminant standards for shipyards) and § 1926.55 (air contaminant standards for construction). Ethylene is not listed in 29 CFR § 1910.1000 (general air contaminant standards).

[3] ACGIH issued a proposed TLV for Ethylene in 2003 and a Notice of Intended Change (NIC) in 2004.

Federal Environmental Regulations Overview

Resource Conservation and Recovery Act (RCRA)

RCRA gives EPA authority to control hazardous wastes from generation to disposal. Under RCRA regulations (40 CFR § 261.21), if ethylene becomes a waste material, it would be an Ignitable Hazardous Waste, Hazardous Waste Number D001.

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)

CERCLA, also known as Superfund, established broad federal authority to respond to releases or threats of releases of hazardous substances from vessels and facilities. The list of CERCLA hazardous substances and their reportable quantities (RQs) are found in 40 CFR Part 302. Immediate notification must be made to the National Response Center and state and local response authorities if a CERCLA hazardous substance has been released in a quantity equal to or greater than its RQ. Ethylene is not listed as a hazardous substance under CERCLA and thus is not subject to any special reporting requirements under that law. Reporting of releases may also be required under other applicable laws, including state and local laws or regulations.

Emergency Planning and Community Right-to-Know Act (EPCRA)

Ethylene is subject to community right-to-know reporting requirements under sections 311 and 312 of EPCRA, and annual emissions reporting under section 313. More information concerning these requirements may be obtained from your supplier.

Clean Air Act (CAA)

Ethylene is regulated under the CAA as a Volatile Organic Compound (VOC). EPA has promulgated numerous regulations under CAA section 111 governing the emissions of VOCs, including ethylene. Ethylene is not listed as a Hazardous Air Pollutant (HAP) under section 112 of the CAA. Accordingly, emissions of ethylene are not regulated under that section of the Act.

Toxic Substances Control Act (TSCA)

Ethylene is listed on the TSCA Chemical Substances Inventory (40 CFR §§ 704, 710, 720, and 723).

Prevention of Accidental Releases

An OSHA Process Safety Management Standard (29 CFR § 1910.119) contains requirements for preventing or minimizing the consequences of catastrophic releases of chemicals that are deemed to be "highly hazardous" because of their toxicity, reactivity, flammability, or explosivity. Such releases may result in toxicity, fire, or explosion hazards. Ethylene is not specifically listed as a highly hazardous chemical in the standard. It does, however, meet the definition of a flammable liquid or gas. As a result, a process that involves the use of ethylene on site in one location, in a quantity of 10,000 pounds or more, is subject to the requirements of this standard.

Section 112(r) of the CAA and 40 CFR § 68.130 contain requirements to prevent the accidental release of hazardous substances and minimize the consequences of any such release. Ethylene is listed with a threshold quantity of 10,000 pounds. While this regulation is similar to the OSHA Process Safety Management Standard in many aspects, the CAA requires the EPA to include several elements in its regulations that are not mandated by OSHA.

State/Local Laws/Regulations

Numerous states have adopted laws or regulations governing the manufacture, processing, use or disposal of hazardous materials. For information on the requirements of these or other state or local laws or regulations, the appropriate state or local agency should be contacted. You may also want to consult your legal counsel. Additional information also may be available from your supplier or in your supplier's MSDS.

Canadian Regulations

This section lists a few Canadian regulations that address ethylene. It is not intended to represent a comprehensive listing of the regulations addressing ethylene in Canada.

WHMIS: The Workplace Hazardous Materials Information System (WHMIS) created, in part, criteria for the classification of hazardous substances that are used in the workplace (Can. Gaz.

Part II, Vol. 122, No. 2, Jan. 20, 1988). The WHMIS classifications for ethylene are Class A (Compressed Gas) and B1 (Flammable Gases).

NPRI: Pursuant to Section 16 of the Canadian Environmental Protection Act (CEPA), the National Pollutant Release Inventory (NPRI) established a list of substances required to be reported annually for environmental release purposes. Supplier notification is required for ethylene (128, Can. Gaz., Part I, 1378, Feb. 26, 1994).

DSL: The Canadian Chemical Inventory is called the Domestic Substances List (DSL). Ethylene is listed on the DSL.

Hazard Ratings for Ethylene

National Fire Protection Association (NFPA) Hazard Ratings

NFPA 704 is the Standard System for the Identification of the Fire Hazards of Materials. It addresses the health, flammability, reactivity, and related hazards that could arise during short-term acute exposure to a material in a fire, spill, or similar emergency situation. The intent of the system is to provide basic information to fire-fighting, emergency, and other personnel to aid them in making decisions related to an emergency involving a specific material. The system identifies the hazards of a material in terms of three principal categories: Health, Flammability, and Reactivity. The degree of severity is indicated by a numerical rating that ranges from four (4), indicating severe hazard, to zero (0), indicating no hazard.

Ethylene has the following NFPA hazard ratings:

Health - 1: Materials that, under emergency conditions, can cause significant irritation.

Flammability - 4: Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or that are readily dispersed in air, and which burn readily.

Reactivity - 2: Materials that in themselves are normally unstable and readily undergo violent chemical change, but do not detonate. This includes materials that can undergo violent chemical change at elevated temperatures and pressures.

Transport Classifications

Compressed Ethylene	
Road/Rail:	**U.S. Department of Transportation (DOT)**
Proper shipping name:	Ethylene, compressed
Hazard Class or Division:	2.1
Identification Number:	UN1962
Label/Placard Required:	Flammable Gas

Air:	**International Civil Aviation Organization (ICAO)** **International Air Transportation Association (IATA)**
Proper shipping name:	Ethylene, compressed
Hazard Class or Division:	2.1
Identification Number:	UN 1962
Label/Placard Required:	Flammable Gas

Sea:	**International Maritime Dangerous Goods Code (IMDG)**
Proper shipping name:	Ethylene, Compressed
Hazard Class or Division:	2.1
Identification Number:	UN1962
Label/Placard Required:	Flammable Gas

Cryogenic Ethylene

Road/Rail:	**U.S. Department of Transportation (DOT)**
Proper shipping name:	Ethylene, refrigerated liquid
Hazard Class or Division:	2.1
Identification Number:	UN1038
Label/Placard Required:	Flammable Gas

Air:	**International Civil Aviation Organization (ICAO)** **International Air Transportation Association (IATA)**

Refrigerated liquid ethylene is FORBIDDEN on passenger and cargo aircraft

Sea:	**International Maritime Dangerous Goods Code (IMDG)**
Proper shipping name:	Ethylene, Refrigerated Liquid
Hazard Class or Division:	2.1
Identification Number:	UN1038
Label/Placard Required:	Flammable Gas

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

A variety of restrictions apply to materials subject to these classifications. For example, ethylene is not authorized for shipment via passenger aircraft/rail and there is a 150 kg limit allowed on cargo aircraft. Please refer to the appropriate regulation for specific details regarding classification requirements and restrictions. 46 CFR Parts 150-154 should also be referenced for information regarding U.S. Coast Guard regulations concerning the transportation of ethylene.

PART III - HANDLING, TRANSPORT AND STORAGE INFORMATION

Training

Persons who come into contact with ethylene need to be trained in proper handling and safety in accordance with applicable federal, state, and local laws and regulations. An employer should provide information and training to employees specific to ethylene on its hazards, the methods for detecting releases, and methods of protection from exposure, with adequate consideration of any potential hazards arising from specific plant circumstances related to ethylene. All employees who work with, load, or off-load cryogenic liquids in either tank cars or tank trucks must complete required DOT training for handling this material. The training requirements are listed and explained in 49 CFR 172.700 Subpart H.

> *Note: DOT defines a Cryogenic liquid to mean a refrigerated liquefied gas having a boiling point colder than -90˚C (-130˚F) at 101.3 kPa (14.7 psi) absolute. 49 CFR § 173.115(g) A material meeting this definition is subject to requirements of Subchapter C – Hazardous Materials Regulations (49 CFR Parts 171-180) without regard to whether it meets the definition of a non-flammable, non-poisonous compressed gas*.

This information should be included in a Hazard Communication Training Program. An MSDS is another important source of information and contains labeling information.

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

Personal Protective Equipment

Respiratory Protection

Ethylene is listed as a Simple Asphyxiant by OSHA and ACGIH. (See Part II – Regulatory Overview.) In 2003, ACGIH proposed a TLV-TWA of 100 ppm; a Notice of Intended Change regarding this proposal was published in 2004.

Ethylene is a gas or vapor that displaces oxygen in air. High concentrations displacing oxygen can cause drowsiness, dizziness, unconsciousness, and/or suffocation by asphyxiation.

Ethylene is referenced as having an odor ‘detection’ threshold of 270 ppm and is indicated as having a “grassy” or “faint sweet” odor. A level of odor ‘recognition’ is listed at 418 ppm. (See Table 1.2.) Respiratory protection should be used in accordance with company and applicable regulatory requirements. Persons should not be assigned to tasks requiring the use of respirators unless it has been determined they are physically able to perform the work and are trained to use the equipment.

Chemical Protective Clothing

The purpose of chemical protective clothing (CPC) is to prevent contact with materials that can injure or be absorbed through the skin or eyes. Skin contact with rapidly expanding ethylene gas may cause severe irritation and burns (frostbite). Frostbite would be the result of the cooling effect due to rapid evaporation of the material. The level of protection selected should be based on the potential ethylene concentration and likelihood of contact. It could range from no CPC being required, such as when ethylene is handled in closed systems and there is no personnel exposure, to a fully encapsulating suit with supplied-air respirators for high concentration potential such as large spills or leaks.

Proper use of this type of protective clothing and equipment requires specific skills developed through training and experience. This type of special clothing may protect against one chemical, yet be readily permeated by chemicals for which it was not designed. Protective clothing should not be used unless it is compatible with the material released. This type of protective clothing offers little or no protection against heat and/or cold. Examples of this type of equipment have been described as (1) Vapor Protective Suits (NFPA 1991), also known as Totally-Encapsulating Chemical Protective (TECP) Suits or Level A protection (OSHA 29 CFR § 1910.120, Appendix A & B), and (2) Liquid-Splash Protective Suits (NFPA 1992 & 1993), also known as Level B or C protection (OSHA 29 CFR § 1910.120, Appendix B).

No single protective clothing material will protect against all dangerous goods. Do not assume any protective clothing is resistant to cold and/or heat or flame exposure unless it is certified by the manufacturer (NFPA 1991 5-3 Flammability Resistance Test and 5-6 Cold Temperature Performance Test). When selecting specific products the material manufacturer should be contacted. Thermal insulating properties for frostbite and permeation may be a consideration in CPC material selection.

Eye and Face Protection

Appropriate eye and face protection may be necessary to prevent contact with ethylene. Eye contact with rapidly expanding ethylene gas may cause severe irritation and burns (frostbite). Frostbite would be the result of the cooling effect due to rapid evaporation of the material. A hazard assessment conducted in accordance with the requirements of the OSHA standard for Personal Protective Equipment (29 CFR § 1910.132) can help to determine the level of protection necessary. Further information may be obtained from OSHA's general requirements section of its Eye and Face Protection Standard (29 CFR § 1910.133).

OSHA requires (29 CFR § 1910.133) that protective eye/face devices purchased after July 5, 1994 comply with the 1989 version of American National Standards Institute's (ANSI) Z87.1 Standard. If purchased on or before July 5, 1994, protective devices should at least comply with ANSI Z87.1-1968. In 2003, ANSI issued a new standard for eye protection, ANSI Z87.1-2003, but this standard has not yet been adopted by OSHA and remains voluntary.

Cryogenic Exposures

The eyes are the most sensitive body part to the extreme cold of the liquid and vapors of cryogenic materials. The recommended personal protective equipment for handling cryogens includes a full-face shield over chemical goggles, chemical resistant gloves (insulated PVC or insulated Nitrile), and a chemical resistant suit without cuffs. In addition, chemical resistant boots (PVC, Neoprene, or Nitrile) are recommended for people involved in the handling of ethylene. Depending on the application, special clothing suitable for that application may be advisable.

> ***Special note on insulated gloves***
> *At time of publication, there are no insulated gloves designed to allow hands to be put into a cryogenic liquid. Insulated gloves provide only short-term protection from accidental contact with the liquid.*

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

Exposure Monitoring

A number of methods are available for monitoring employee exposures to ethylene. The following information addresses some of these methods. Please note that this section is not intended to be a complete review and evaluation of ethylene sampling and analytical methods. The employer is responsible for assuring the accuracy and precision of a method relevant to the unique conditions of the specific workplace, no matter which method is chosen. For more information contact your supplier.

Detector Tubes

A number of detector tubes for use with volumetric pumps to measure ethylene concentrations are commercially available. These colorimetric-indicating tubes provide a direct reading of the ethylene concentration. A specified amount of air is drawn through the tube, and the ethylene present in the air reacts with the solid sorbent to produce a color change whose length-of-stain is directly proportional to the ethylene concentration. Detector tube limits are from 0.1 ppm to 2500 ppm, for 3 to 40 strokes.

Interferences and sampling time are other issues, which need to be considered with the use of colorimetric detector tubes. Chemical substances that may interfere with these tubes include other compounds with C=C double bonds (butylene, propylene, etc.), H_2S (hydrogen sulfide), and CO (carbon monoxide). The presence of these chemicals may cause false positive results. Current colorimetric tubes can require 4 to 30 minutes of sample acquisition time to determine a reading.

Direct Reading, Portable Instruments

Photo ionization (PID) detectors can be used to measure for ethylene in low- to sub-ppm concentrations. One potential concern is that these instruments will respond to a wide range of hydrocarbons. A specific response factor should be utilized with the correct lamp to maximize the approximate value of reading for ethylene. Note that the non-specificity for ethylene can be affected by the presence of other hydrocarbons.

Direct reading portable infrared (IR) and gas chromatography (GC) instruments may also be used to monitor for ethylene in the field. Extreme care should be utilized with these instruments in the field. Alternatively, a collection device such as a syringe, bag, or vacuum canister can acquire the sample and be brought to the instrument in a safe environment.

Bench Scale Analytical Instruments

As noted, the presence of other hydrocarbons or certain gases may significantly interfere with the readings obtained by detector tubes, or the intrinsic safety of portable field instruments may cause concern or difficulty in reading samples in the field. Laboratory scale gas chromatographs, infrared spectrophotometers or gas chromatograph-mass spectrophotometers can be used to quantitate ethylene in samples. Field acquisition of ethylene in air can be, as stated earlier, by syringe, sample bag, or vacuum canister. Most frequently ethylene is analyzed by gas chromatography using a flame ionization detector. Any column that is suitable for hydrocarbon analysis may be used. Air analysis is done by direct injection into the gas chromatograph. A capillary column under cryogenic conditions may be more efficient.

Charcoal Methods

Most exposure monitoring methods for organic materials use charcoal tubes with sampling pumps, or passive diffusion badges with a charcoal sorbent. The devices are then desorbed with a solvent followed by analysis of the samples using gas chromatography (GC). These methods are *not recommended* for ethylene, because charcoal does not produce reproducible results with ethylene. There currently are no known validated methods for ethylene on charcoal.

Passive Diffusion Tube

A second type of passive monitoring device available for some organic material sampling is a passive diffusion tube. This is a colorimetric method whereby the organic material concentration can be read directly by the length of the color stain in the pre-calibrated tube, which has been produced by a chemical reaction. One tube available is primarily a 1,3-butadiene tube that has a secondary application for ethylene with an applied correction factor. The measurement range for ethylene is listed as 12 – 240 ppm-hrs. It should be noted that such color stain methods might have interferences from other materials. The documents accompanying such devices should be reviewed prior to use.

Transport of Ethylene

Most ethylene is transported by pipeline to or from various production sites, but, in certain cases, it must be transported by cargo tanks or tank cars to reach its destination. Transportation by truck or rail is highly regulated by DOT due to the hazards of the material.

Transport by Pipeline

The DOT, along with various state regulatory agencies, regulates the transport of ethylene by pipeline as noted in 49 CFR Parts 190-199.

For pipeline movements of ethylene, consider several safety measures. One primary measure utilized is a “line integrity metering” system. The pipelines are continually monitored by control centers that are staffed 24 hours per day. Any discrepancy between the amounts entering and exiting the pipeline is investigated.

In addition, pipelines carrying ethylene are required to have a periodic patrol program to observe surface conditions on or adjacent to the pipeline right-of-way for indication of leaks, construction activity, and other factors affecting safety and operations.

The frequency of the patrols is determined by numerous factors, but intervals between patrols may not be longer than prescribed by DOT and state regulations. Methods of patrolling the pipeline include walking, driving, flying, or other appropriate means of traversing the right-of-way.

Pipeline markers containing the name of the contents of the pipeline and a 24-hour emergency number to call are located at periodic intervals along the pipeline and at all road and stream crossings. If any digging is to be done near the pipelines, notification by calling the listed phone number on the pipeline marker (or a suitable local “One Call” system number) is required. Once the number is called, the pipeline operator dispatches a specialist to the site to mark the exact pipeline location before excavation starts.

Transport by Cargo Tank

Cargo Tank refers to the liquid container, insulation, supports and outer jacket that are attached to a trailer used to transport cryogenic liquids over the road. 49 CFR § 173.318 refers to Cryogenic Liquids in Cargo Tanks.

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

Transport by Rail Tank Cars

"Ethylene, Refrigerated Liquid" is transported in specially built tank cars for that service. It may be transported in two different types of tank cars, DOT-113C120W and DOT-113D120W. These cars are of special design so the product remains refrigerated during the transportation of the material to the consignee. 49 CFR 174 refers to Carriage by Rail.

A separate product stewardship manual concerning the handling of cryogenic ethylene (refrigerated liquid ethylene) has been prepared by the Cryogenic Ethylene Transportation Safety Panel of the American Chemistry Council. The reader should consult that document for additional information pertaining to cryogenic ethylene.

Storage of Ethylene

Storage facilities for light hydrocarbons such as ethylene are highly specialized. Qualified engineering firms should be employed for their design. The following information describes some of the factors that should be addressed for storage of ethylene. Many factors discussed in this section are required by applicable regulations, while other factors represent common industry practices. For additional information, consult your supplier or a qualified engineer.

Storage System Design and Operation

Type of Vessel

There are two basic types of vessels used to store ethylene: pressurized or cylindrical (bullet tanks) and flat bottom storage tanks. The most common way to store liquid ethylene is in flat bottom insulated tanks at atmospheric pressure (temperature is -150°F). For smaller capacities, liquid ethylene can be stored in pressurized vessels (cylinders or spheres). They are generally constructed to ASME Boiler & Pressure Vessel Code Section VIII. Check with local jurisdiction for applicable laws and regulations.

Ethylene is also stored as a supercritical fluid (ambient temperature, pressure in excess of 1000 psig) below ground in caverns created within dense salt dome formations. A cavern is formed by drilling into the salt formation and then washing the cavern with fresh water. This practice is highly regulated and is outside the scope of this document.

Materials

Care must be exercised to select the proper material of construction for the storage tank. Carbon steel is typically used for pressurized spheres when subjected to the proper tests for impact and ductility. There exists a wide variety in grades of steel; generally, carbon steel will be suitable for temperatures down to -50° F. Older installations may be suitable only for temperatures down to -25° F. Stainless steel or other low temperature alloys must be used for storage at lower temperatures.

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Design

All vessel types must have a foundation suitable for the tank design. They are generally constructed from concrete or steel and are designed to transmit all loads to the earth. When the support is constructed from steel, it should be protected from fire exposure. It should also have the same impact properties at low temperatures as the pressurized portion of the vessel. All vessels must be electrically grounded to prevent the accumulation of static electrical discharges, which could result in a fire.

The vessel should be placed in an area that is large enough to allow for secondary containment or the installation of a dike. A typical arrangement uses an earthen dike to provide for the total volume of liquid equivalent to a tank full of product. Concrete is another common form of dike construction. It is necessary to consider individual features and conditions when selecting an impoundment concept. The method chosen depends on topography, the surrounding property, the proximity and type of adjacent buildings and their uses, exposure to the public at work or at home, and local jurisdictional requirements.

Flat bottom tank foundations in low temperature service present an additional issue. Unless the foundation is heated, eventually a large quantity of soil will reach temperatures below freezing. Moisture in the soil will freeze and some “heaving” could occur. Soil temperature should be maintained above 32° F.

Single wall tanks will have insulation on the outside of the tank, covered with some type of weather barrier. Double wall tanks have a non-combustible insulating material between the two walls.

When designing a refrigerated system, a choice is made between single wall and double wall tanks for use in atmospheric pressure storage systems. Help from a competent engineering firm will be beneficial with this decision.

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Operation

When filling a storage tank, allowance must be made to properly handle thermal expansion. The total capacity of the storage vessels must be calculated in order to contain the product in its normal and expanded states. If provisions are not made for thermal expansion, liquid leakage through pressure relief valves could occur, resulting in a fire hazard.

A thorough understanding of the level gauge is necessary for safe operation to prevent overfilling the storage tank. It is recommended that the operator become acquainted with the manufacturer's instructions regarding the operation of the level gauge.

All storage vessels should be supplied with overpressure relief valves and/or vacuum relief. The set point of these valves should not exceed the maximum allowable working pressure (MAWP) of the storage vessel. Double wall tanks should have overpressure protection on both the inner storage area and the annular space between the walls. Frequent inspection of relief devices is advisable to determine if they are plugged by debris that would render them inoperable. Relief devices should be tested and calibrated on a regular basis in accordance with manufacturer's instructions.

Handling, Safety, and Health Information

The flammability and explosion risks of ethylene are widely recognized and well documented, and ethylene liquid or vapor in high concentrations can potentially result in certain safety and health risks to workers. The safety hazards, industrial health risks, and exposure limits for ethylene may be updated or modified through studies and regulatory changes. Standards frequently vary from country to country.

OSHA regulations (29 CFR § 1910.1200(g)) require all ethylene manufacturers to provide customers with the latest Material Safety Data Sheets (MSDS) for ethylene. The MSDS also can be used to notify users of applicable regulations. Users should disseminate such information in accordance with the OSHA regulations to give warning of possible hazards to all appropriate persons.

In general terms, these documents contain physical data on the product, information for safety and emergency situations, recommended procedures for immediate medical treatment, identification of fire and explosion hazards, current hazard information, and current occupational health, exposure, and protection guidelines. The regulations require that the MSDS be updated to reflect significant new information in these areas. 29 CFR § 1910.1200(g)(5).

For more detailed information regarding safety, health, and/or toxicity data for ethylene, refer to your supplier's MSDS for ethylene. Consult the supplier's MSDS for specific recommendations on handling ethylene under regular operations and in emergencies. Supervisory and operating staff must have access to the MSDS and receive training on hazardous chemicals in their work area (29 CFR § 1910.1200(h)).

Handling and Disposal of Samples

Care must be taken in the handling and disposal of laboratory-sized and larger samples of ethylene. Laboratory and sample storage facilities should be appropriate for the associated risks. Test and handling procedures should be clear and the laboratory and operating personnel well trained.

Methods for in-plant disposal of samples include venting to a control device such as a flare or controlled incineration at a remote site with remote control of the ignition source to help protect personnel and property.

Where disposal of large quantities is involved, the help of a competent specialist is recommended. There are several chemical disposal companies specializing in the transportation and disposal of hazardous materials. These companies have the proper equipment and trained personnel to handle the disposal safely.

Emission Sources and Controls

Ethylene is normally stored under pressure as a liquefied or compressed gas. It is transported by railroad in tank cars, by roadway in cargo tank trucks, and over land by pipeline. Ethylene may be released during manufacture, storage, and use due to mechanical failure of a pump seal, valve pack, pipe connection, or gasket. These fugitive emissions are the most common form of industrial release. Releases of this type are regulated and controlled by federal and state rules as well as operating permits. The applicable regulations require frequent monitoring and require repair of leaking components within a specified period of time. Ethylene may leak from piping at points where the integrity of pipeline sealing is compromised. Such losses can be minimized by the use of suitable packing materials and pump sealing technology. Ethylene emission reduction activities that have been planned, completed or are in progress at some sites include those listed below. These are provided as examples of the various ways that ethylene releases can be further reduced. Other fugitive emission monitoring programs may include:

- Leak detection and repair (LDAR) program for valves, pumps and flanges.
- Pump seal replacement (design changed to double seals).
- Analyzer replacement (fewer connections).
- Analyzer vents to closed systems (flare).
- Rupture disks under relief valves.
- Equipment safeguarding (process changes to better control pressure).
- Closed loop sampling systems.
- Reduced ethylene flaring via improved source control (flares are not 100% efficient combustors of ethylene).

Reactivity/Incompatibilities

Ethylene forms explosive mixtures in air. The lower explosive limit (LEL) and upper explosive limit (UEL) values are 2.3% and 32.3% by volume of air, respectively. (See Table 1.2) Its reaction with fluorine is explosively violent (ΔH = -112 kcal/mol).

Ethylene is also incompatible or reacts violently with a number of other substances. A partial list of examples is provided below:

- Ethylene may undergo a reaction explosive at room temperature over the oxides of mercury or silver [Mellor 1946, Suppl. 1956].

- Acid-catalyzed addition of hydrogen peroxide to ethylene may produce ethyl hydroperoxide, which is unstable and explodes on heat or shock [Patnaik, Pradyot Ph.D., et al., A Comprehensive Guide To The Hazardous Properties of Chemical Substances, Second Ed., New York, et al.: Wiley, 1999, p. 467]:

$$CH_2{=}CH_2 + H_2O_2 \rightarrow CH_3\text{-}CH_2\text{-}O\text{-}OH$$

- Explosions have been reported from ethylene and carbon tetrachloride (under pressure in the presence of organic peroxide catalysts), [Bolt 1947; Joyce 1947], bromotrichloromethane, nitromethane and aluminum chloride [National Fire Protection Association, 1997], and nitrogen dioxide.

- Ethylene undergoes a variety of reactions to form highly toxic and/or flammable substances. It catalytically oxidizes to ethylene oxide; reacts with chlorine and bromine to form ethylene dichloride and ethylene dibromide; reacts with hypochlorite to form ethylene chlorohydrin; reacts with chlorine in the presence of HCl and light or chlorides of copper; and hydrates in the presence of H_2SO_4 to form diethyl ether. [Patnaik, Pradyot Ph.D., A Comprehensive Guide To The Hazardous Properties Of Chemical Substances, Second Ed., New York, et al.: Wiley, 1999, p. 467]

- Ethylene can react vigorously with oxidizing materials. [Fire Protection Guide to Hazardous Materials. 12 ed. Quincy, MA: National Fire Protection Association, 1997, p. 49-66]

- Ethylene can react vigorously with aluminum chloride. [Sax, N.I. Dangerous Properties of Industrial Materials. 6th Ed. New York, NY: Van Nostrand Reinhold, 1984. p. 1337]

- In absence of nitrogen as a diluent, interaction with trifluoromethyl hypofluorite and ethylene is explosive on mixing. [Bretherick, L. Handbook of Reactive Chemical Hazards. 4th ed. Boston, MA: Butterworth-Heinemann Ltd., 1990, p. 127]

- An explosive reaction between ethylene and chlorine is possible. [Fire Protection Guide to Hazardous Materials. 12 ed. Quincy, MA: National Fire Protection Association, 1997, p. 49-66]

- A violent explosion was reported to have occurred when a mixture of tetrafluoroethylene and excess ethylene was heated at 160° C and 480 bar. Traces of oxygen must be vigorously excluded. [Bretherick, L. Handbook of Reactive Chemical Hazards. 4th ed. Boston, MA: Butterworth-Heinemann Ltd., 1990, p. 261]

Hazardous Polymerization:

- Hazardous polymerization may occur. [Fire Protection Guide to Hazardous Materials. 12 ed. Quincy, MA: National Fire Protection Association, 1997, p. 49-66]

- Polymerization of ethylene in presence of metallic copper becomes violent above a pressure of 54 bar at about 400° C, with much carbon being deposited. [Bretherick, L. Handbook of Reactive Chemical Hazards. 4th ed. Boston, MA: Butterworth-Heinemann Ltd., 1990, p. 260]

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Ethylene Decomposition:

At elevated temperature (typically greater than 300° F) and pressure (typically greater than 1000 psig) ethylene can decompose to carbon and methane. The reaction is exothermic, releasing heat which further fuels the decomposition. Unless steps are taken immediately to stop decomposition (depressuring, removing heat, lowering temperature), the elevating temperature can result in failure of the containment vessel with corresponding release of unreacted ethylene. The higher the pressure, the lower the temperature needed to initiate the decomposition reaction.

Examples of events that can initiate an ethylene decomposition include:

- Sudden pressurization of a vessel or pipeline with ethylene, or of one containing ethylene.

- Heat (steam, flame) added to a vessel or pipeline containing ethylene, such as a flame impinging on a pipeline or vessel containing ethylene under elevated pressure.

- Polymerization of ethylene in a pressurized vessel, without adequate heat removal, can generate sufficient heat to initiate the decomposition reaction.

- Heat of adsorption from addition of ethylene to an adsorbent bed (where the adsorbent has pore size sufficient to adsorb ethylene) under elevated pressure can release sufficient heat to initiate an ethylene decomposition.

For more information on ethylene decompositions, refer to:

Britton, Laurence G., Taylor, D. Alex and Wobser, Donald C., "Thermal Stability of Ethylene at Elevated Pressures," Plant/Operations Progress (Vol. 5, No. 4), October 1986.

Worrell, G. R., "Theory of Ethylene Decomposition", Presented at the Texas Chemical Council Symposium of Ethylene Decomposition, May 17-18, 1983.

And to read about some ethylene decomposition incidents, refer to:

McKay, F.F., Worrell, G.R., "If an Ethylene Pipe Line Ruptures…", Hydrocarbon Processing, November, 1977.

Worrell, G. R., "If Ethylene Decomposes in Pipe…", Hydrocarbon Processing, April, 1979.

Coleman, S. T., and Knickerbocker, R. L., "Ethylene Pipeline Decomposition Incident", Proceedings of the 13th Annual Ethylene Producers' Conference, AIChE National Spring Meeting, Houston, TX, April 25, 2001.

PART IV - FIRE SAFETY AND EMERGENCY RESPONSE

Fire and Explosion Hazard

Ethylene presents a significant fire and explosion hazard based on its physical properties, including flashpoint, vapor pressure, and boiling point. It can quite readily form explosive mixtures in air as a result of its high vapor pressure. Therefore, preventive measures must be taken to minimize the potential for a fire or explosion.

Ethylene is extremely flammable and is classified as a flammable gas by OSHA and DOT. Ethylene concentrations in air of between 2.3% and 32.3% can form explosive mixtures. If an ignition source is present, a fire and/or explosion can result. At temperatures of approximately 842^{o} F or above, this material can autoignite. In other words, it can spontaneously ignite without the application of flame or spark if it is heated above this temperature.

Vapors of ethylene are slightly lighter than air (0.975 w/air =1). A vapor with a vapor density less than 1 is lighter than air and would tend to rise in air. The stratification based on vapor density is most significant while the vapor or gas is being introduced to a space. Given sufficient time, gases will diffuse throughout the space. An ethylene gas release may produce a visible fog when it is escaping in a non-fire emergency situation such as a spill or leak. The fog is the result of the liquid vaporization, which condenses water vapor from air. It should be noted that the fog is only an approximate indicator of the amount of ethylene in the area. The invisible, ignitable ethylene/air mixture can extend up to a half mile beyond the visible fog from the source of a large leak. In a fire situation, conditions can develop which could lead to explosions and further fire propagation. The build-up of pressure in closed containers of ethylene caused by elevated temperatures can result in container failure. Ethylene will polymerize but only at elevated temperature and pressure in the presence of a catalyst.

A particular concern for ethylene pipeline maintenance is the possible overheating and consequent initiation of a decomposition reaction in the pipeline. After offline maintenance is conducted on the pipeline, it normally is purged with nitrogen prior to refilling with ethylene. Care must be taken when refilling the pipeline to avoid rapid compression of the ethylene vapor as the pipeline is filled up to the vapor pressure of approximately 750 psig. Repressuring gradually allows heat dissipation and prevents the ethylene from reaching autodecomposition temperature. The decomposition reaction, if started, will almost certainly result in a pipeline failure.

Fire Prevention

Some general guidelines for fire prevention are included in Table 4.1.

Table 4.1: General Guidelines for Fire Prevention, Ethylene

1.	Storage and handling areas should be located with consideration given to neighboring properties as well as nearby plant operations. All potential sources of ignition should be reviewed.
2.	Storage and handling equipment should be designated and maintained in conformance with applicable regulations and codes (ASME, OSHA, API, DOT, National Electrical Code, etc.)
3.	Smoking should not be permitted in areas near where ethylene is stored or handled.
4.	Stringent hot work practices and systems that fully address ethylene's fire and explosion hazards should be in place. (Hot work is defined as including but not limited to welding, cutting and burning.) The use of non-sparking tools while working on or near ethylene-containing equipment should be among these practices.
5.	Preventive measures against the accumulation of static electricity should be employed. In accordance with applicable codes and regulations, fixed equipment must be grounded. Appropriate bonding and grounding also needs to be employed during transfer operations.
6.	Electrical devices and installations should be suitable for Class I, Group B hazardous locations (as defined by Articles 500 and 501 of the National Electrical Code).
7.	Storage and handling facilities should conform to local ordinances and with the requirements of underwriters and insurance companies.

Firefighting

In general, firefighting measures for ethylene are similar to those for Liquified Petroleum Gases. If there is an ethylene fire or ethylene is located in a fire area, to prevent injury the fire area should be cleared of unauthorized and/or unprotected personnel and isolated. For fire incidents involving a tank, rail car or cargo tank truck, the DOT Emergency Response Guide Number 115 for ethylene refrigerated liquid, and Guide Number 116P for ethylene gas-flammable-unstable, indicate to isolate the area for one mile (1600 meters) in all directions. Firefighters should wear full bunker gear at a minimum (helmet with face shield, bunker coats, gloves and rubber boots) and a positive pressure, NIOSH-approved, self-contained breathing apparatus (SCBA) as necessary to prevent exposure to smoke and other combustible products.

As outlined in the DOT Emergency Response Guidebook, the following procedures should be taken into account when fighting a fire involving ethylene:

- A container of ethylene exposed to intense heat from fires should be cooled with large quantities of water to minimize pressure build-up in the container, which could result in container failure and/or weakening of the container structure. Water should be applied from a safe distance and until well after the fire is out. If possible, this should be done with unmanned hose holders or monitor nozzles. Large volumes of water should continue to be used to cool containers even if the fire is out.

- If water supplies are limited or not available, firefighters should be withdrawn and the fire allowed to burn.

- Unless the gas flow can be safely shut off, the gas should be allowed to burn. Disperse the vapor cloud with a sustained flow of water fog. Keep liquid and vapor away from heat, sparks and flames. Surfaces that are sufficiently hot may ignite ethylene even in the absence of sparks or flame. Precautions must be taken to eliminate all potential sources of ignition.

- Immediate withdrawal of fire-fighting personnel should take place in case of a rising sound from a venting safety device, or any discoloration of the tank due to fire.

If a company opts to fight fires with an internal fire brigade, compliance with the requirements of OSHA's Fire Brigade Standard (29 CFR § 1910.156) is required. Under these requirements, part of the training provided to the fire brigade members should include information on the hazards of ethylene, quantities present, and location(s). Similarly, if a facility is to utilize community fire companies for fire response, they should be provided with the same types of information and training as appropriate.

In the event of residual ethylene contamination (e.g., in a container or enclosed space) after a fire has been extinguished, the clean-up activities must be conducted in accordance with the requirements of the OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) standard (29 CFR § 1910.120).

Emergency Response

During transport, and also during normal plant operations, a release may occur from an incident that damages the container and results in an ethylene leak. Gases or liquefied gases of this type are normally processed in equipment and stored in tanks equipped with pressure relief devices. These devices are designed to release a small amount of the material if the pressure in the tank goes above a preset limit. Use of pressure relief devices greatly reduces the risk of a tank or vessel rupture in the event of pressure building inside the tank. Use of flares or other control devices to which the relief devices can discharge can reduce the risk of releases to the atmosphere. When released from a tank to the atmosphere, liquid ethylene will become a gas. Due to the storage pressure and low temperature of the material, it can appear like steam. Because it is lighter than air, it will rise and then mix with the air and seem to disappear. When these releases occur, emergency response measures need to be set in motion as appropriate for the size of the release.

When ethylene is transferred from transport vessels into site storage and distribution pipelines, leakage may occur as a result of ethylene entrapment in the connecting hose and on the atmospheric side of valves. Although purging with nitrogen is partially effective, experience indicates that substantial ethylene loss may still result. Leaks of ethylene during procedures that result in breaks of containment may be more effectively reduced by the use of dry-break coupling technology.

Emergency Response Planning

Adequate emergency response capability, including an emergency response plan, is necessary for the responsible management of a hazardous chemical such as ethylene. Preparation in advance of an emergency situation is the most important part of an effective emergency response plan. Part II of this document (see Prevention of Accidental Releases) refers to OSHA and EPA emergency planning and response requirements for employers. For example, the OSHA Process Safety Management standard (29 CFR § 1910.119) requires employers to develop and implement an emergency action plan. This emergency action plan must also include procedures for handling small releases.

A thorough plan will address all aspects of an ethylene emergency, including problems that may be specific to a particular site. Effective emergency response plans are generally tested through periodic drills that involve emergency response personnel both on-site and in the local community. Appropriate response procedures for responding to spills may include the following measures:

- Remove or shut off all sources of ignition.
- Prevent spill from entering sewers and waterways.
- Wear goggles, respirators, rubber overclothing, and gloves.
- Evacuate area in case of large discharge.
- Stay upwind and use water spray to disperse vapors.
- Notify fire department and local health and pollution control agencies.

Also see DOT's Emergency Guidebook (Guides 115 and 116) for more information.

CHEMTREC®

If a transportation incident involving ethylene does occur, the Chemical Transportation Emergency Center (CHEMTREC) is available for immediate assistance. CHEMTREC is a public service organization established by the American Chemistry Council and its members to provide assistance in hazardous materials incidents. It is recognized by DOT as a central clearinghouse for transportation emergencies including hazardous materials.

CHEMTREC's toll-free emergency assistance number is 1-800-424-9300. Ships at sea can contact CHEMTREC through the international and maritime number, 1-703-527-3887. The CHEMTREC center is staffed 24-hours a day, 7-days a week by trained communicators.

CHEMTREC uses a two-step approach in responding to emergencies involving hazardous materials. First, immediate emergency response information for the product involved in the incident is provided to the caller. This information is generally obtained from a manufacturer's Material Safety Data Sheet (MSDS) for the product in question. A reference library with over 1,000,000 MSDS' is maintained by CHEMTREC. DOT's Emergency Response Guidebook may also be used as a reference. Guides 115 and 116 of that document apply to emergency actions for ethylene incidents.

The second step is for CHEMTREC to notify the 24-hour emergency contact designated by the shipper or manufacturer of the material involved in the incident. Ethylene producers have emergency response procedures in place to provide additional technical advice and assistance. Trained emergency response personnel capable of responding to an ethylene incident are located at various production facilities throughout the United States.

A mutual aid program known as the Chemical Industry Mutual Aid Network (CHEMNET®) covers ethylene. CHEMNET was established by CHEMTREC to enable a chemical industry respondent to be on the scene of a chemical emergency as soon as possible. The network consists of emergency response teams from participating chemical companies and commercial contractors under contract to the American Chemistry Council.

The mutual aid agreement permits a shipper who is a member of the network, but is not able to promptly respond to an incident because of distance or other reasons, to have CHEMTREC link the shipper with the response team nearest to the scene able to provide assistance. The response team will then provide assistance on behalf of the shipper until the shipper is able to relieve the response team.

While this section focuses on ethylene transportation incidents, please be aware that CHEMTREC can also be contacted for non-transportation and medical incidents.

PART V - APPENDIX

GLOSSARY OF TERMS, ABBREVIATIONS, AND ORGANIZATIONS

A	
ACC	American Chemistry Council (Formerly the Chemical Manufacturers Association)
ACGIH®	American Conference of Governmental Industrial Hygienists
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
B	
Bonding	The connection of two or more conductive objects by means of a conductor (most commonly a wire or metal plate)
BTU	British Thermal Unit
C	
C#	The number of carbon atoms present in a molecular composition
CAA	Clean Air Act
CANUTEC	Canadian Transport Emergency Centre
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CG	Coast Guard
CHEMNET®	Chemical Industry Mutual Aid Network
CHEMTREC®	Chemical Transportation Emergency Center
CNS	Central Nervous System
Confined Space	An area that by design has limited openings for entry and exit. A confined space has unfavorable natural ventilation and is not intended for continuous worker occupancy.
CPC	Chemical Protective Clothing
D	
DIPPR	Design Institute for Physical Property Data (AIChE)
DOT	Department of Transportation
DSL	Domestic Substances List (Canada)

E	
EC	European Community
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
ESD	Electrostatic discharge
EU	European Union
F	
Flashpoint	The minimum temperature at which a liquid gives off vapor in sufficient concentrations to form an ignitable mixture with air near the surface of a liquid.
G	
GC	Gas Chromatography
GDP	Gross Domestic Product
GLP	Good Laboratory Practices
Grounding	The connection of one or more conductive objects to the ground: a specific form of bonding. Grounding is also referred to as “earthing.”
H	
HAP	Hazardous Air Pollutant
HMIS	Hazardous Materials Identification System
HAZWOPER	Hazardous Waste Operations and Emergency Response
HON	Hazardous Organic NESHAP
I	
IDLH	Immediately Dangerous to Life or Health
IARC	International Agency for Research on Cancer
ISO	International Standards Organization
J	
K	
L	
LEL	Lower Explosive Limit
LFL	Lower Flammability Limit
LLDPE	Linear Low Density Polyethylene
LPGs	Liquefied Petroleum Gases

M	
MSDS	Material Safety Data Sheet
N	
NDE	Nondestructive Evaluation
NDT	Nondestructive Testing
NEC	National Electrical Code
newton	Unit of force in the meter-kilogram-second system equal to the force required to impart an acceleration of one meter per second to a mass of one kilogram.
NFPA	National Fire Protection Association
NGLs	Natural Gas Liquids
NIOSH	National Institute for Occupational Safety and Health
NPRI	National Pollutant Release Inventory
NTP	National Toxicology Program
O	
OSHA	Occupational Safety and Health Administration
P	
PEL	Permissible Exposure Limit
PM	Preventative Maintenance
PPE	Personal Protective Equipment
ppm	parts per million
ppmv	parts per million by volume
ppmw	parts per million by weight
psia	Absolute pressure in pounds per square inch.
psig	pounds per square inch gauge.
Q	
R	
REL	Recommended Exposure Limit (NIOSH)
RCRA	Resource Conservation and Recovery Act
RQs	Reportable Quantities
S	
SCBA	Self-Contained Breathing Apparatus
SCC	Standards Council of Canada
SOCMI	Synthetic Organic Chemicals Manufacturing Industry
STEL	Short Term Exposure Limit

T	
TLV®	Threshold Limit Value (ACGIH)
TLV-TWA	Threshold Limit Value, Time Weighted Average (ACGIH)
TOC	Total Organic Carbon
TPQ	Threshold Planning Quantity
TRI	Toxics Release Inventory
TSCA	Toxic Substances Control Act
TWA	Time-Weighted Average
U	
UEL	Upper Explosive Limit
UL	Underwriters Laboratory
Ullage	Amount by which a packaging falls short of being liquid full
UN	United Nations
USCG	United States Coast Guard
V	
Vapor Pressure	The pressure exerted by a volatile liquid while under defined equilibrium conditions. Vapor pressure is usually measured in millimeters of mercury (mm Hg).
VOC	Volatile Organic Chemical
W	
WHMIS	Workplace Hazardous Materials Information System (Canada)
XYZ	

Additional References

As the Legal Notice to this Guide observes, this Guide is not intended to present comprehensive information regarding the topic, but to provide general information to persons who may handle or store ethylene. For more information regarding specific handling or storage requirements, readers may wish to consult their supplier(s) or some of the many additional references cited in this document or otherwise available.