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Office of Air Quality
Planning And Standards
Research Triangle Park, NC 27711

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LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF ETHYLENE DICHLORIDE

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning an Standards
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SECTION 1
PURPOSE OF DOCUMENT

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

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

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

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

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

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

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

Section 3 of this document provides a brief summary of the physical and chemical characteristics.of ethylene dichloride, its commonly occurring forms and an overview of its production and uses. A chemical use tree summarizes the quantities of vinylidene chloride consumed in various end use categories in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

Section 4 of this document focuses on major industrial source categories that may discharge ethylene dichloride air emissions. This section discusses the production of ethylene dichloride and its use as an industrial feedstock. For each major industrial source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for ethylene dichloride emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production or use of ethylene dichloride, based primarily on trade publications.

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

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

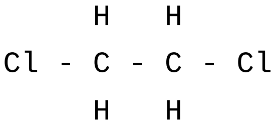
Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Noncriteria Emissions Section
Air Management Technology Branch
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

SECTION 3
BACKGROUND

NATURE OF POLLUTANT

Ethylene dichloride (EDC) is a clear, colorless oily liquid with a pleasant chloroform-like sweet odor and taste. The chemical name for ethylene dichloride is 1,2-dichloroethane, the molecular formula is ClCH2CH2Cl, and the structure is as follows:



$$\begin{array}{ccccccc} & & H & & H & & \\ Cl & - & C & - & C & - & Cl \\ & & H & & H & & \end{array}$$

Ethylene dichloride should be distinguished from 1,2-dichloroethylene which has double-bonded carbon atoms and the molecular formula ClCH=CHCl. Ethylene dichloride is soluble in hydrocarbon solvents, miscible with other chlorinated solvents, and has a high solvency for fats, greases, and waxes. However, it has only a limited solubility in water.[1] Physical properties of EDC are listed in Table 1.

Dry EDC is stable at room temperature but decomposes slowly when exposed to air, moisture, and light, forming hydrochloric acid and other corrosive products. The decomposing liquid becomes darker in color and progressively acidic. It can thus corrode iron or steel containers. Decomposition can be prevented by adding a small amount of alkylamine. EDC that is sold as a solvent is normally treated in this manner; however, as an intermediate chemical, EDC is usually not stabilized.[2]

Both of the chlorine atoms in the ethylene dichloride molecule are reactive and can be removed by heat or replaced by other substituents. The economic importance of ethylene dichloride is based in part on the ease with which hydrogen chloride can be removed to form vinyl chloride with the application of heat. The chemical nature of EDC also makes it useful in the manufacture of condensation polymers and ethylene diamine.[1]

TABLE 1. PHYSICAL PROPERTIES OF ETHYLENE DICHLORIDE[3,4]

Synonyms: 1,2-Dichloroethane, EDC, glycol dichloride, ethylene chloride, sym-dichloroethane, brocide, borer sol, destruxol borer-sol, di-chlor-mulsion, dutch liquid, ent 1,656, freon 150, NCI-C00511

Chemical Formula	$ClCH_2CH_2Cl$
CAS Registry Number	107-06-2
Molecular Weight	98.97
Boiling Point, °C	83.7
Melting Point, °C	-35.3
Density at 20°C, g/l	1.2529
Refractive index at 20°C, for Sodium Light	1.4451
Viscosity at 20°C, mPa•s	0.84
Surface Tension at 20°C, mN/m	31.38
Specific Heat at 20°C, J/(g•K)	
liquid	1.288
gas	1.066
Latent Heat of Vapor at 20°C, J/g	323.42
Latent Heat of Fusion, J/g	88.36
Critical Temperature, °C	290
Critical Pressure, MPa	5.36
Critical Density, g/L	0.44
Flash Point, °C	
closed cup	17
open cup	21
Explosive Limits in Air at 25°C, % by Vol.	6.2-15.6
Autoignition Temperature in Air, °C	413
Thermal Conductivity, liq• at 20°C, W/(m•K)	0.143
Heat of Combustion, kJ/g	12.57
Heat of Formation, kJ/(g•mol)	
liquid	157.3
vapor	122.6

TABLE 1. (Continued)

Dielectric Constant	
liquid, 20°C	10.45
vapor, 120°C	1.0048
Dipole Moment, C•m	5.24×10^{-30}
Coefficient of Cubical Expansion, mL/g, 0-30°C	0.00116
Vapor Pressure, kPa	
10°C	5.3
20°C	8.5
30°C	13.3
Solubility at 20°C, g	
1,2-dichloroethane in 100 g H_2O	0.869
H_2O in 100 g 1,2-dlchloroethane	0.160
Azeotropes, bp, °C	
with 19.5% H_2O	72
with 5% H_2O and 17% ethanol	66.7

OVERVIEW OF PRODUCTION AND USES

Since the mid-1940s, ethylene dichloride has been used principally as a raw material in the synthesis of other compounds, particularly vinyl chloride, methyl chloroform, trichloroethylene, perchloroethylene, vinylidene chloride, and ethyleneamines.[1] Ethylene dichloride is produced in the United States mainly by 12 manufacturers in 19 production facilities.[5] The production of EDC from these plants is flexible and highly responsive to economic conditions. The combined annual capacity of these plants in 1983 was estimated to be 9,205,700 Megagrams5 while actual production in 1982 was estimated at a level of 3,451,488 Megagrams.[6] Exports of EDC in 198l were estimated at 277,000 Megagrams.[7]

Ethylene dichloride is manufactured in the United States by direct chlorination of ethylene, oxychlorination of ethylene, or a combination of these methods. In the direct chlorination process ethylene is treated with chlorine in the presence of a catalyst to produce EDC. Either vapor- or liquid-phase reactions may be used, but undesirable side products are obtained unless conditions are controlled carefully. In one vapor-phase procedure, product yields of 96 to 98 percent are obtained by treating ethylene at 40°C to 50°C with chlorine containing traces of ethylene dibromide, which acts as a catalyst. Other direct chlorination procedures exist that differ primarily in reaction conditions and catalyst. Catalysts mentioned most often in the patent literature include ferric, aluminum, cupric, and antimony chlorides. In 1974 the direct chlorination of ethylene accounted for 58 percent of the U.S. production of ethylene dichloride.[1]

Ethylene dichloride is also manufactured commercially by treating ethylene with anhydrous hydrogen chloride and oxygen (or air) in a fluidized bed of finely divided particles containing cupric chloride. Typically, the reactive pressure and temperature are maintained at 20 to 70 psig and 200°C to 315°C, respectively.[1]

Where EDC is produced for use in the manufacture of vinyl chloride, the oxychlorination and direct chlorination processes are often used together in what is know as the balanced process. In the balanced process, EDC is synthesized by the direct chlorination process and is then dehydrochlorinated, resulting in the production of vinyl chloride monomer and byproduct HCl. Manufacturers take advantage of the byproduct HCl by using it in the oxychlorination process to produce more EDC.

Ethylene dichloride is used primarily as a chemical intermediate in the synthesis of other compounds. The current uses of EDC are listed in Figure 1, along with the percentage of the total product devoted to each use. Synthesis of vinyl chloride accounts for 81 percent of the annual United States consump- tion of EDC while the synthesis of methyl chloroform (1,1,1-trichloroethane), ethyleneamines, perchloroethylene, trichloroethylene, and vinylidene chloride (1,1-dichloroethene) accounts for another 14 percent of consumption.[4]

Ethylene dichloride is also used as a scavenger for lead in gasoline. The EDC decomposes during combustion, with the chlorine atoms binding to the lead in the gasoline to form gaseous lead species. Thus, engine fouling with lead oxides or other solid lead species is prevented. The use of EDC as a lead scavenger in gasoline accounted for about l percent of the 1980 production. However, this use declined by 30 percent in 198O and is expected to decline further because of the decreasing production of leaded gasolines.[7]

Minor uses of ethylene dichloride are in textile cleaning and processing, in formulations of acrylic-type adhesives, as a product intermediate for polysulfide elastomers, as a constitutent of polysulfide rubber cements, in the manufacture of grain fumigants, and as a cleaning and extraction solvent. Of the estimated consumption of EDC by minor uses, about 28 percent is used in the manufacture of paints, coatings, and adhesives. Extracting oil from seeds, treating animal fats, and processing pharmaceutical products account for 23 percent. An additional 19 percent is consumed in cleaning textile products and polyvinyl chloride manufacturing equipment. Nearly 11 percent is used in the preparation of polysulfide compounds. Grain fumigation requires about 10 percent. The remaining 9 percent is used as a carrier for amines in leaching copper ores, in the manufacture of color film, as a diluent for pesticides and herbicides, and for other miscellaneous purposes.[1]

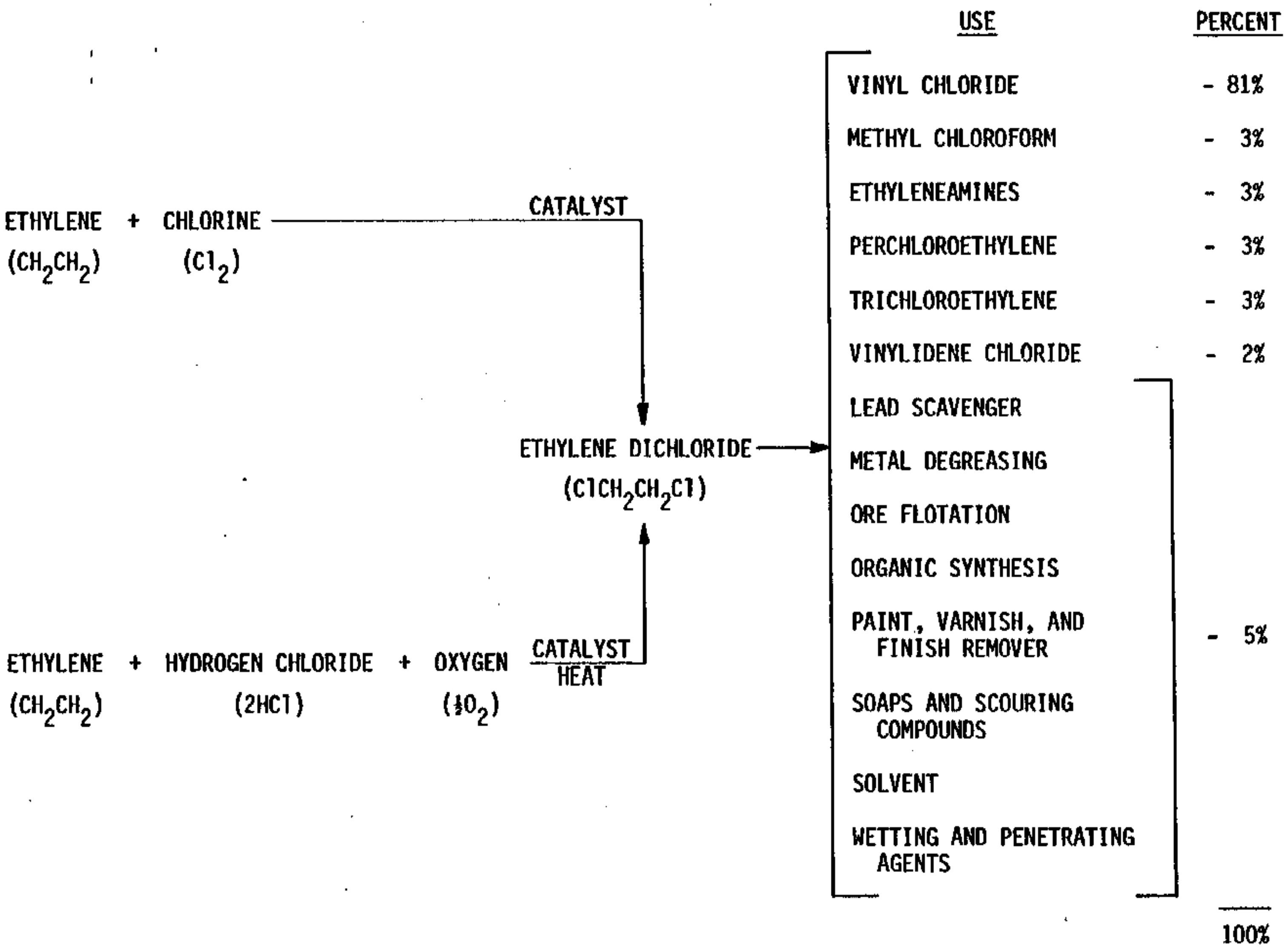


Figure 1. Chemical use tree for ethylene dichloride.[4]

SECTION 4

ETHYLENE DICHLORIDE EMISSION SOURCES

This section discusses ethylene dichloride (EDC) emissions from direct sources such as production of EDC, production of chemicals using EDC as a feedstock, and miscellaneous uses of EDC. Process and emissions information are presented for each source for which data were available.

ETHYLENE DICHLORIDE PRODUCTION

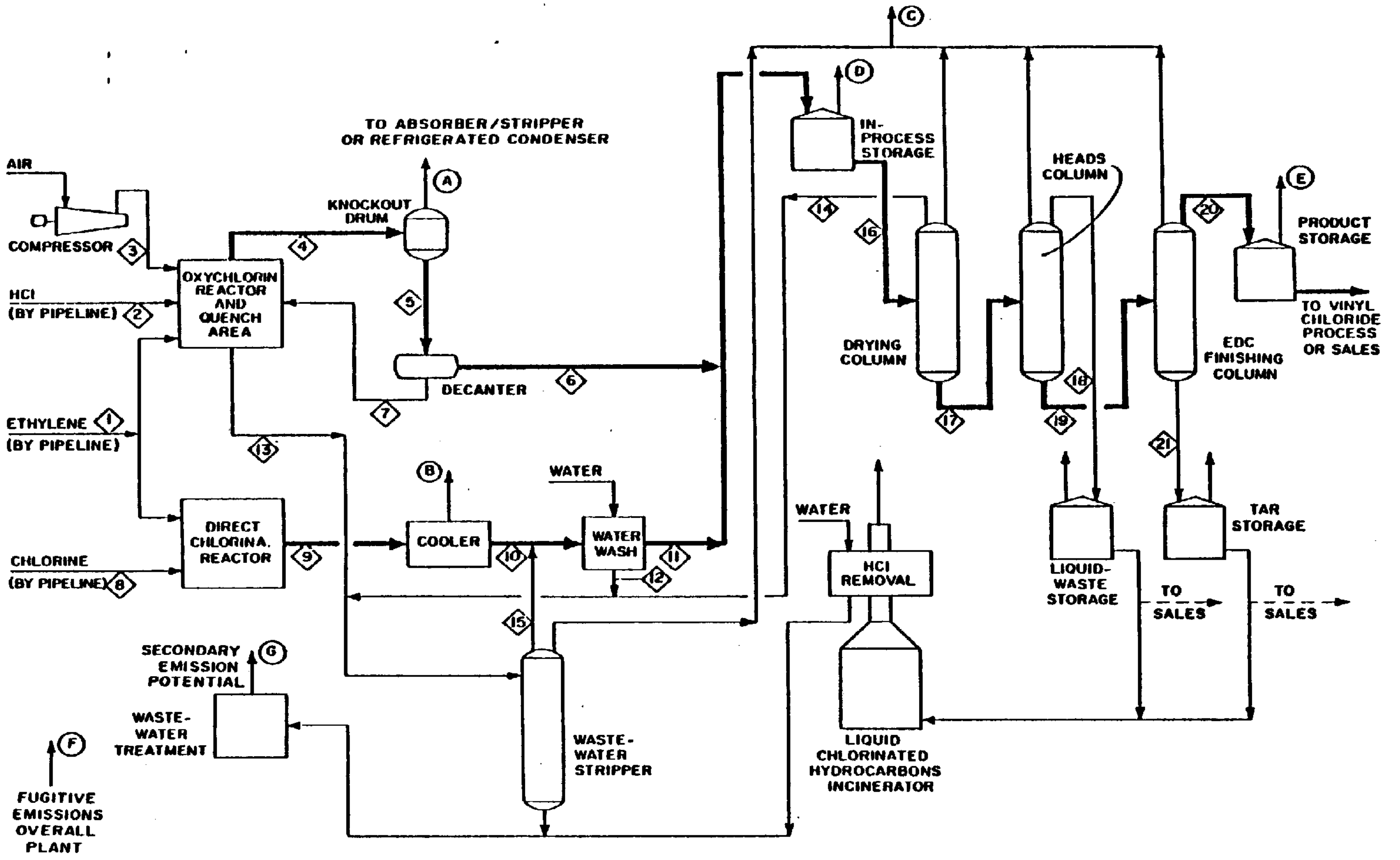
Ethylene dichloride (EDC) Is produced from ethylene and chlorine by direct chlorination, and from ethylene and hydrogen chloride (HCl) by oxychlorination. At most production facilities, these processes are used together in what is known as the balanced process. This section discusses EDC emissions from this process.

The balanced process generally is used wherever EDC and vinyl chloride monomer (VCM) are produced at the same facility. As noted in Section 1, about 81 percent of the EDC produced domestically is used in the manufacture of VCM.4 In VCM production, EDC is dehydrochlorinated to yield VCM and byproduct HCl. In the balanced process, byproduct HCl from VCM production via the-direct chlorination/dehydrochlorination process is used in the oxychlorination/dehydrochlorination process.

Process Description

The balanced process consists of an oxychlorination operation, a direct chlorination operation, and product finishing and waste treatment operations. The raw materials for the direct chlorination process are chlorine and ethylene. Oxychlorination involves the treatment of ethylene with oxygen and HCl. Oxygen for oxychlorination generally is added by feeding air to the reactor, although some plants use purified oxygen as feed material.[8]

Basic operations that may be used in a balanced process using air for the oxychlorination step are shown in Figure 2. Actual flow diagrams for production facilities will vary. The process begins



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 2. Basic operations that may be used for ethylene dichloride production by the balanced process, with air-based oxychlorination.[8]

with ethylene (Stream 1) being fed by pipeline to both the oxychlorination reactor and the direct chlorination reactor. In the oxychlorination reactor the ethylene, anhydrous hydrogen chloride (Stream 2), and air (Stream 3) are mixed at molar proportions of about 2:4:1, respectively, producing 2 moles of EDC and 2 moles of water. The reaction is carried out in the vapor phase at 200 to 315°C in either a fixed-bed or fluid-bed reactor. A mixture of copper chloride and other chlorides is used as a catalyst.[8]

The products of reaction from the oxychlorination reactor are quenched with water, cooled (Stream 4), and sent to a knockout drum, where EDC and water (Stream 5) are condensed. The condensed stream enters a decanter, where crude EDC is separated from the aqueous phase. The crude EDC (Stream 6) is transferred to in-process storage, and the aqueous phase (Stream 7) Is recycled to the quench step. Nitrogen and other inert gases are released to the atmosphere (Vent A). The concentration of EDC in the vent stream is reduced by absorber and stripper columns or by a refrigerated condenser (not shown in Figure 2).[2,8]

In the direct-chlorination step of the balanced process, equimolar amounts of ethylene (Stream 1) and chlorine (Stream 8) are reacted at a temperature of 38 to 49°C and at pressures of 69 to 138 kPa. Most commercial plants carry out the reaction in the liquid phase in the presence of a ferric chloride catalyst.[8]

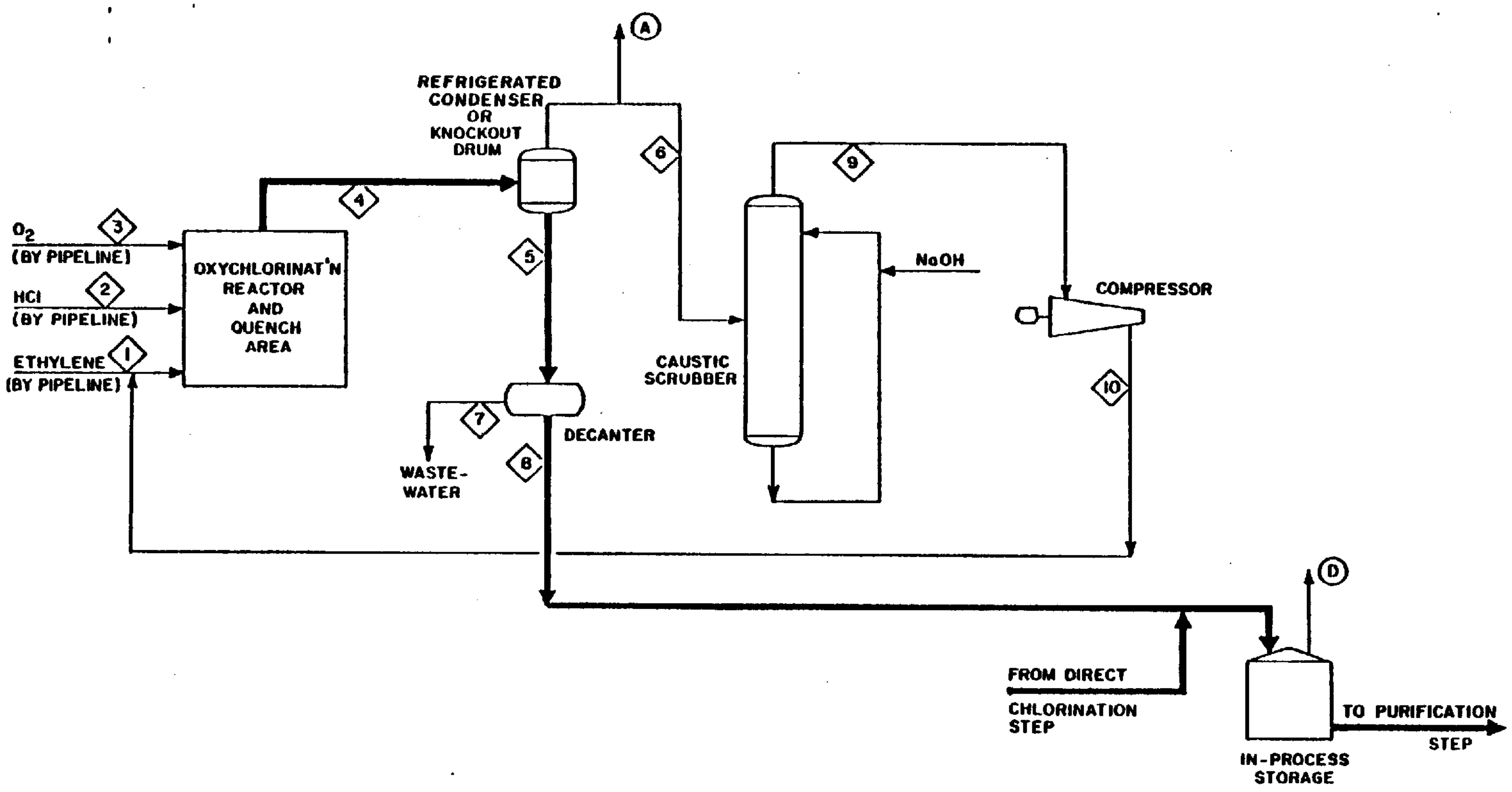
Products (Stream 9) from the direct chlorination reactor are cooled and washed with water (Stream 10) to remove dissolved hydrogen chloride before being transferred (Stream 11) to the crude EDC storage facility. Any inert gas fed with the ethylene or chlorine is released to the atmosphere from the cooler (Vent B). The waste wash water (Stream 12) is neutralized and sent to the wastewater steam stripper along with neutralized wastewater (Stream 13) from the oxychlorination quench area and the wastewater (Stream 14) from the drying column. The overheads (Stream 15) from the wastewater steam stripper, which consist of recovered EDC, other chlorinated hydrocarbons, and water, are returned to the process by adding them to the crude EDC (Stream 10) going to the water wash.[8]

Crude EDC (Stream 16) from in-process storage goes to the drying column, where water (Stream 14) Is distilled overhead and sent to the wastewater steam stripper. The dry crude EDC (Stream 17) goes to the heads column, which removes light ends (Stream 18) for storage and disposal or sale. Bottoms (Stream 19) from the heads column enter the EDC finishing column, where EDC (Stream 20) goes overhead to product storage. The tars from the EDC finishing column (Stream 21) are taken to tar storage for disposal or sale.[8]

Two domestic EDC producers use oxygen as the oxidant in the oxychlorination reactor. The process details are considered to be confidential by both producers. Although conceptual descriptions of such processes are given in the literature, it is not known how the actual processes compare with those described in the literature. One producer has released data showing that the plant is not truly balanced; that is, the ratio of EDC from oxychlorination and direct chlorlnation differs from that of a balanced plant. However, because both producers have direct chlorination, EDC purification and cracking, and VCM purification steps at the same site, both plants probably can be considered to have integrated processes.[8] Another producer uses only the oxychlorination process and does not use direct chlorination.[2]

Figure 3 shows basic operations that may be used in an oxygen-based oxychlorination process as presented in the literature.8 For a balanced process plant, the direct chlorination and purification steps are the same as those shown in Figure 2, and, therefore, are not shown again in Figure 3. Ethylene (Stream 1) is fed in large excess of the amount used in the air oxychlorination process, that is, 2 to 3 times the amount needed to fully consume the HCl feed (Stream 2). Oxygen (Stream 3) is also fed to the reactor, which may be either a fixed bed or a fluid bed. After passing through the condensation step in the quench area, the reaction products (Stream 4) go to a knockout drum, where the condensed crude EDC and water (Stream 5) produced by the oxychlorination reaction are separated from the unreacted ethylene and the inert gases (Stream 6). From the knockout drums the crude EDC and water (Stream 5) go to a decanter, where wastewater (Stream 7) is separated from the crude EDC (Stream 8), which goes to in-process storage as in the air-based process. The wastewater (Stream 7) Is sent to the steam stripper in the direct chlorination step for recovery of dissolved organics.[8]

The vent gases (Stream 6) from the knockout drum go to a caustic scrubber for removal of HCl and carbon dioxide. The purified vent gases (Stream 9) are then compressed and recycled (Stream 10) to the



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 3. Basic operations that may be used for ethylene dichloride production by the oxygen process (oxychlorination step).[8]

oxychlorination reactor as part of the ethylene feed. A small amount of the vent gas (Vent A) from the knockout drum is purged to prevent buildup of the inert gases entering with the feed streams or formed during the reaction.[8]

Emissions

Uncontrolled EDC emission factors for the balanced process are listed in Table 2. Also listed in this table are potentially applicable control techniques and associated emission factors for controlled emissions. The emission factors were developed for a hypothetical plant with a total EDC production capacity of 400,000 Mg/yr, based on 8760 hours of operation annually. Of the total production capacity, 2l5,000 Mg/yr is produced by direct chlorination and 185,000 Mg/yr by oxychlorination.[9] Because of variations in process design, age of equipment, and so on, actual emissions vary for each plant.

Process Emissions--

Ethylene dichloride process emissions originate from the purging of inert gases from the oxychlorination vent (Vent A, Figure 2 and Figure 3) and the direct chlorination vent (Vent B, Figure 2). The level of EDC in the oxychlorination vent gas is reduced by either an absorber/stripper combination or a refrigerated condenser. Average EDC emission rates of 3.24[9] and 3.58[10] kg/Mg of EDC produced have been reported from the absorber column. Emissions from the refrigerated condenser of one EDC producer were calculated to be 2.40 kg/Mg of EDC produced.[2] These emission factors are presented in the "uncontrolled EDC emission factor" column in Table 2 because the use of either the absorber/stripper combination or the refrigerated condenser is considered an integral part of the process design of some EDC production facilities. Somewhat higher oxychlorination and chlorination pressures are also reported to help lower EDC emissions.[2]

Many plants incinerate vent gases from the oxychlorination and direct chlorination reactors to reduce atmospheric emissions of EDC and VCM. This includes plants using the air-based as well as the oxygen-based oxychlorination processes,[11] although in air units a much larger incinerator must be used because of high levels of nitrogen in the oxychlorination vent.[2] Thermal oxidation is estimated to reduce EDC emissions by 98 percent or more.[12] Incineration destruction efficiency varies with emission stream properties and incinerator operating

TABLE 2. ETHYLENE DICHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL EDC PRODUCTION PLANT (BALANCED PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled EDC emission factor[c] (kg/Mg)	Potentially applicable control technique	% reduction	Controlled EDC emission factor[c] (kg/Mg)
Oxychlorination					
Air process	A				
Absorber/stripper, or		3.24[d,e]	Thermal oxidizer	98+[g]	≤0.0648[h]
		3.58[e,f]	Catalytic oxidizer	92.2[f]	≤0.280[f]
Refrigerated condenser		2.40e,f	Thermal oxidizer	98+[g]	≤0.0480[h]
Oxygen process	A[j]	0.462[d]	Thermal oxidizer	98+[g]	≤0.0092[h]
			Refrigerated condenser	85[k]	0.0693[h], 0.17[i]
Direct chlorination vent	B	1.08[d]	Thermal oxidizer	98+[g]	≤0.0216[h]
			Refrigerated condenser	86k	0.162[h],0.26[i]
Column vents	C	3.00[d]	Thermal oxidizer	98+[g]	≤0.0600[h]
Storage vents					
In-process	D	0.0149[d]	Thermal oxidizer	98+[g]	≤0.0003[h]
			Refrigerated condenser	85k	0.0022[h]
Product	E	0.0733[d]	Thermal oxidizer	98+[g]	≤0.0015[h]
			Refrigerated condenser	85k	00110[h]
Process fugitive	F	0.265[d]	Detection & correction of major leaks	72[k,l]	0.106[h]
Secondary					
Wastewater biotreatment	G	0.002-0.06[i,m]	None		0.002-0.06[i,m]

[a] Any given EDC production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 2.

[c] Emission factors in terms of kg/Mg refer to kilogram of EDC emitted per Megagram of EDC produced by balanced process. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all (at each) of these operations within the hypothetical facility.

[d] Reference 8, p.IV-3.

[e] The use of the absorber/stripper combination or refrigerated condenser is sometimes used for EDC recovery as an integrated part of the process. Per Reference 2,2 one producer reports uncontrolled EDC emissions of 40 kg/Mg. Emissions from newer plants are generally significantly lower.

[f] Reference 10.

[g] The control efficiency for thermal oxidation (i.e. incineration) varies depending on the design of the incinerator and the compound which is burned. The 99 percent level is an estimate of the control efficiency of an incinerator with a residence time of about 0.75 seconds and a temperature of about 870°C, for a compound which is difficult to incinerate. Incinerators operating at longer residence times and higher temperatures may achieve higher efficiences. Reference 12.

[h] Calculated by applying the control efficiency to the uncontrolled emission factor.

[i] Reference 2.

[j] See Figure 3 for this vent source; see Figure 2 for all others.

[k] Reference 13.

[l] Detection and correction of major leaks is estimated to achieve emission reductions of 75 percent for pumps, 90 percent for vapor-service valves, 70 percent for liquid service valves, and 62 percent for relief valves, for an overall reduction of 72 percent. Emission reductions of up to 100 percent can be achieved for pumps and relief valves by installing double mechanical sealed pumps and rupture disks on relief valves.

[m] Emissions data are not available for deep well injection or neutralization. Reference 2.

[n] Steam stripping is sometimes used as an integrated part of the EDC production process for the recovery of EDC from wastewater, as shown in Figure 2. Information was not available on the use of controls beyond steam stripping.

parameters. The 98 percent efficiency level is based on incinerator operation at 870°C and 0.75 second residence time for a compound which is difficult to incinerate.[12] The emission reduction may be greater than 98 percent for incineration of EDC with these operating parameters. In addition, the efficiency may be higher for longer residence times or higher operating temperatures.[12] Catalytic incineration is used by one plant to reduce EDC emissions from reactor vents by 92.2 percent.[10] Refrigerated vent condensers may also be used to control direct chlorination vent emissions, as reported by one EDC producer.[2]

In an oxygen process, the purge gas can be dried and the contained ethylene can be chlorinated in a separate direct chloripator to produce additional EDC. The small vent from this direct chlorinator can be combined with the vent from the other direct chlorinator and other vents from the process and incinerated. This treatment is reported to essentially eliminate all emissions of EDC and VCM.[2]

Process emissions of EDC also result from the release of gases from the column vents (Vent C, Figure 2). Column vents include vents from the wastewater steam stripper, the drying column, the heads column,and the EDC finishing column.[9] Incineration reduces EDC emissions by at least 98 percent.[12]

Storage Emissions--

Ethylene dichloride emissions result from the storage of EDC during in-process and final product stages. Sources for the hypothetical plant are shown in Figure 2 (Source D and source E). The emissions in Table 2 are based on fixed-roof tanks, half full, and 11°C diurnal temperature variation.[9]

Emissions may be controlled by use of refrigerated vent condensers. The control efficiency for a refrigerated condenser is dependent on the properties of the uncontrolled emission stream and on the condenser operating parameters. The 85 percent efficiency level for storage vents is based on an uncontrolled emission temperature of 20°C and a condenser operating temperature of -15°C. Greater efficiency can be achieved by using a lower operating temperature.[13]

Handling Emissions--

No handling emissions occur in the hypothetical plant, as all raw materials, product, and waste byproducts are transported by pipeline. This may not be the case in existing plants, where loading and unloading operations could result in additional emissions.[9]

Fugitive Emissions--

Fugitive emissions of EDC and other volatile organics result from leaks in process valves, pumps, compressors, and pressure relief valves. The plant is estimated to have 38 pumps handling EDC or other light liquids. There are an estimated 40 pressure relief valves in volatile organics service and 900 process valves handling EDC or other liquids.[9] Fugitive emission quantities for specific production facilities are dependent on age of equipment, level of preventative maintenance, and leak detection programs.

Secondary Emissions--

Secondary emissions can result from the handling and disposal of process waste-liquid streams (Source G in Figure 2). Wastewater treatment at an EDC production plant may consist of neutralization and steam stripping followed by either deep well injection or biotreating. Use of an open-pit neutralization system may result in substantial EDC air emissions.[2] Handling of wastewater prior to deep well injection may also result in EDC emissions; however, emissions after injection are negligible.

Emissions of EDC from a biotreater are affected strongly by the biotreater process configuration, temperature of ambient air and wastewater, type of aeration device used, degree of aeration, and hydraulic retention time of the system.[2,10] EDC wastewater to a biotreater originates from several sources, as designated in Figure 2, as well as from spills, drips, stormwater runoff from concrete pads under process equipment and washing down of equipment.[2,10] In an activated sludge biotreating system, EDC is not a readily biodegradable compound.[2]

Most biotreater activated sludge systems consist of an open tank with surface mixers for aeration and mixing. The removal of EDC by air stripping in these systems can be extremely high (over 99 percent). The emisssion factor range in Table 2 is from biotreater emission data reported by two EDC production facilities.[2] The emission factors were based on production rates of approximately 1.1 x 10^3 Mg/day. Emission data were not available for neutralization or deep well injection.

Source Locations

Major EDC producers and production locations are listed in Table 3. In addition, the Chemical Division of Olin Corporation is listed as a producer of EDC by the U.S. International Trade Commission.[14]

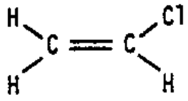
TABLE 3. PRODUCTION OF ETHYLENE DICHL0RIDE[2,5]

Manufacturer	Location
Atlantic Richfield Co.	
ARCO Chem. Co., div.	Port Arthur, TX
Diamond Shamrock	Deer Park, TX
Dow Chem. U.S.A.	Freeport, TX
	Oyster Creek, TX
	Plaquemine, LA
E.I. duPont de Nemours & Co., Inc.	
Conoco inc., subsid.	
Conoco Chems. Co. Div.	Lake Charles, LA
Ethyl Corp.	
Chems. Group	Baton Rouge, LA
	Pasadena, TX
Formosa Plastics Corp., U.S.A.	Baton Rouge, LA
	Point Comfort, TX
Georgia-Pacific Corp.	
Chem. Div.	Plaquemine, LA
The BF Goodrich Co.	
BF Goodrich Chem. Group	La Porte, TX
	Calvert City, KY
	Convent, LA
PPG indust., Inc.	
Indust. Chem. Div.	Lake Charles, LA
Shell Chem. Co.	Deer Park, TX
Union Carbide Corp.	
Ethylene Oxide Derivatives Div.	Taft, LA
	Texas City, TX
Vulcan Materials Co.	
Vulcan Chems., div.	Geismar, LA

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

VINYL CHLORIDE MONOMER PRODUCTION

Vinyl chloride monomer (VCM) Is produced domestically by the dehydrochlorination of ethylene dichloride (EDC). It is used primarily in the production of polyvinyl chloride (PVC). Vinyl chloride has the following structure:



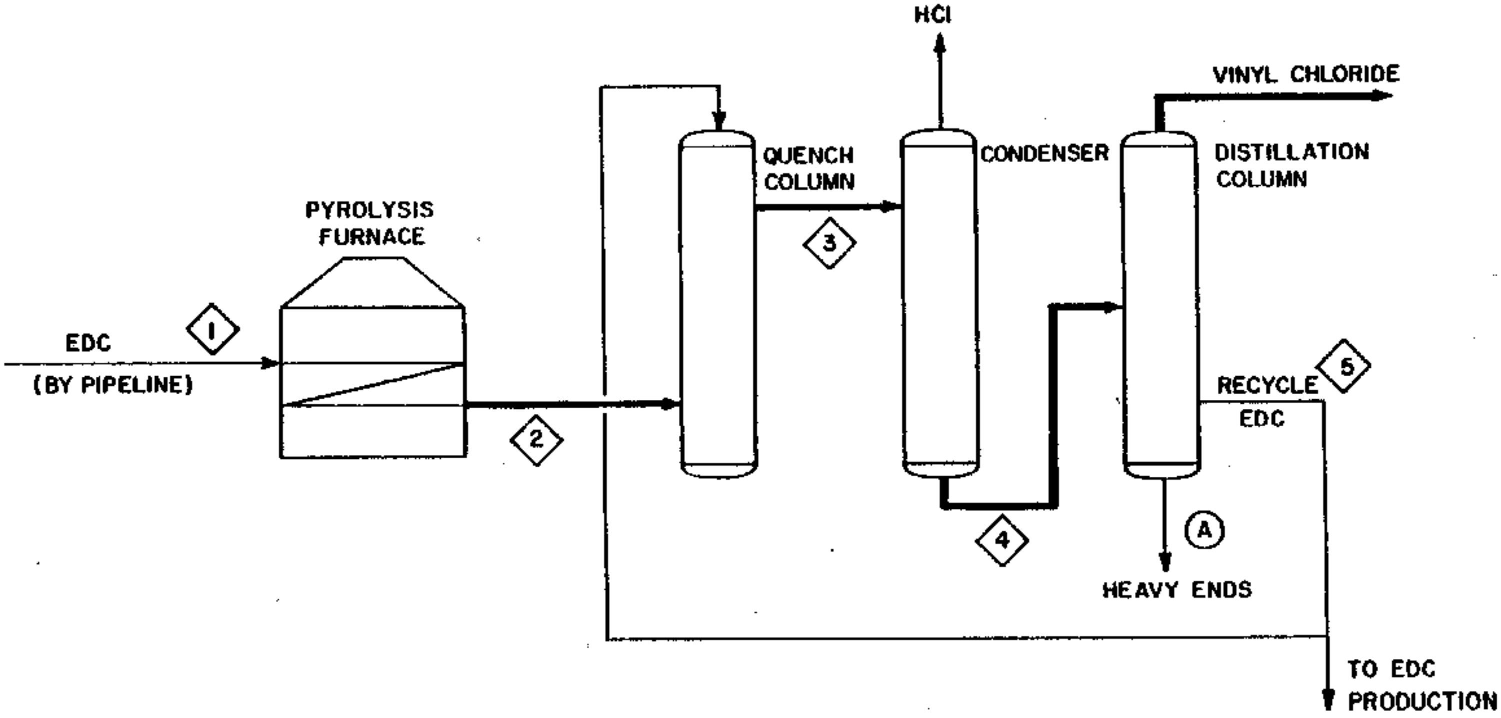
Process Description

A typical flow diagram for EDC dehydrochlorination is shown in Figure 4. Ethylene dichloride (Stream 1) is introduced into the pyrolysis furnace where it is cracked in the vapor phase at temperatures of 450 to 620°C and pressures of 450 to 930 kPa. About 50 percent conversion of EDC to VCM is achieved in the reaction.[15]

The product gas stream from the furnace (Stream 2), containing VCM, EDC, and HCl is quenched with liquid EDC, and fed to a condenser. Hydrogen chloride is removed from the condenser in the gas phase, and is recovered for use on site, generally in EDC production. The liquid stream from the condenser (Stream 4) is fed to a distillation column, where it is separated into VCM product, unreacted EDC, and heavy ends. The unreacted EDC (Stream 5) is recycled either to the quench column or to the finishing section of an EDC plant (generally onsite). Vinyl chloride product is used either on-site or sold, and heavy ends are incinerated.[15]

Emissions

In the EDC dehydrochlorination process, losses of EDC to the environment can occur in the heavy ends from the vinyl chloride separation unit (Source A in Figure 4). Uncontrolled EDC emissions from the heavy ends stream are reported as 0.6 - 0.8 kg/Mg.[2,15]



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 4. Basic operations that may be used for vinyl chloride production by ethylene dichloride dehydrochlorination.[15]

The heavy ends usually are incinerated along with other solid wastes generated by the VCM manufacturing process. Assuming that a removal efficiency of at least 98 percent is achieved by incineration,12 the controlled emission factor for EDC would be $\leq$0.016 kg of EDC per Mg of vinyl chloride produced. Fugitive and process vent emissions of EDC from VCM production are expected to be minor because of control measures which are taken to prevent emissions of vinyl chloride.[15]

VCM production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm technology at a particular facility prior to estimating emissions therefrom.

Source Locations

A list of vinyl chloride production facilities, and locations is presented in Table 4.

TABLE 4. PRODUCTION OF VINYL CHLORIDE MONOMER[2,5]

Manufacturer	Location
Borden inc. Borden Chem. Div. Petrochems. Div.	Geismar, LA
Dow Chem. U.S.A.	Oyster Creek, TX Plaquemine, LA
E.I. duPont de Nemours & Co., Inc. Conoco inc., subsid. Conoco Chems. Co. Div.	Lake Charles, LA
Ethyl Corp. Chems. Group	Baton Rouge, LA
Formosa Plastics Corp. U.S.A.	Baton Rouge, LA Point Comfort, TX
Georgia-Pacific Corp. Chem. Div.	Plaquemine, LA
The BF Goodrich Co. BF Goodrich Chem. Group	Calvert City, KY La Porte, TX
PPG indust., Inc. Chems. Group Chem. Division-U.S.	Lake Charles, LA
Shell Chem. Co.	Deer Park, `TX

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

METHYL CHLOROFORM PRODUCTION

Methyl chloroform (Cl_3C-CH_3), also known as 1,1,1-trichloroethane, is used predominantly as a metal-cleaning solvent.16 It is produced in the United States by three processes. It has been estimated that about 60 percent of the methyl chloroform produced in the U.S. Is derived from vinyl chloride and about 30 percent is made from vinylidene chloride. The remaining 10 percent of methyl chlorform produced is derived from ethane.[17] Because Because there are no documented EDC emissions from the production of methyl chloroform from ethane, this process is not discussed in this section.

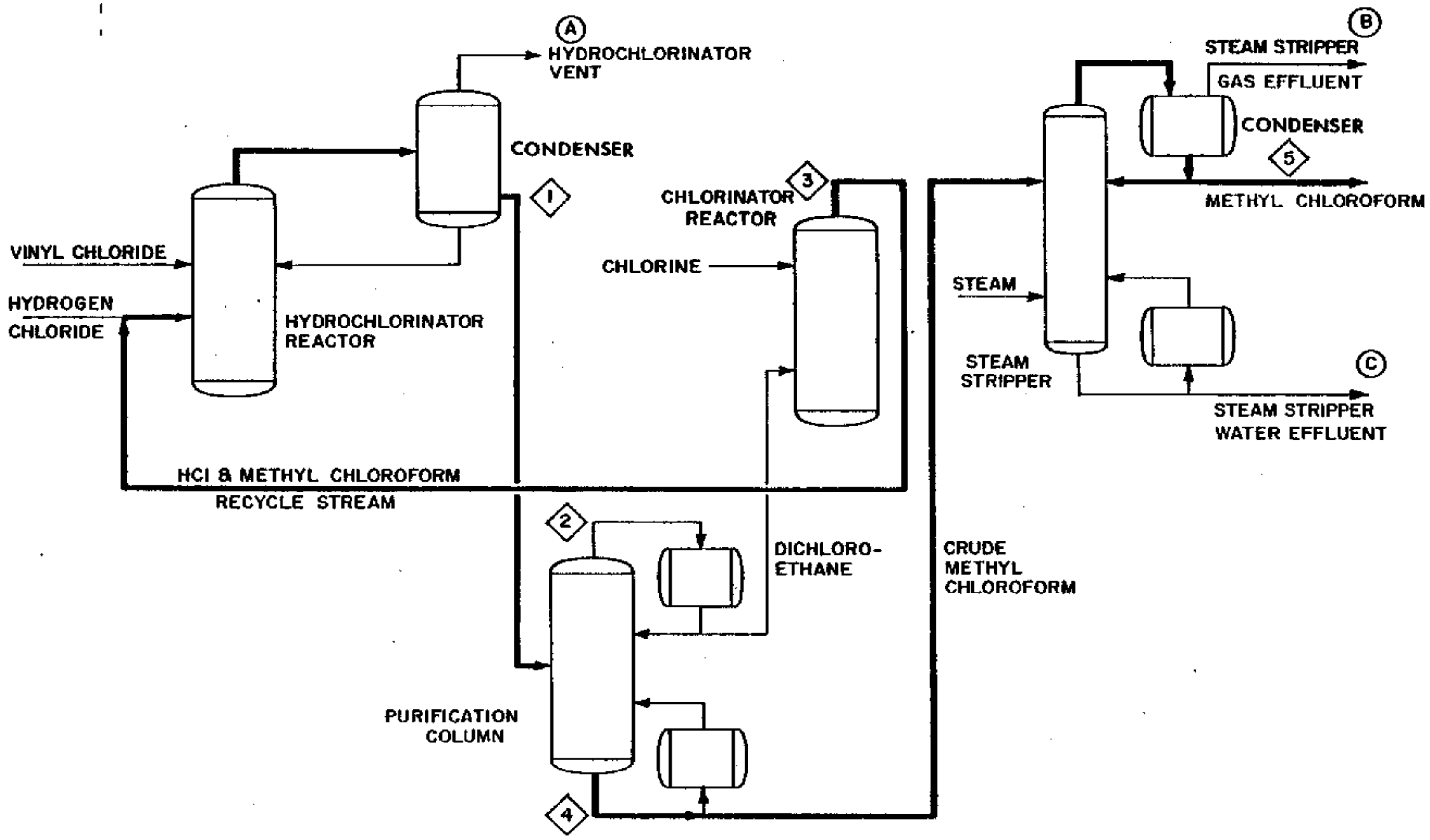
Methyl chloroform may be produced from vinyl chloride by a two-step process involving the hydrochlorination of vinyl chloride to form 1,1-dichloroethane and the thermal chlorination of this intermediate to produce methyl chloroform. In the vinylidene chloride process, vinylidene chloride is hydrochlorinated in the presence of a catalyst to form methyl chloroform.[18]

Process Description

Vinyl Chloride Hydrochlorination/1,1-Dichloroethane Chlorination Process----

Basic operations that may be used for production of methyl chloroform from vinyl chloride are presented in Figure 5. Vinyl chloride, hydrogen chloride (HCl), recycled methyl chloroform, and ferric copper catalyst are combined in a tower-type reactor. In the reactor, a hydrochlorination reaction between vinyl chloride and HCl takes place at temperatures of 35 to 40°C, producing 1,1-dichloroethane.[18]

After being cooled in a condenser, the reaction products (Stream 1) are fed to a purification column. The dichloroethane fraction is removed as an overhead stream (Stream 2) from the column, and fed to a chlorination reactor. There, the dichloroethane is reacted with chlorine gas at atmospheric pressure and about 400°C to produce methyl chloroform and byproduct hydrogen- chloride. The entire product stream from the chlorination reactor, containing methyl chloroform, HCl, and a small amount of unreacted 1,1-dichloroethane, is recycled to the hydrochlorinator reactor (Stream 3).[18]



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 5. Basic operations that may be used for methyl chloroform production by the vinyl chloride hydrochlorination/1,1-dichloroethane chlorination process.[18]

The recycled methyl chloroform is removed in the purification column as a high boiling fraction (Stream 4), and is sent to a stripper column where it is steam-stripped and distilled to yield a purified product (Stream 5). The product yield is over 95 percent.[18] One company reports that it does not use a steam stripper, eliminating Vent B and vent C, but has a solids dump (not shown in Figure 5) from the hydrochlorinator filter.[2]

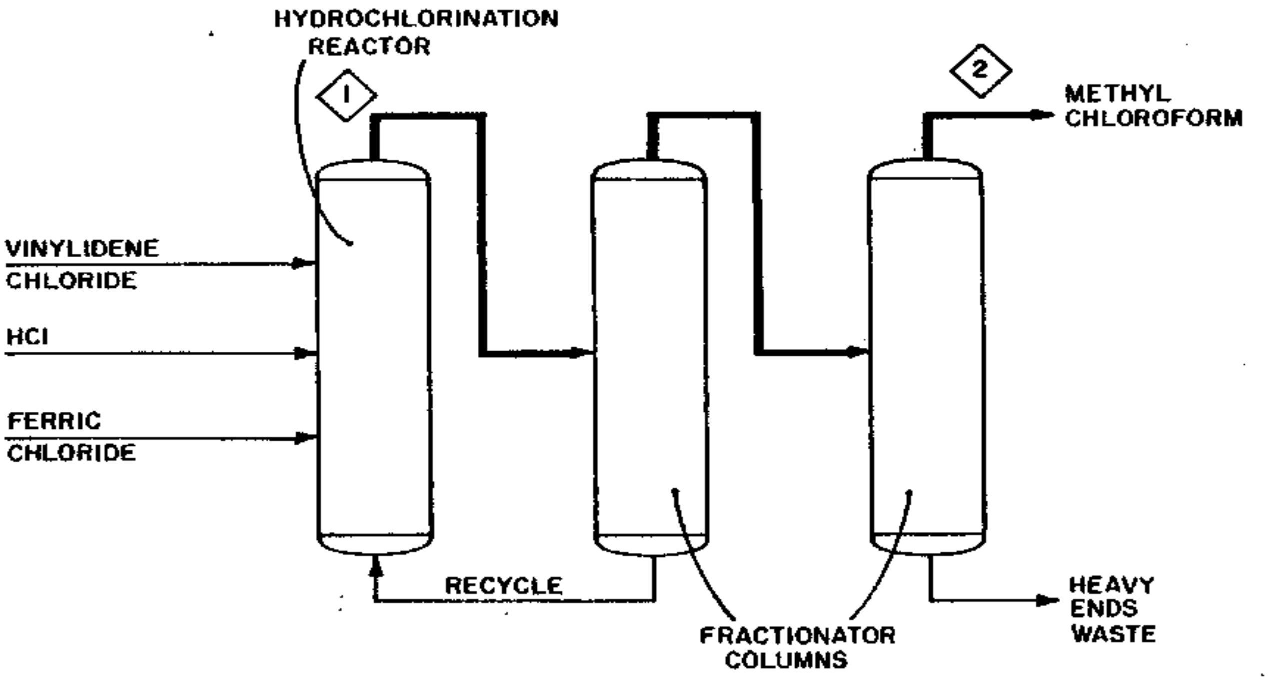
Vinylidene Chloride Hydrochlorination Process--

Figure 6 shows basic operations that may be used for the production of methyl chloroform from vinylldene chloride. Vlnylidene chloride, hydrochloric acid, and small quantity of ferric chloride catalyst are fed to the hydrochlorination reactor. The reaction is conducted in the liquid phase at 25 to 35°C. Crude methyl chloroform product is withdrawn continuously from the hydrochlorinatlon reactor (Stream 1) and purified by fractional distillation. The purified product (Stream 2) is treated to remove moisture and is combined with appropriate stabllizers to make the material suitable for commercial use. The yield of product is over 98 percent.[18]

Emissions

Figure 5 shows possible sources of gas and liquid wastes (Sources A, B, and C) for the methyl chloroform production process from the vinyl chloride method. The two major sources of EDC emissions to the atmosphere from the vinyl chloride method are: (1) the hydrochlorinator vent (Vent A), and (2) the steam stripper gas effluent vent (Vent B). The emissions of EDC may result from the presence of EDC as an impurity in vinyl chloride or the production of EDC in the hydrochlorination and chlorination reactions. The emission factors for EDC emissions from the hydroctilorinator vent condenser and the steam stripper vent condenser are 8.5 kg/Mg and 0.5 kg/Mg, respectively.[17] The emission factors refer to kg of EDC emitted per Mg of methyl chloroform produced.

One methyl chloroform producer is reported to incinerate gases in the hydrochlorinator vent.[2] This would reduce EDC losses by at least 98 percent,12 resulting in an emission rate of $\leq$0.17 kg/Mg, and in some facilities below 0.001 kg/Mg.[2] No information was available on techniques used by industry to control emissions from the stream stripper gas vent.



NOTE: The numbers in this figure refer to process streams, as discussed in the text. The heavy lines represent final product streams through the process.

Figure 6. Basic operations that may be used for methyl chloroform production by the vinylidene chloride hydrochlorination process.[18]

Information on EDC emissions from the vinylidene chloride-based production process of methyl chloroform is not available. It is thought that EDC may be present in the heavy ends waste stream and the aqueous effluent waste stream discharged by the vinylidene chloride-based process.[17] Data are not currently available to quantify atmospheric discharges from the handling of these waste streams.

Methyl chloroform production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

A list of methyl chloroform production facilities and locations is presented in Table 5. Manufacturing processes used in each of the facilities are not listed in the available literature.

TABLE 5. PRODUCTION OF METHYL CHLOROFORM[2,5]

Manufacturer	Location
Dow Chem U.S.A.	Freeport, TX
PPG indust., Inc. Indust. Chem. Div.	Lake Charles, LA
Vulcan Materials Co Vulcan Chems., Div.	Geismar, LA

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

ETHYLENEAMINES PRODUCTION

Ethyleneamines are used in the production of carbamate fungicides, chelating agents, dimethylethylene urea resins, and diaminoethylethanol.[19]

Process Description

The only reported process used in the production of ethyleneamines is shown in Figure 7. Ethyleneamines may be produced by reacting EDC with ammonia in either the liquid phase or the vapor phase. The major product of both of these reactions is ethylenediamlne. Byproducts of the reactions include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and higher polymers.[20]

In the vapor phase reaction, EDC and an excess of anhydrous ammonia are reacted at 150°C and 9.0 MPa. Anhydrous ethylenediamine hydrochloride is formed, which, on treatment with caustic soda at 100°C, yields free ethylenedlamine ($NH_2CH_2CH_2NH_2$). Ethylenediamine vapors, steam, and unreacted ammonia are fed to a dehydrating column (not shown) where the diamine is dried and condensed.[20]

In the liquid phase process, EDC is treated with excess aqueous ammonia at 100°C and 1.0 MPa. The aqueous product solution containing ethylenediamine hydrochloride, ammonium chloride, and ammonia is heated with caustic soda and fractionated. The ethylenediamine is drawn off and the ammonium chloride is recycled to the reaction vessel.[20]

The ethyleneamines are separated into a number of marketable products, the composition of which varies from producer to producer.[10]

Emissions

Reactor pressure vents, dehydration columns, and fractionating (distillation) columns are possible sources of unreacted EDC emissions. Waste water streams from dehydrochlorination and drying operations may contain quantities of unreacted EDC.[20]

Emissions of EDC from ethyleneamine production facilities using typical controls have been estimated at 600 Megagrams for 1976.[19] Typical control techniques used by industry in the production of ethyleneamines are not

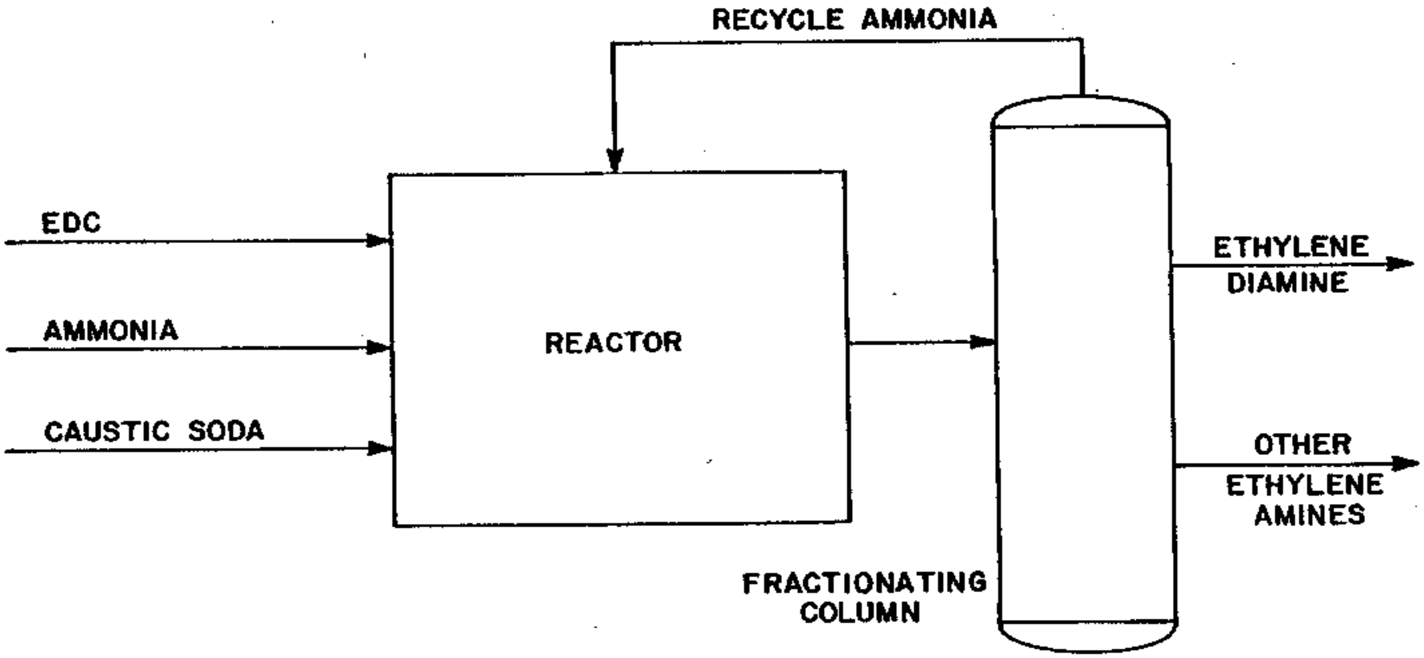


Figure 7. Basic operations that may be used in the production of ethyleneamines.[19]

discussed in the published literature. The total production of ethyleneamines in 1976 was estimated at a level of 66,012 Megagrams.[19] From these two values, average EDC emissions per unit ethyleneamine production are estimated at 9.09 kg per Mg. Data are not available on the derivation of the total nationwide emissions estimates, nor are data available to break down EDC emissions between specific sources.

Ethyleneamine production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

A list of major ethyleneamine production facilities and locations is presented in Table 6.

TABLE 6. PRODUCTION OF ETHYLENEAMINES[a,b] [2,5]

Manufacturer	Location
Dow Chem. U.S.A.	Freeport, TX
Union Carbide Corp. Ethylene Oxide Derivatives Div.	Taft, LA

[a] Ethylenediamine is the principal product, although a mixture of various ethyleneamines is obtained.

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

TRICHLOROETHYLENE PRODUCTION

Trichloroethylene (TCE) is used primarily as a metal-cleaning solvent and is produced domestically by either chlorination or oxychlorination of EDC or other chlorinated ethanes. Trichloroethylene, $Cl_2C{=}CHCl$, can be produced separately or as a coproduct of perchloroethylene (PCE), $Cl_2C{=}CCl_2$, by varying raw material ratios.[21]

TCE was once manufactured predominantly by the chlorination of acetylene. However, because of a decrease in the supply of acetylene, EDC chlorination became the preferred method for producing TCE. The last acetylene-based TCE plant was shut down in late 1977.[22]

Process Description

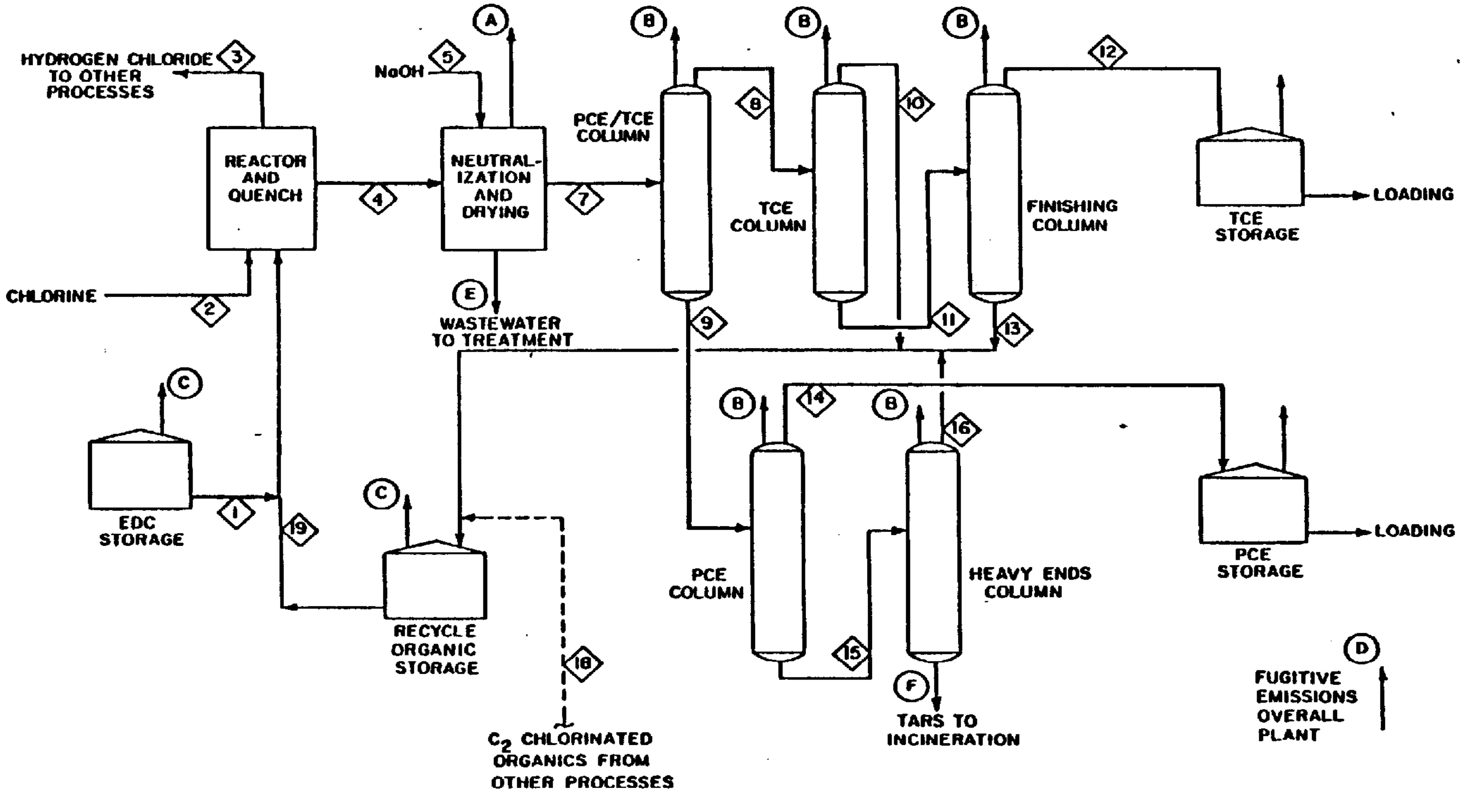
Ethylene Dichloride Chlorination Process--

The major products of the EDC chlorination process are TCE, PCE, and hydrogen chloride (HCl). Basic operations that may be used in the production of TCE and PCE by EDC chlorination are shown in Figure 8.

EDC (Stream 1) and chlorine (Stream 2) vapors are fed to a chlorination reactor. The chlorination is carried out at a high temperature (400 to 450°C), slightly above atmospheric pressure, without the use of a catalyst. Other chlorinated C_2 hydrocarbons or recycled chlorinated hydrocarbon byproducts may be fed to the chlorinator.[21]

The product stream from the chlorination reaction consists of a mixture of chlorinated hydrocarbons and HCl. Hydrogen chloride (Stream 3) is separated from the chlorinated hydrocarbon mixture (Stream 4) and used in other processes. The chlorinated hydrocarbon mixture (Stream 4) is neutralized with sodium hydroxide solution (Stream 5) and is then dried. Spent caustic is transferred to a wastewater treatment plant.[21]

The dried crude product (Stream 7) is separated by a PCE/TCE column into crude TCE (Stream 8) and crude PCE (Stream 9). The crude TCE (Stream 8) is fed to a TCE column, where light ends (Stream 10) are removed overhead. Bottoms from this column (Stream 11), containing TCE and heavies, are sent to the finishing column, where TCE (Stream 12) is removed overhead and sent to TCE storage. Heavy ends (Stream 13) are combined with light ends (Stream 10) from the TCE column and stored for eventual recycling.[21]



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

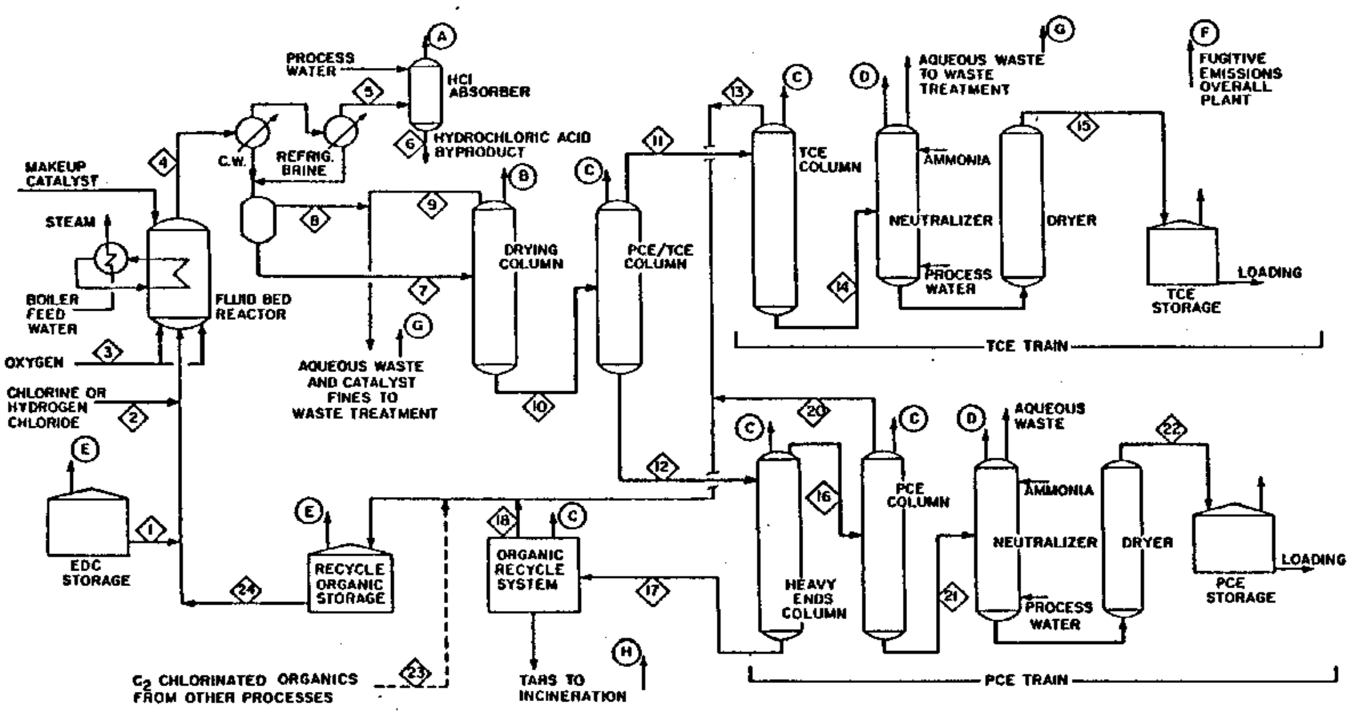
Figure 8. Basic operations that may be used for trichloroethylene (TCE) and perchloroethylene (PCE) production by ethylene dichloride chlorination.[21]

The crude PCE (Stream 9) from the PCE/TCE column is fed to a PCE column, where PCE (Stream 14) goes overhead to PCE storage. Bottoms from this column (Stream 15) are fed to a heavy ends column. Overheads from the heavy ends column (Stream 16) are recycled and bottoms, consisting of tars, are incinerated.[21] These bottoms, called "hex wastes", may be processed further or heated to recover more volatilizable materials, with the resulting tars sent to disposal, often by incineration. This additional step recovers 80 to 90 percent of the bottoms.[10]

Ethylene Dichloride Oxychlorination Process--

The major products of the EDC oxychlorlnation process are TCE, PCE, and water. Side reactions produce carbon dioxide, hydrogen chloride (HCl), and several chlorinated hydrocarbons. Figure 9 shows basic operations that may be used for EDC oxychlorination. The crude product contains 85 to 90 weight percent PCE plus TCE and 10 to 15 weight percent byproduct organics. Essentially all byproduct organics are recovered during purification and are recycled to the reactor. The process is very flexible, so that the reaction can be directed toward the production of either PCE or TCE in varying proportions.[21]

EDC (Stream 1), chlorine or hydrogen chloride (Stream 2), oxygen (Stream 3) and recycled byproducts are fed to a fluid-bed reactor in the gas phase. The reactor contains a vertical bundle of tubes with boiling liquid outside the tubes to maintain the reaction temperature at about 425°C. The reaction takes place at pressures slightly above atmospheric. Copper chloride catalyst is added continuously to the tube bundle. The reactor product (Stream 4) is fed to a water-cooled condenser and then a refrigerated condenser. Condensed material and catalyst fines drain to a decanter. The noncondensed inert gases (Stream 5), consisting of carbon dioxide, hydrogen chloride, nitrogen, and a small amount of uncondensed chlorinated hydrocarbons, are fed to a hydrogen chloride absorber, where HCl is recovered by absorption in process water to make byproduct hydrochloric acid. The remaining inert gases are purged (Vent A).[21]



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 9. Basic operations that may be used for trichloroethylene (TCE) and perchloroethylene (PCE) production by ethylene dichloride oxychlorination.

In the decanter the crude product (Stream 7) Is separated from an aqueous phase. The aqueous phase, containing catalyst fines (Stream 8), is sent to a waste treatment plant (G). Crude product is fed to a drying column where dissolved water is removed by azeotropic distillation. The water (Stream 9) from the drying column is sent to the waste treatment plant (G) and the dried crude product (Stream 10) is separated into crude TCE (Stream 11) and crude PCE (Stream 12) in a PCE/TCE column.[21]

Crude TCE (Stream 11) is sent to a TCE column, where the light ends (Stream 13) are removed overhead and stored for recycle. The bottoms (Stream 14) are neutralized with ammonia and then dried to produce finished TCE (Stream 15), which is sent to storage.[21]

The crude PCE (Stream 12) from the PCE/TCE is fed to a heavy ends column where PCE and light ends (Stream 16) are removed overhead. Heavy ends (Stream 17), called "hex wastes," are sent to an organic recycle system, where the organics that can be recycled (Stream 18) are separated from tars, which are incinerated. The PCE and light ends (Stream 16) from the heavies column are fed to a PCE column, where the light ends (Stream 20) are removed overhead and sent to the recycle organic storage tank. The PCE bottoms (Stream 21) are neutralized with ammonia and then dried to produce finished PCE (Stream 22) which is sent to storage.[21]

Emissions

Potential sources of EDC process emissions for the EDC chlorination process (Figure 8) are the neutralization and drying area vent (Vent A), which releases inert gases from the chlorine and EDC feeds, and the distillation column vents (Vents B), which release noncondensable gases. Storage emission sources (Vents C) include raw material storage and recycle storage. Fugitive emissions (D) occur when leaks develop in valves or in pump seals. When process pressures are higher than the cooling-water pressure, VOCs can leak into the cooling water and escape as fugitive emissions from the quench area. Secondary emissions can occur when wastewater containing VOCs is sent to a wastewater treatment system or lagoon and the VOCs evaporate (E). Another source of secondary emissions is the combustion of tars in the incinerator where VOCs are emitted with the flue gases (F).[21]

In the EDC oxychlorination process (Figure 9), the hydrogen chloride asbsorber vent (Vent A), which releases the inert gases from the oxygen, chlorine, and hydrogen chloride feeds, is a potential source of EDC process emissions. Other potential sources of EDC process emissions are the dr.ying column vent (Vent B) and the distillation column vents (Vent C), which release primarily noncondensable gases, and the TCE and the PCE neutralizer vents (Vent D), which relieve excess pressure of the nitrogen pads on the systems. Storage emission sources (Vent E) are raw material storage and recycle storage. Fugitive emissions (F) occur when leaks develop in valves or in pump seals. Secondary emissions (G and H) occur as described above for the chlorination process (see Vent E and Vent F in Figure 8).[21]

Atmospheric emissions of EDC in 1977 from the TCE production processes were estimated at 610 Mg.[23] The total domestic production of TCE in 1977 was estimated at 135,000 Mg, of which 90 percent was from EDC.[23] The emission factor for the controlled EDC emissions from the production of TCE can be calculated by dividing the EDC emissions by 90 percent of the total TCE production quantity. From these values, the controlled emission factor is about 5.0 kg of EDC per Mg of TCE produced. Data are not available on the derivation of the total annual EDC emissions estimate, nor are sufficient data available to break down EDC emissions between various sources. One reference states that EDC emissions for the process as a whole are practically zero when volatiles are recovered from the hex wastes and since EDC conversion is 100 percent in the reactor.[2]

TCE production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

A list of trichloroethylene production facilities and locations is presented in Table 7.

TABLE 7. PRODUCTION OF TRICHLOROETHYLENE[5]

Manufacturer	Location
Dow Chem U.S.A.	Freeport, TX
PPG indust., Inc. Indust. Chem. Div.	Lake Charles, LA

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

PERCHLOROETHYLENE PRODUCTION

Perchloroethylene (PCE) is used primarily as a dry-cleaning and textile-processing solvent. It is also used as a metal-cleaning solvent.[16] PCE is produced domestically by three processes. Two of the processes involve the chlorination and oxychlorination of EDC or other chlorinated hydrocarbons having two carbon atoms. PCE and trichloroethylene (TCE) are manufactured separately or as coproducts by the chlorination or oxychlorination process with the raw material ratios determining the proportions of PCE and TCE.[21] PCE is also manufactured as a coproduct with carbon tetrachloride by the chlorinolysis of hydrocarbons such as propane and propylene.[24]

PCE was once manufactured predominantly by the chlorination of acetylene. However, as acetylene production declined, EDC chlorination and hydrocarbon chlorinolysis became the preferred methods of production. The last acetylene-base PCE plant was shut down in late 1977.[25]

Process Description

Ethylene Dichloride Chlorination Process--

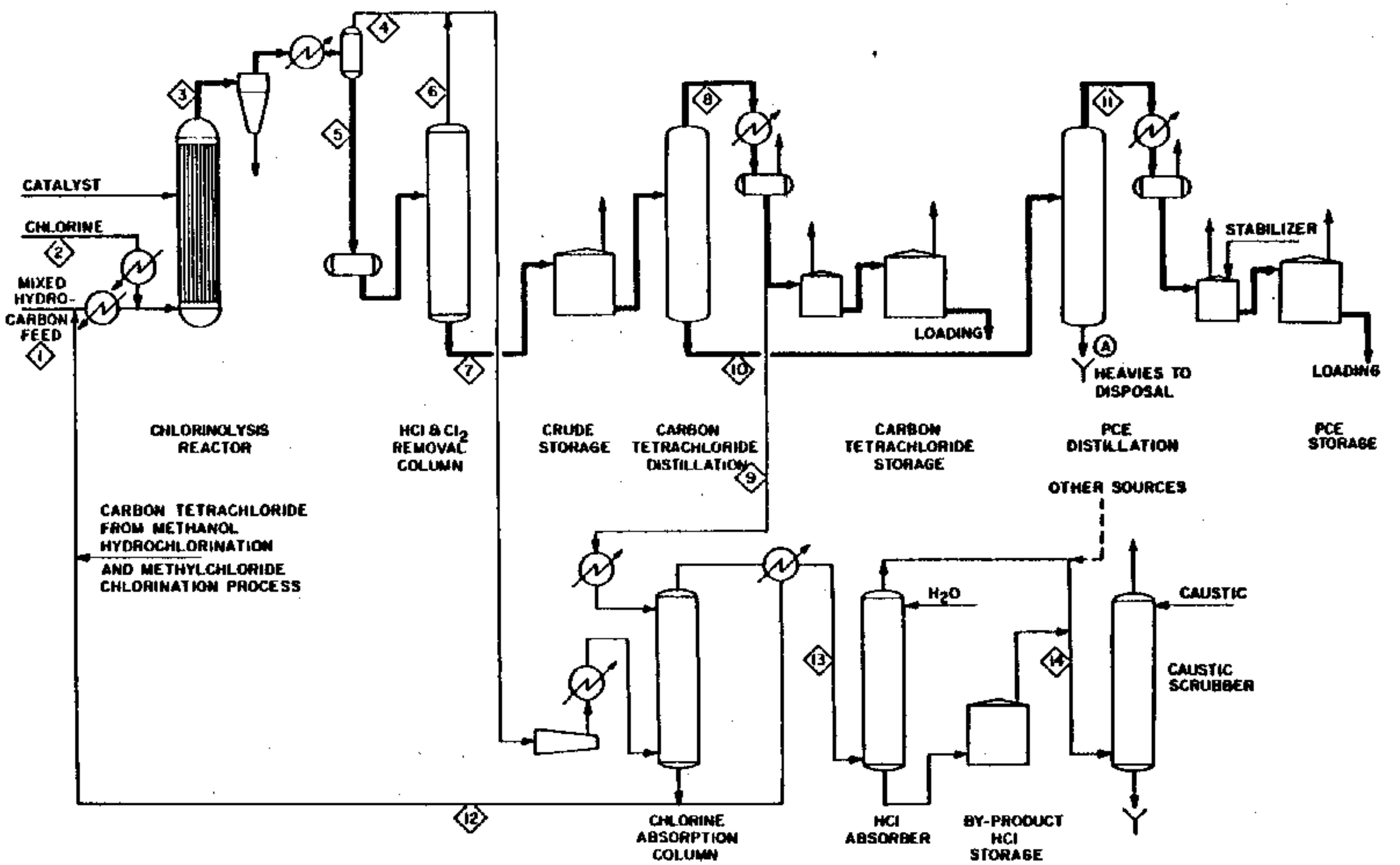
A discussion of the EDC direct chlorination process for producing PCE and TCE is presented in the subsection titled TRICHLOROETHYLENE PRODUCTION.

A discussion of the EDC oxychlorination process for producing PCE and TCE is presented in the subsection titled TRICHLOROETHYLENE PRODUCTION.

Hydrocarbon Chlorinolysis Process--

The major products of the hydrocarbon chlorlnolysis process are PCE, carbon tetrachloride, and hydrogen chloride (HCl). Basic operations that may be used in this process are shown in Figure 10. Preheated hydrocarbon feed material (Stream 1) and chlorine (Stream 2) are fed to a chlorinolysis reactor, which is a fluid-bed reactor maintained at about 500°C.[24]

The reaction products, consisting of carbon tetrachloride, PCE, HCl, and chlorinated hydrocarbon byproducts, (Stream 3) pass through a cyclone for removal of entrained catalyst and then on to a condenser. Uncondensed materials (Stream 4), consisting of hydrogen chloride, unreacted chlorine,



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 10. Basic operations that may be used for the production of perchloroethylene by hydrocarbon chlorinolysis.[24]

and some carbon tetrachloride, are removed to the hydrogen chloride purification system. The condensed material (Stream 5) Is fed to a hydrogen chloride and chlorine removal column, with the overheads (Stream 6) from this column going to hydrogen chloride purification. The bottoms (Stream 7) from the column are fed to a crude storage tank. Material from crude storage is fed to a distillation column, which recovers carbon tetrachloride as overheads (Stream 8). The bottoms (Stream 10) from the carbon tetrachloride distillation column are fed to a PCE distillation column. The overheads (Stream 11) from the PCE distillation column are taken to PCE storage and loading, and the bottoms are incinerated.[24] These bottoms, called "hex wastes," may be processed further or heated to recover more volatilizable materials, with the resulting tars sent to disposal, often by incineration. This additional step recovers 80 to 90 percent of the bottoms.[10]

The feed streams (Stream 4 and Stream 6) to hydrogen chloride purification are compressed, cooled, and scrubbed in a chlorine absorption column with chilled carbon tetrachloride (Stream 9) to remove chlorine. The bottoms and condensable overheads (Stream 12) from this column are combined and recycled to the chlorinolysis reactor. Uncondensed overheads (Stream 13) from the chlorine absorption column are contacted with water to produce a hydrochloric acid solution. This solution is stored for eventual reprocessing and use in a separate facility. Overheads from the absorber and vented gases from byproduct hydrochloric acid storage are combined (Stream 14) and passed through a caustic scrubber for removal of residual hydrogen chloride. Inert gases are vented from the scrubber.[24]

Emissions

Potential emission sources for the EDC chlorination and oxychlorination processes are shown in Figure 8 and Figure 9, respectively, and discussed in the TRICHLOROETHYLENE PRODUCTION subsection. It is estimated that 910 Mg of EDC were released to the atmosphere from the PCE production process in 1977.[26] The majority of these emissions were from EDC oxychlorination and chlorination. The total domestic production of PCE in 1977 was 279,000 Mg, of which 65 percent of PCE production was from EDC.[26] Thus, the nationwide emissions estimate corresponds to a controlled EDC emission factor for EDC chlorination and oxychlorination of about 5.0 kg of EDC per Mg of PCE produced. Data are not available on the derivation of the nationwide annual EDC emissions estimate, nor are sufficient data available to break down EDC emissions between specific emission points. One reference states that EDC emissions for the process as a whole are practically zero when the volatiles are recovered from the hex wastes and since EDC conversion is 100 percent in the reactor.[2]

Potential emission sources for the hydrocarbon chlorinolysis process are shown in Figure 10. Since EDC is not used as a feedstock in this process, as it is in the EDC chlorination and oxychlorination processes, the only emissions of EDC can result from the handling and disposal of hex wastes from the PCE distillation column (Source A in Figure 10). The EDC is produced in the chlorinolysis reaction. The uncontrolled EDC emission factor for the hex waste handling is about 0.026 kg of EDC per Mg of PCE and carbon tetrachloride produced.[27]

Hex wastes may be processed further or heated to recover more volatilizable materials, with the resulting tars sent to disposal. This additional step recovers 80 to 90 percent of the bottoms,[10] and the EDC emissions from the dumping of the hex wastes are essentially zero.[2] Alternatively, a vapor-balance system and refrigerated condenser have been used to control emissions from hex wastes with an emission reduction of approximately 99 percent.[28] Thus, the controlled EDC emission factor for the secondary emissions is 0.00026 kg of EDC per fig of PCE and carbon tetrachloride produced. These EDC emission factors were developed for a hypothetical plant with the capacity to produce 50,000 Mg/yr PCE and 30,000 Mg/yr carbon tetrachloride operating 8760 hours per year.[29]

PCE production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

A list of perchloroethylene production facilities and locations is presented in Table 8.

TABLE 8. PRODUCTION OF PERCHLOROETHYLENE[2,5]

Manufacturer	Location
Diamond Shamrock Corp. Indust. Chems. and Plastics Unit Electro Chems. Div.	Deer Park, TX
Dow Chem. U.S.A.	Pittsburg, CA Plaquemine, LA
E.I. duPont de Nemours & Co., Petrochems. Dept. Freon(R) Products Div.	Corpus Christi, TX
PPG indust., Inc. Indust. Chem. Div.	Lake Charles, LA
Vulcan Materials Co. Vulcan Chems., Div.	Geismar, LA Wichita, KS

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

VINYLIDENE CHLORIDE PRODUCTION

Process Description

Vinylidene chloride, or 1,1-dichloroethene, is used primarily in the production of polyvinylidene copolymers such as Saran® and some modacrylic fibers.16 It is manufactured domestically by a two step process as shown in Figure 11. The first step involves the chlorination or oxychlorination of EDC to produce 1,1,2-trichloroethane. The second step is dehydrochlorination of 1,1,2-trichloroethane to produce vinylidene chloride. Little data are available on the specific steps used in the production of 1,1,2-trichloroethane; however the process used to produce vinylidene chloride from 1,1,2-trichloroethane is described extensively in published literature.[30]

Most 1,1,2-trichloroethane is made by chlorination of EDC. The reaction is carried out in the liquid phase at 120°C and 345 kPa. The major products are hydrogen chloride (HCl) and 1,1,2-trichloroethane. Where 1,1,2-trichloroethane is made by oxychlorination the reactants are EDC, HCl, and oxygen. Reaction conditions vary from one process to another. Water and 1,1,2-trichloroethane are the major products of this reaction.[31] After 1,1,2-trichloroethane is produced, it is dehydrochlorinated with aqueous sodium hydroxide at about 70°C. Major products of the reaction are vinylidene chloride, sodium chloride, and water.[30]

Emissions

The primary source of emissions from the EDC chlorination process are the waste streams from the HCl scrubber. Waste water streams may contain chlorine, HCl, spent caustic, and various chlorohydrocarbons, including EDC, trichloroethane and reaction byproducts. Hydrogen chloride and a number of organic chlorides are probably present in the waste gas.[31]

Emissions from the EDC oxychlorination process originate from waste water and vent gases from the separator which contain a number of chlorohydrocarbons, including EDC, trichloroethane, and byproducts. Scrubbing of the crude product to remove unreacted acid is another source of waste water which may contain EDC.[31]

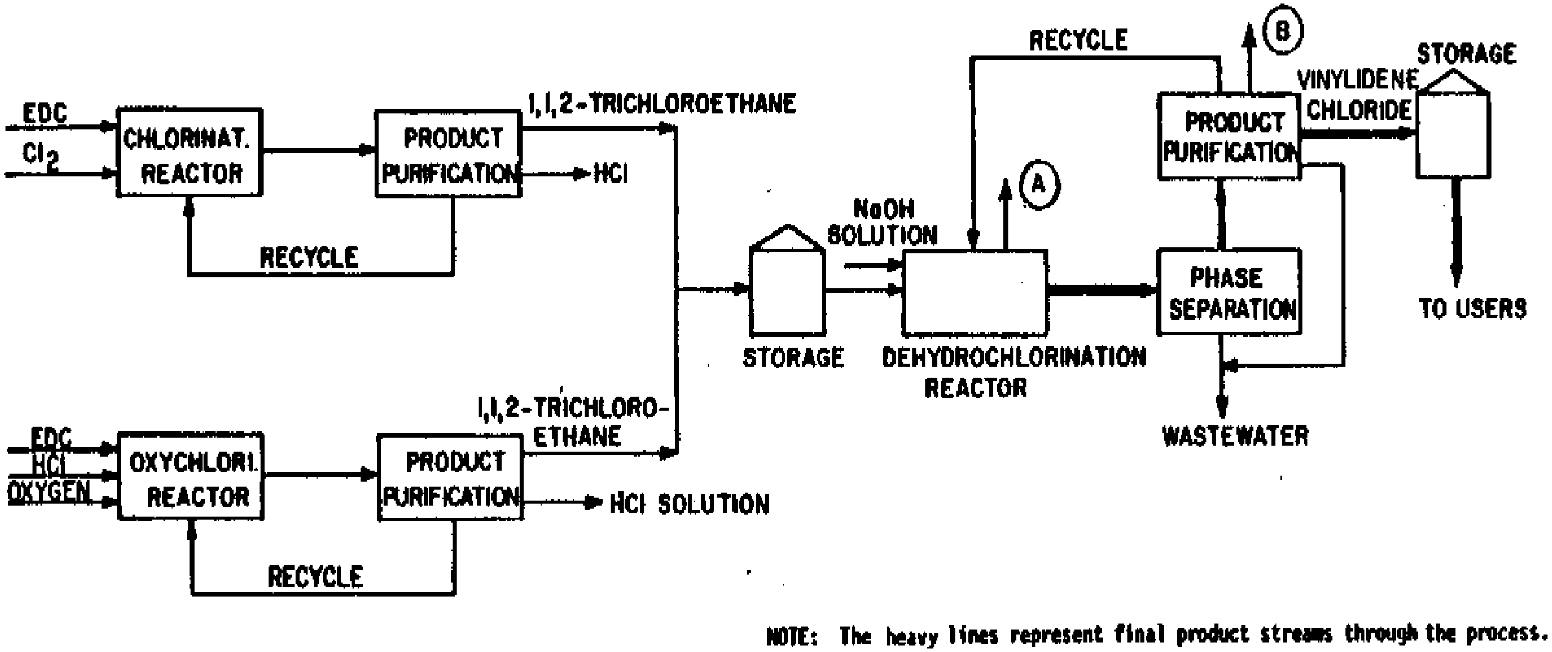


Figure 11. Basic operations that may be used for the production of vinylidene chloride.[30,31]

Potential sources of EDC emissions for the dehydrochlorination of 1,1,2-trichloroethane are the dehydrochlorination reactor purge vent (A in Figure 11) and the distillation column vents (B), which release noncondensable gases. Secondary EDC emissions can occur from desorption of VOCs during wastewater treatment.[30]

It is estimated that 600,000 kg of EDC were released to the atmosphere from the production of vinylidene chloride in 1977.[32] The total U.S. production of vinylidene chloride in 1977 was estimated at 105,000 Mg.32 From these values, the controlled EDC emission factor for vinylidene chloride production is calculated to be 5.7 kg of EDC per Mg of vinylidene chloride produced. Data are not available on the derivation of the annual EDC emissions estimate for vinylidene chloride production, nor are sufficient data available to break down EDC emissions between specific emission points.

Vinylidene chloride production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

Major vinylidene chloride production facilities and their locations are listed below.[5]

• Dow Chemicals U.S.A.	Freeport, TX Plaquemine, LA
• PPG industries, Inc. Industrial Chemicals Div.	Lake Charles, LA

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

ETHYL CHLORIDE PRODUCTION

About 90 to 95 percent of ethyl chloride produced domestically is manufactured by the hydrochlorination of ethylene. This reaction takes place in the presence of EDC and a catalyst such as aluminum chloride. Ethyl chloride is also produced by the thermal chlorination of ethane or by a combination of ethane chlorination and ethylene hydrochlorination. EDC is a by-product of ethyl chloride production by both of these processes.[33]

Process Description

Basic operations that may be used in the production of ethyl chloride by the hydrochlorination of ethylene are presented in Figure 12. Ethylene gas and hydrogen chloride are mixed in equimolar proportions before being fed to a reactor which contains EDC or a mixture of EDC and ethyl chloride. Hydrochlorination of ethylene occurs in the presence of an aluminum chloride catalyst. The gaseous reaction products are charged to a separation column or flash drum to remove heavy polymer bottoms and then to a fractionation column for final product purification.[34]

Emissions

There is little information available in the published literature on EDC emissions from ethyl chloride production. Emissions may occur from process air vents. EDC emissions from ethyl chloride production via ethylene hydrochlorination were estimated to be 2313 x 10^3 kg in 1978.[35] From this total emission estimate and the level of ethyl chloride production for 1978 (244,800 Mg),[36] the EDC emission factor for ethyl chloride production was calculated to be 9.45 kg/Mg.

Ethyl chloride production plants may vary in configuration and level of control. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

Major ethyl chloride producers and locations are listed in Table 9.

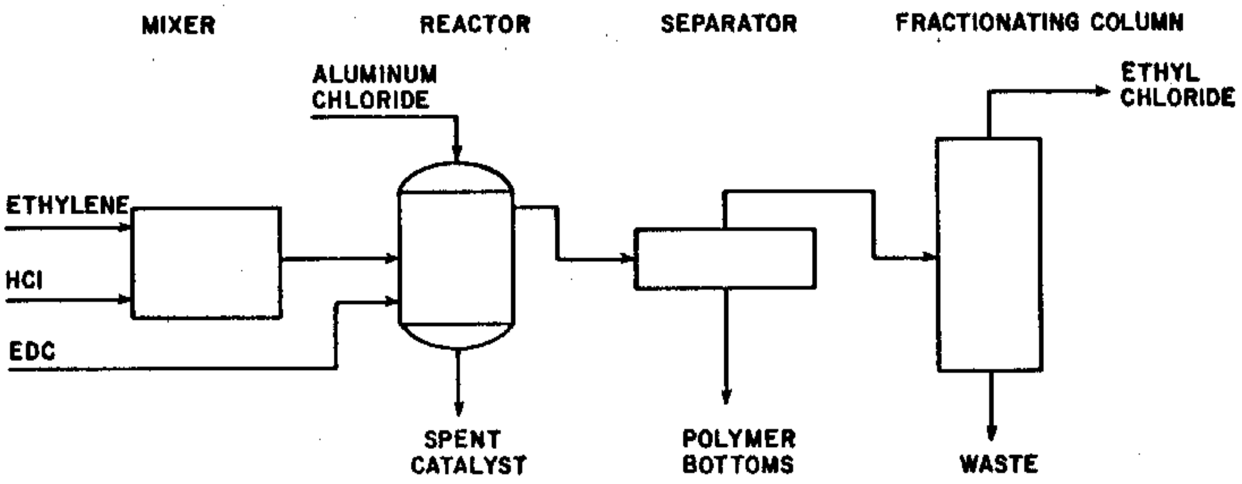


Figure 12. Basic operations that may be used in the production of ethyl chloride by ethlene hydrochlorination.[34]

TABLE 9. PRODUCTION OF ETHYL CHLORIDE5

Manufacturer	Location	Process
Dow Chem. U.S.A.	Freeport, TX	Hydrochlorination of ethylene
E.I. duPont de Nemours & Co., Inc. Petrochems. Dept. Freon(R) Products Div.	Deepwater, NJ	Hydrochlorination of ethylene
Ethyl Corp. Chems. Group	Pasadena, TX	Hydrochlorination of ethylene
Hercules inc. Operations Div.	Hopewell, VA	Hydrochlorinaiion of ethylene
PPG indust., Inc. Indust. Chem. Div.	Lake Charles, LA	Hydrochlorination of ethylene

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

POLYSULFIDE RUBBER PRODUCTION

Process Description

Polysulfide rubber is a synthetic rubber polymer which is used in the manufacture of caulking putties, cements, sealants, and rocket-fuel. It is produced by the reaction between aliphatic halides, such as EDC, and alkali polysulfides such as Na_2S_4. The main products of the reaction are the polysulfide rubber chain, $(CH_2CH_2\text{-}S_4)_n$, and sodium chloride.[37]

Emissions

Based on yields for similar industrial chemical reactions it has been estimated that 94 percent of the EDC used during the manufacturing of polysufide rubber becomes incorporated in the end product.[37] It is estimated that 5 percent of the EDC used in the process is released to the atmosphere via leaks, spills and fugitive emissions associated with the overall polysulfide manufacturing process. The remaining 1 percent of EDC remains dissolved in the mother liquor from which the polymer is produced. The mother liquor may be discharged as solid waste and stored in landfills.[37]

From the stoichiometry of the polysulfide production reaction and the percentages of EDC consumed and emitted,[37] the average controlled EDC emission factor for polysulfide rubber manufacture is 33.8 kg of EDC per Mg of polysulfide rubber produced.

Source Locations

The Specialty Chemicals Division of Morton Thikol incorporated in Moss Point, Mississippi, is currently listed as the only producer of polysulfide rubber by the SRI Directory of Chemical Producers for 1983.[5] This information is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of this or other facilities by consulting current listings and/or the plants themselves. The level of EDC emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

LIQUID PESTICIDE FORMULATION

Ethylene dichloride is used in a number of liquid pesticide formulations. These formulations generally are mixtures of EDC and other active ingredients such as carbon tetrachloride and carbon disulfide.[38]

Process Description

Pesticide formulation systems are typically batch mixing operations. A typical liquid pesticide formulation unit is presented in Figure 13. Technical grade pesticide is usually stored in its original shipping container in the warehouse section of the plant until it is needed. If the material is received in bulk, it is transferred to holding tanks for storage. Solvents are normally stored in bulk tanks.

Batch mixing tanks are typically closed vessels. The components of the formulation are fed into the tank, measured by weight, and mixed by circulation with a tank pump.[2] The formulated material is then pumped to a holding tank before being put into containers for shipment.

The blend tank is vented to the atmosphere through a vent dryer, which prevents moisture from entering the tank.[2] Storage and holding tanks and container-filling lines may be provided with an exhaust connection or hood to remove any vapors. The exhaust from the system may be vented to a control device or directly to the atmosphere.[39]

Emissions

Sources of EDC emissions from pesticide formulation include storage vessels, mixing vessel vents, and leaks from pumps, valves, and flanges. insufficient information is available for the development of EDC emission factors for liquid pesticide formulation facilities.

Source Locations

Registrants and applicants for registration of pesticide products containing EDC are listed in Table 10. Some of the listed companies may buy a preformulated or prepackaged product from larger producers and, therefore, may not be actual sources of emissions. In addition, this list may change as facility ownership changes or plants are closed down.

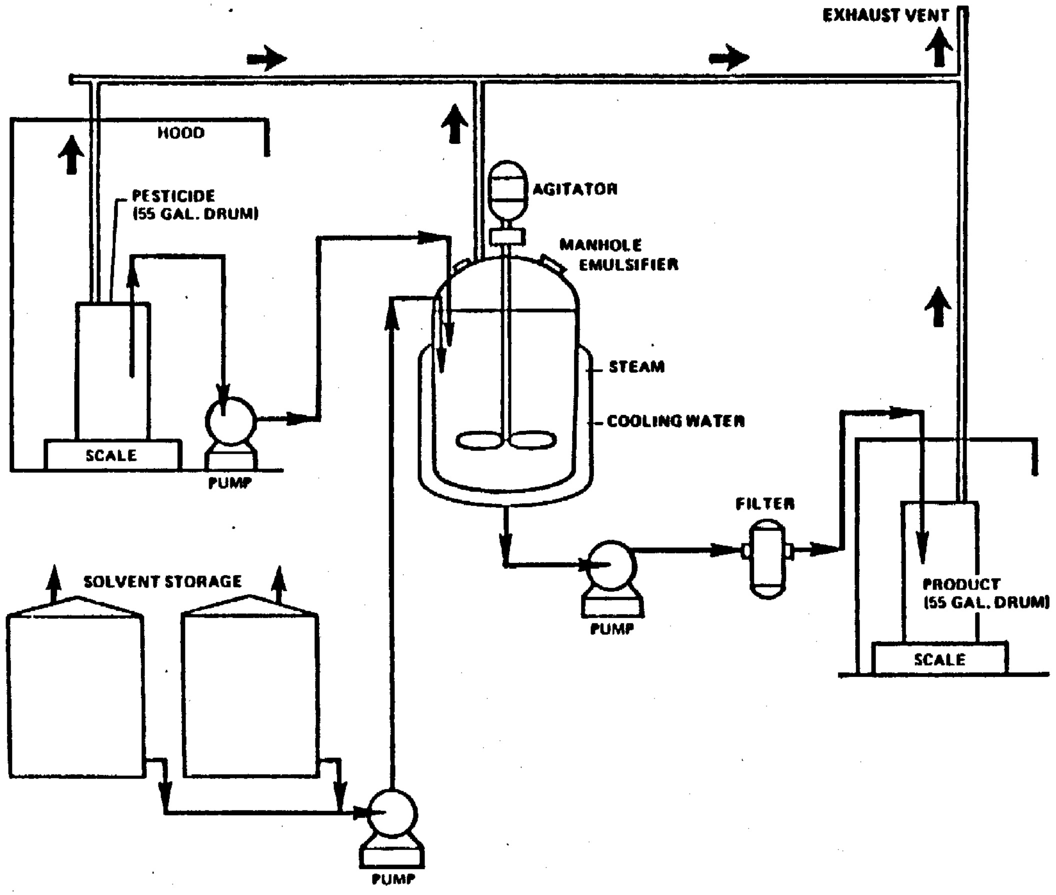


Figure 13. Basic operations that may be used for liquid pesticide formulation.[39]

TABLE 10. COMPANIES WHICH HOLD REGISTRATIONS ON PESTICIDE FORMULATIONS CONTAINING ETHYLENE DICHLORIDE[40]

Company	Location
Southland Pearson & Co.	Mobile, AL
Vulcan Materials Co.	Birmingham, AL
Cardinal Chemical Co.	San Francisco, CA
Cooke Laboratory Products	Commerce, CA
Coyne Chemical Co.	Los Angeles, CA
Dexol industries	Torrance, CA
Hacienda Enterprises	San Jose, CA
Hockwaldchem, Division of Oxford Chemicals	Brisbane, CA
James Chem Co.	San Francisco, CA
Master Nurseymens Assn.	Concord, CA
Dettelbach Chemicals Corp.	Atlanta, GA
Hill Manufacturing, Inc.	Atlanta, GA
Lester Laboratories	Atlanta, GA
Oxford Chemicals	Atlanta, GA
The Selig Chemical industries	Atlanta, GA
Stephenson Chemical Co., Inc.	College Park, GA
Wool folk Chemical Works, Inc.	Ft. Valley, GA
Riverdale Chemical Co.	Chicago Heights, IL
Carmel Chemical Corp.	Westfield, IN
Brayton Chemicals, Inc.	West Burlington, IA
Industrial Fumigant Co.	Olathe, KS
Research Products Co.	Salina, KS
Central Chemical Corp.	Hagerstown, MD
Dow Chemical USA	Midland, MI[a]

(CONTINUED)

TABLE 10. (Continued)

Company	Location
Haertel Walter Co.	Minneapolis, MN
E.N. Leitte Co.	Stlllwater, MN
The Agriculture & Nutrition Co.	Kansas City, KS
Bartels & Shores Chemical Co.	Kansas City, MO
Farmland industries, Inc.	Kansas City, MO
Ferguson Fumigants	Hazelwood, MO
The Huge Co., Inc.	St. Louis, MO
Knox Chemical Co.	St. Louis, MO
Patterson Chemical Co., Inc.	Kansas City, MO
PBI-Gordon Corp.	Kansas City, MO
Stewart Sanitary Supply Co., Ltd.	St. Louis, MO
Falls Chemicals, Inc.	Great Falls, MT
Ling Fuang industries, Inc.	Gardnerville, NV
Rochester Midland Corp.	Rochester, NY
Prentis Drug & Chemical Co., Inc	New York, NY
Bernard Sirotta Co., Inc.	Brooklyn, NY
Big F insecticides, Inc.	Memphis, TN
Weil Chemicals Co.	Memphis, TN
J-Chem, A Division of Fumigators, Inc.	Houston, TX
The Staffel Co.	San Antonio, TX
Voluntary Purchasing Group, Inc.	Bonham, TX
Atomic Chemical Co.	Spokane, WA
Chemical Formulators, Inc.	Nitro, WV

(CONTINUED)

TABLE 10. (CONTINUED)

Note: The companies listed are registrants of pesticidal products containing EDC. Some of these companies may buy a preformulated or prepackaged product and, therefore may not be actual sources of emissions. In addition, the list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF ETHYLENE DICHLORIDE IN GRAIN FUMIGATION

Ethylene dichloride is used as a component of fumigant mixtures that are applied to control insect infestations in grains during storage, transfer, milling, distribution and processing. Ethylene dichloride comprises 7.1 percent of the total weight of fumigant active ingredients applied to stored grain. Annual usage of EDC in grain fumigants ranged from 870 to 1570 Mg/yr during the period from 1976 to 1979.[38]

Due to its flammability, EDC is used in fumigant mixtures with carbon tetrachloride, which decreases the fire and/or explosion hazard of the mixture. A product containing three parts EDC to one part carbon tetrachloride has been used widely. Other grain fumigant formulations containing EDC are:

- Ethylene dichloride 64.6 percent, carbon tetrachloride 27.4 percent, ethylene dibromide 5.0 percent
- Ethylene dichloride 10.0 percent, carbon tetrachloride 76.5 percent, ethylene dibromide 3.5 percent, carbon disulfide 10.0 percent
- Ethylene dichloride 29.2 percent, carbon tetrachloride 63.6 percent, ethylene dibromide 7.2 percent
- Ethylene dichloride 64.7 percent, carbon tetrachloride 27.4 percent, ethylene dibromide 7.9 percent
- Ethylene dichloride 12.0 percent, carbon tetrachloride 83.8 percent, ethylene dibromide 1.2 percent.38

Table 11 lists brand names of pesticide products containing EDC.

Process Description

Liquid grain fumigants are used on approximately 12 percent of the grain grown in the United States. Fumigants are used during binning (placement in storage) and turning (shifting from one storage facility to another) operations or at any time during storage when infestation occurs. Fumigants have a period of effectiveness of only a few days. Thus, they kill existing insect populations but do not prevent later reinfestation. Newly harvested grain typically is fumigated 6 weeks after binning. Corn grown in the southern regions of the U.S. usually is fumigated immediately following binning, because of field infestation by weevils.[41]

TABLE 11. ETHYLENE DICHLORIDE PESTICIDE BRAND NAMES[40]

Big F "LGF" Liquid Gas Fumigant

Best 4 Servis Brand 75-25 Standard Fumigant

Brayton 75-25 Grain Fumigant

Brayton Flour Equipment Fumigant for Bakeries

Brayton EB-5 Grain Fumigant

Bug Devil Fumigant

Cardinal Fume

Chemform Brand Bore-Kill

Cooke Kill-Bore

Coop New Activated Weevil Killer Fumigant

Crest 15 Grain Fumigant

De-Pester Weevil Kill

De-Pester Grain Conditioner and Weevil Killer

Diweevil

Dowfume EP-15 Inhibited

Dowfume 75

Dowfume EB-5 Effective Grain Fumigant

Dowfume F

Dowfume EB-59

Dynafume

Excelcide Excel fume

FC-7 Grain Fumigant

(CONTINUED)

TABLE 11. (CONTINUED)

FC-13 Mill Machinery Fumigant

Formula MU-39

Formula 635 (FC-2) Grain Fumigant

Fume-O-Death Gas No. 3

Fumisol

Gas-o-cide

Grain Fumigant (Dettelbach Chemicals)

Grainfume MB

Hill's Hilcofume 75

Hydrochlor Fumigant

Hydrochlor GF Liquid Gas Fumigant

Infuco 50-50 Spot Fumigant

Infuco Fumigant 75

Iso-Fume

J-Fume-20

J-Fume-75

KLX

Koppersol

Leitte Spotfume 60

Max Spot Kill Machinery Fumigant

Max Kill 75-25

Max Kill Spot - 59 Spot Fumigant for Mills and Milling Machinery

Parson Lethogas Fumigant

Patterson's Weevil Killer

(CONTINUED)

TABLE 11. (CONTINUED)

Pearson's Fumigraln P-75
Pioneer Brand Grain Fumigant
Riverdale Fumigant
Security Di-Chlor-Mulsion
Selig's Selcofume
Selig's Grain Fumigant No. 15
Selig's Grain Storage Fumigant
Serfume
Sirotta's Sircofume Liquid Fumigating Gas
Spray-Trol Brand insecticide Fumi-Trol
Spot Fumigant
Standard 75-25 Fumigant
Staffel's Boraway
Stephenson Chemicals Stored Grain Fumigant
Vulcan Formula 635 (FC-2) Grain Fumi•gant
Vulcan Formula 72 Grain Fumigant
Waco-50
914 Weevil Killer and Grain Conditioner

A variety of structures are used for grain storage. Farm grain storage facilities are mostly metal with some wooden bins of flat, older and loose-fitting construction. Country elevators are of two types: small banked concrete silos and flat storages. At mills, banked silos are predominant. Terminal elevators are banked silos. Grain transportation vehicle's include trucks, rail cars (box, freight, hopper), inland barges, ocean barges and ships. Subterminal and terminal elevators and shipholds are usually almost air tight, while farm grain storage facilities generally allow considerable air flow.[38,41] On-farm facilities typically have a capacity of about 3,000 bushels, while country elevators have a capacity of about 300,000 bushels. Terminal elevators have an average capacity of 4 million bushels.[42]

Grain fumigants are applied primarily by the "gravity distribution" method by either surface application or layering. This method is practiced both on-farm and off-farm. A second method of fumigant application is "outside of car" application, where the fumigant is either poured from one or five gallon containers through vents located in the roof of the car or sprayed into the car with a power sprayer.[43]

Equipment used to apply fumigants includes common garden sprinkling cans with spray heads removed; 3 to 5 gallon capacity compressed air sprayers from which the nozzles have been removed; high capacity motor driven pumps which apply large volumes of liquid materials directly from large drums; metering devices which treat streams of moving grain; and distribution tube and pressure reduction valve systems for discharging of liquids stored under pressure.[41]

The rate of application of fumigants is dependent on the type of grain and the type of storage facility. Table 12 presents general application rates for various types of grain for both on-farm and off-farm storage. The application rates for off-farm storage are lower since these types of facilities are typically more tight-fitting than on-farm storage.[38]

After application of fumigants, grain generally is left undisturbed for at least 72 hours. The usual practice is to leave the grain for a much longer period. Fumigants are often left on the grain until the normal turning procedure is undertaken. Alternatively, the grain may be aerated by

TABLE 12. FUMIGANT APPLICATION RATES[38]

Grain	Application rate $(gal/10^3\ bu)$ On-farm	Application rate $(gal/10^3\ bu)$ Off-farm
Wheat	3 - 4	2 - 3
Corn	4 - 5	3 - 4
Rice, Oats, Barley, Rye	3 - 4	2 - 3
Grain sorghum	5 - 6	4 - 5

turning after completion of the required treatment period. In tight-fitting facilities equipped with recirculation or forced distribution blowers, the fumigant is ventilated from the grain with fresh air by operating the blowers for 3 to 4 hours.[41]

Emissions

Emissions of EDC from fumigant mixtures occur during fumigant application and when fumigated grain is exposed to the atmosphere, for instance, during turning or loading. The rate of emissions of EDC from fumigant use depends on a number of factors including the type of grain, the type and concentration of fumigant applied, the type of storage (whether loose or tight-fitting), the manner in which the grain is handled, and the rate of release of fumigant residues in and on the grain. Although high sorption efficiencies (84 percent) have been reported for certain cereals, it is generally concluded that by the time the grain is processed, essentially all of the retained EDC will have been dissipated to the atmosphere.[44]

Source Locations

The Standard industrial Classification (SIC) code for farms at which grain may be stored are as follows:

0111 - Agricultural production of wheat
0112 - Agricultural production of rice
0115 - Agricultural production of corn
0116 - Agricultural production of soybeans
0119 - Agricultural production of other grains
0191 - General farms

Table 13 lists the on-farm grain storage capacity by state and the percentage of total U.S. capacity by region.

SIC codes for off-farm storage facilities, are as follows:

4221 - Grain elevators, storage only
5153 - Wholesale grain merchants (includes country and terminal elevators and other merchants marketing grain)
4463 - Marine cargo handling (includes terminal elevators

TABLE 13. ON-FARM GRAIN STORAGE[42]

Region and State	Capacity (10^3 bu)	Regional percentage	
Northeast:	142,698	2%	
Maine	2,866		
New Hampshire	0		
Vermont	0		
Massachusetts	9,654		
Rhode island	0		
Connecticut	222		
New York	39,204		
New Jersey	5,190		
Pennsylvania	62,498		
Delaware	2,057		
Maryland	21,007		
Lake States:	1,357,597	17%	
Michigan	116,462		
Wisconsin	244,827		
Minnesota	996,338		
Corn Belt:	2,982,755	37%	80%
Ohio	225,279		
Indiana	429,981		
Illinois	947,208		
Iowa	1,071,203		
Missouri	309,084		
Northern Plains:	2,132,264	26%	
North Dakota	681,397		
South Dakota	394,381		
Nebraska	715,594		
Kansas	340,892		
Appalachian:	236,607	3%	
Virginia	37,554		
West Virginia	5,685		
North Carolina	100,938		
Kentucky	49,237		
Tennessee	43,193		
Southeast:	159,132	2%	
South Carolina	31,437		
Georgia	87,720		
Florida	12,145		
Alabama	27,830		

TABLE 13. ON-FARM GRAIN STORAGE (Continued)

Region and State	Capacity (10^3 bu)	Regional percentage
Delta States:	131,593	1%
Mississippi	41,588	
Arkansas	50,095	
Louisiana	39,910	
Southern Plains:	315,160	4%
Oklahoma	76,685	
Texas	238,472	
Mountain:	507,357	6%
Montana	278,783	
Idaho	77,960	
Wyoming	19,519	
Colorado	97,216	
New Mexico	9,136	
Arizona	6,404	
Utah	15,220	
Nevada	3,119	
Pacific:	151,622	2%
Washington	60,011	
Oregon	33,552	
California	58,059	
	=========	====
Total	8,116,815	100%

Table 14 lists the number of off-farm grain storage facilities and the total capacity of these facilities by State.

TABLE 14. OFF-FARM GRAIN STORAGE[42]

State	Number of facilities	Capacity (10^3 bu)
Alabama	37,290	178
Arizona	33,890	76
Arkansas	179,180	283
California	115,710	226
Colorado	91,500	209
Delaware	17,200	27
Florida	6,070	27
Georgia	56,700	344
Idaho	64,070	231
Illinois	775,260	1,177
Indiana	245,550	804
Iowa	635,000	1,141
Kansas	830,000	1,086
Kentucky	49,580	202
Louisiana	87,010	131
Maryland	36,940	64
Michigan	90,240	351
Minnesota	366,440	894
Mississippi	76,350	183
Missouri	204,140	611
Montana	54,000	298
Nebraska	484,600	740
Nevada	300	4
New 3ersey	2,200	24
New Mexico	17,550	27
New York	70;270	243
North Carolina	63,420	465
North Dakota	140,070	580
Ohio	228,800	713
Oklahoma	203,520	400
Oregon	65,530	238
Pennsylvania	26,900	337
South Carolina	33,470	177
South Dakota	83,820	386
Tennessee	43,180	106
Texas	720,350	896
Utah	17,170	55
Virginia	29,920	241
Washington	186,370	324
West Virginia	530	9
Wisconsin	118,920	428
Wyoming	5,580	49
Other States	5,170	80
Total	6,600,030	15,065

EDC USE IN LEADED GASOLINE

General

Ethylene dichloride is used in conjunction with ethylene dibromide (1,2-dibromoethane) as a lead scavenger in leaded gasoline. The addition of these compounds prevents the fouling of the engine combustion chamber with lead oxides. Ethylene dichloride and ethylene dibromide react with lead during combustion to form lead chloride ($PbCl_2$) and lead bromide ($PbBr_2$) which remain in the gas phase and-are expelled with exhaust gases. About 1.0 mole of EDC and 0.5 mole of ethylene dibromide are added to gasoline per mole of alkyl lead added.[45] Current EPA regulations limit lead in gasoline to 0.29 grams (.0014 moles) per liter.[46] Thus, no more than 0.0014 moles or 0.14 grams of EDC are added per liter. Higher lead and EDC levels were added in previous years.

Emissions

Sources of EDC emissions from its use in leaded gasoline include blending oPerations at refineries, bulk gasoline marketing and transportation service stations, gasoline combustion, and evaporation from the vehicles themselves.

Blending--

EDC emissions from blending operations at refineries result from evaporation during storage and handling of EDC and blended product. It is estimated in the literature that about 1 kg of EDC is emitted to the atmosphere per fig of EDC used in blending.[47] This corresponds to an emission factor of about 0.14 mg EDC/1 of leaded gasoline produced.

Bulk Marketing and Transportation--

Estimates of EDC emissions from bulk loading, storage, and transportation of leaded gasoline are presented in Table 15. These EDC emission factors were developed based on published VOC emission factors.[48] Data were not available to calculate emissions of EDC from loading and ballasting of marine vessels, submerged loading of tank cars and trucks, and storage and loading in fixed roof tanks. Emissions of EDC from splash loading of tank cars and trucks, and from floating roof

TABLE 15. EDC EMISSIONS FROM BULK L0ADING, STORAGE, AND TRANSPORTATI0N OF LEADED GASOLINE[48]

Emission source	Emission rate or factor
<u>Gasoline storage and loading</u>	
Fixed roof tanks	[a]
Floating roof tanks [b]	438 g/yr
<u>Tank car/truck loading</u>	
Submerged loading normal service	[a]
Submerged loading balance service	[a]
Splash loading normal service	0.269 mg/1 transferred
Splash loading balance service	0.192 mg/1 transferred
<u>Marine vessel loading</u>	
Ship loading	
Cleaned tank	[a]
Ballasted tank	[a]
Uncleaned tank	[a]
Average tank condition	[a]
Ocean barge loading	
Cleaned tank	[a]
Ballasted tank	[a]
Uncleaned tank	[a]
Barge loading	
Cleaned tank	[a]
Uncleaned tank	[a]
Average tank condition	[a]
Tanker ballasting	[a]

[a] Information was not available to calculate emissions of EDC from these sources.

[b] The following assumptions were made for floating roof tanks emissions: external floating roof with metallic shoe primary seal, diameter is 62 feet, height is 40 feet, shell condition is light rust, 10 turnovers/year, wind speed is 10 miles/hour, gasoline density is 6.1 lb/gallon.

tanks, were calculated using the assumption that the EDC concentration in emissions is the same as that in the bulk liquid.

Service Stations--

Estimates of EDC emissions from service stations are presented in Table 16. These emission factors were developed based on published emission factors for gasoline. Data was not available for estimation of EDC emissions from underground tank filling by submerged loading and tank breathing. Emissions from splash loading of underground tanks, vehicle refueling, and spillage were developed with the assumption that emissions have the same composition as the stored liquid.

Combustion in Motor Vehicles--

Most of the EDC added to leaded gasoline is destroyed during combustion, reacting with lead and oxygen to produce lead chloride, hydrogen chloride, water, and carbon dioxide. It is estimated in published literature that about 1 percent of the EDC added is not destroyed during combustion and is emitted to the atmosphere with vehicle exhaust.[47] This corresponds to an emission factor of about 1.4 mg EDC/liter of leaded gasoline burned.

Motor Vehicle Evaporation--

In addition to EDC emissions from motor vehicle exhaust, evaporative emissions occur in the crankcase, carburetor, and fuel tank. Crankcase emissions result from the crankcase as the engine is running. Hot soak losses are produced as fuel evaporates from the carburetor system at the end of a trip. Diurnal changes in ambient temperature result in expansion of the air-fuel mixture in a partially filled fuel tank. As a result, gasoline vapor is expelled into the atmosphere and EDC is emitted with the vapor.[49]

Evaporative EDC emission factors for motor vehicles are not available.

TABLE 16. EDC EMISSI0NS FROM SERVICE STATIONS[48]

Emission source	Emission factor (mg/1 transferred)
Filling underground tank	
Submerged filling	[a]
Splash filling	0.26
Balanced submerged filling	[a]
Underground tank breathing and emptying	[a]
Vehicle refueling operations	
Displacement losses (uncontrolled)	0.21
Displacement losses (controlled)	0.021
Spillage	0.016

[a] Information was not available to calculate emissions of EDC from these sources.

Source Location

Blending of leaded gasoline generally occurs at petroleum refineries. A list of active petroleum refineries in the United States and their locations is presented in Table 17.

Bulk gasoline loading facilities and service stations are too numerous to list here. Terminal and bulk stations can be found within Standard industrial Classifications (SIC) code 5171. Gasoline service stations can be found within SIC 5541. Terminals and bulk plants are commonly identified individually as point sources in many emission inventories such as EPA's National Emissions Data System (NEDS). Service stations and other gasoline outlets are usually treated collectively as area sources in these inventories, as are mobile sources.

EDC USE iN PAINTS, COATINGS, AND ADHESIVES

General

It is estimated that about 1,400 Mg of EDC per year are used in the manufacture of paints, coatings, and adhesives. This amounts to about 0.03 percent of total EDC consumption. Although specific uses of EDC in paints and coatings are not known, EDC is thought to be used as a solvent in paints and coatings which use vinyl polymers, particularly polyvinyl chloride. EDC use in adhesives is restricted to adhesives using acrylics.[51]

Emissions

Because EDC is used as a solvent in paints, coatings, and adhesives, it is estimated that all of the EDC used in these products is eventually emitted to the atmosphere.[51] Data are not available on the relative amounts of EDC emitted during formulation and use of these products.

Source Locations

Standard industrial Classification (SIC) codes for manufacturing and uses of paints, coatings, and adhesives are listed below:

- painting, paper hanging, decorating - 172
- paint and allied product manufacturing - 285
- adhesives and sealants manufacturing - 2891

TABLE 17. PETROLEUM REFINERIES[50]

Company and location
Alabama
Hunt Oil Co.--Tuscaloosa
Louisiana Land and Exploration Co.--Saraland
Marion Corp.--Theodore
Mobile Bay Refining Co.--Chickasaw
Warrior Asphalt Co. of Alabama Inc.--Holt
Alaska
Atlantic Richfield Corp.--Prudhoe Bay
Chevron U.S.A. Inc.--Kenai
North Pole Refining. Div. of Mapco--North Pole
Tesoro Petroleum Corp.--Kenai
Arizona
Arizona Fuels Corp. --Fredonia
Arkansas
Berry Petroleum, Division of Crystal Dll Co. --Stevens
Cross Oil & Refining Co. of Arkansas--Smackover
Macmillan Ring-Free Oil Co.--Norphlet
Tosco Corp.--El Dorado
California
Anchor Refining CI--McKittrick
Atlantic Richfield Co.--Carson
Beacon Oil Co. --Hanford
Champlin Petroleum Co.--Wilmington
Chevron U.S.A. Inc.--Bakersfield
El Segundo
Richmond
Douglas Oil Co.--Santa Maria
Eco Petroleum inc.--Signal Hill
Edgington Oil CI--Long Beach
Exxon Co.--Benlcia
Fletcher Oil & Refining Co.--Carson
Getty Refining & Marketing Co.--Bakersfield
Golden Bear Division, Wltco Chemical Corp. --Oildale
Golden Eagle Refining Co.--Carson
Gulf Oil Co.--Santa Fe Springs
Huntway Refining Co. --Benicia
Wilmington
Independent Valley Energy Co.--Bakersfield
Kern County Refinery inc.--Bakersfield
Marlex Oil & Refining inc.--
Mobil Oil Corp.--Torrance
Newhall Refining CI--Newhall
Oxnard Reflnery--Oxnard
Pacific Oasis--Paramount
Pacific Refining Co.--Hercules
Powerine Oil Co.--Santa Fe Springs
Long Beach
Sabre Refining inc.--Bakersfield
Shell Oil Co.--Martinez
Wilmington
Sunland Refining Corp.--Bakersfield
Texaco inc.--Wilmington
Tosco Corp.--Bakersfield
Martinez
Union Oil Co. of California--Los Angeles
Rodeo
USA Petrochem Corp.--Ventura
Colorado
Asamera Oil U.S. Inc.--Commerce City
Conoco inc. --Commerce City
Gary Refining Co.--Fruita
Delaware
Getty Refining and Marketing Co. --Delaware City
Georgia
Amoco Oil Co.--Savannah
Young Refining Corp.--Douglasville
Hawaii
Chevron U.S.A. Inc.--Barber's Point
Hawaiian independent Refinery Inc. --Ewa Beach
Illinois
Clark Oil & Refining Corp.--Blue island
Hartford
Marathon Oil Co.--Robinson
Mobile Oil Corp.--Joliet
Shell 011 Co.--Hood River
Texaco inc.--Lawrenceville
Union Oil Co. of California--Lemont
Indiana
Amoco Oil Co.--Whiting
Gladieux Refinery inc. --Ft. Wayne
Indiana Farm Bureau Cooperative Association inc.--Ht. Vernon
Laketon Refining Corp. --Laketon
Rock island Refining Corp.--Indianapolis
Kansas
Derby Refining Co.--Wichita
Farmland industries inc. --Coffeyville
Getty Refining & Marketing Co. --El Dorado
Mobile Oil Corp.--Augusta
National Cooperative Refinery Association--McPherson
Pester Refining Co.--El Dorado
Total Petroleum--Arkansas City

TABLE 17. PETROLEUM REFINERIES (Continued)

Company and location

Kentucky

Ashland Petroleum Co.--Catlettsburg
Louisville
Somerset Refinery inc.--Somerset

Louisiana

Atlas Processing Co., Division of Pennzoil--Shreveport
Calumet Refining Co.--Princeton
Canal Refining Co.--Church Point
Celeron Oil & Gas--Mermentau
Cities Service Co.--Lake Charles
Claiborne Gasoline Co.--Lisbon
Conoco inc.-Lake Charles
Cotton Valley Refinery (Kerr-McGee Refining Corp.)--Cotton Valley
CPI Refining inc.--Lake Charles
Exxon Co.--Baton Rouge
Gulf Oil Corp.--Belle Chasse
Hill Petroleum Co.--Krotz Springs
Kerr McGee Corp.--Dubach
Mallard Resources inc.--Gueydon
Marathon Oil Co.--Garyville
Murphy Oil Co.--Meraux
Placid Refining Co.--Port Allen
Port Petroleum inc.--Stonewall
Shell Oil Co.--Norco
Tenneco Oil Co.--Chalmette
Texaco inc. --Convent

Maryland

Chevron U.S.A. Inc.--Baltimore

Michigan

Crystal Refining Co.--Carson City
Lakeside Refining Co.--Kalamazoo
Marathon Oil Co.--Detroit
Total Petroleum inc.--Alma

Minnesota

Ashland Petroleum Co.--St. Paul Park
Koch Refining Co. --Rosemount

Mississippi

Amerada-Hess Corp.--Purvis
Chevron U.S.A. Inc.-Pascagoula
Ergon Refining inc.--Vicksburg
Natchez Refining inc.--Natchez
Southland Oil Co.--Lumberton
Sandersville

Montana

Cenex--Laurel
Conoco inc.--Billings
Exxon Co.--Billings
Flying J inc.--Cut Bank
Kenco Refining inc.--Wolf Point
Simmons Refining Co.--Great Falls

Nevada

Nevada Refining Co.--Tonopah

Company and location

New Jersey

Chevron U.S.A.--Perth Amboy
Exxon Co.--Linden
Mobil Oil Corp.--Paulsboro
Seavlew Petroleum inc.--Thorofare
Texaco inc.--Westville

New Mexico

Giant industries inc. --Ciniza
Farmington
Navajo Refining Co.--Artesia
Plateau inc.--Bloomfield
Southern Union Refining Co.--Lovington
Thriftway Co.--Bloomfield

North Dakota

Amoco Oil Co.--Mandan
Flying J inc.--Wllliston

Ohio

Ashland Petroleum Co.--Canton
Gulf Oil Co.--Cincinnati
Standard Oil Co. of Ohio--Lima
Toledo
Sun CI--Toledo

Oklahoma

Allied Material Corp.--Stroud
Champlin Petroleum Co. --Enid
Conoco inc. --Ponca City
Kerr-McGee Refining Corp. --Wynnewood
Oklahoma Refining Co.--Cyril
Custer Country
Sun CI--Tulsa
Tonkawa Refining Co.--Arnett
Tosco--Duncan
Total Petroleum Corp. --Ardmore

Oregon

Chevron U.S.A. Inc.--Portland

Pennsylvania

Atlantic Richfield Co.--Philadelphia
BP Oil Corp.--Marcus Hood
Gulf Oil Co.--Philadelphia
Kendall-Amalie Division Witco Chemical Co.--Bradford
Penzoil Co. --Rouseville
Quaker State Oil Refining Corp.--Farmers Valley
Sun CI--Marcus Hook
United Refining Co. --Warren
Valvoline Oil Co., Division of Ashland Oil Co.--Freedom

Tennessee

Delta Refining Co.--Memphis

TABLE 17. PETROLEUM REFINERIES (Continued)

Company and location

Texas

- Amber Refining Co.--Fort Worth
- American Petrofina inc.--
  - Big Spring
  - Port Arthur
- Amoco Oil Co.--Texas City
- Atlantic Richfield Co.--Houston
- Champlin Petroleum Co.--
  - Corpus Christi
- Charter international Oil Co. --Houston
- Chevron U.S.A. Inc.--El Paso
- Coastal States Petroleum Co.--
  - Corpus Christi
- Crown Central Petroleum Corp.--Houston
- Diamond Shamrock Corp. --Sunray
- Dorchester Refining Co.--
  - Mt. Pleasant
- Eddy Refining Co.--Houston
- Exxon Co. U.S.A. --Baytown
- Flint Chemical Co.--San Antonio
- Gulf Oil Co.--Port Arthur
- Howell Hydrocarbons inc.--San Antonio
- Koch Refining Co.--Corpus Christi
- LaGloria Oil & Gas Co.--Tyler
- Liquid Energy Corp.--Bridgeport
- Marathon Oil Co.--Texas City
- Mobil Oil Corp.--Beaumont
- Phillips Petroleum Co.--
  - Borger
  - Sweeny
- Pride Refining inc.--Abilene
- Quintana Petrochemical Co.--
  - Corpus Christi
- Saber Energy inc. --Corpus Christi
- Shell Oil Co.--Deer Park
  - Odessa
- Sigmor Refining Co.--Three Rivers
- South Hampton Refining Co.--Silsbee
- Southwestern Refining CI--
  - Corpus Christi
- Tesoro Petroleum Corp.--
  - Carrizo Springs
- Texaco inc.--Amarillo
  - El Paso
  - Port Arthur
  - Port Neches
- Texas City Refining inc.--Texas City
- Uni Refining inc.-- Ingleside
- Union Oil Co. of California--
  - (Beaumont), Nederland

Company and location

Utah

- Amoco Oil Co.--Salt Lake City
- Caribou Four Corners inc.--Woods Cross
- Chevron U.S.A.--Salt Lake City

- Crysen Refining Co.--WoodsCross
- Husky Oil Co.--North Salt Lake City
- Phillips Petroleum Co.--Woods Cross
- Plateau inc.--Roosevelt

Virginia

- Amoco Oil Co.--Yorktown

Washington

- Atlantic Richfield Co.--Ferndale
- Chevron U.S.A. Inc. --Seattle
- Mobile Oil Corp.--Ferndale
- Shell Oil Co.--Anacortes
- Sound Refining inc. --Taco:
- Texaco inc. --Anacortes
- U.S. Oil & Refining Co.--Tacoma

West Virginia

- Quaker State Oil Refining Corp. --
  - Newell
  - St. Mary's

Wisconsin

- Murphy Oil Corp. --Superior

Wyoming

- Amoco Oil Co.--Casper
- Husky Oil Co.--Cheyenne
- Little America Refining Co.--Casper
- Mountaineer Refining CI--LaBarge
- Sinclair Oil Corp.--Sinclair
- Wyoming Refining Co. --Newcastle

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

EDC USE AS AN EXTRACTION SOLVENT

General

EDC is used in a number of solvent extraction applications. Major applications include the extraction of oil from seeds, the processing of animal fats, and the processing of pharmaceutical products. It is estimated that EDC use as an extraction solvent accounts for about 1.1 Mg EDC/year or about 0.02 percent of total EDC consumption.[52]

Emissions

The solvent used in extraction processes is generally recovered by low pressure distillation. Some solvent is lost to the atmosphere from valves, pumps, and compressors; in spills; and during transfer operations. It is estimated that in published literature that about 95 percent of the EDC consumed in solvent extraction processes is emitted to the atmosphere, while about 5 percent is discharged with solid wastes. These solid wastes are generally incinerated.[52]

Source Locations

Standard industrial Classification (SIC) codes for uses of extraction solvents are listed below:

- Manufacturing of fats and oils - 207
- Manufacturing of pharmaceutical preparations - 2834

EDC USE IN CLEANING SOLVENTS

General

Solvents containing EDC are used in cleaning equipment in the polyvinyl chloride and textile manufacturing industries. It is estimated that this use accounts for about 910 Mg/year or about 0.02 percent of total EDC consumption.[53] Data are not available on the equipment cleaned, the specific nature of the cleaning operations, or the compositions of the solvents used.

Emissions

Although no emissions data are available for solvent cleaning uses of EDC, it is estimated in the literature that about 95 percent of the EDC consumed is ultimately emitted to the atmosphere, while the remaining 5 percent is discharged with solid wastes.[53] These solid wastes are generally incinerated.

Source Locations

Standard industrial Classification (SIC) codes for uses of cleaning solvents are listed below:

- Manufacturing of plastics materials and synthetics - 282
- Manufacturing of textile mill products - 22
- Manufacturing of apparel and other textile products - 23

MISCELLANEOUS EDC USES

General

EDC is used in the manufacture of color film, as a diluent in pesticides and herbicides, and as an amine carrier in the leaching of copper ores. The total amount of EDC used in these applications is 460 Mg/year or about 0.01 percent of total domestic consumption.[54] Very little information is available in published sources regarding the details of these processes.

Emissions

It is estimated in published literature that all of the EDC used in the manufacture of pesticides, herbicides, and color film is emitted to the atmosphere, while nearly all of the EDC used in copper leaching is either consumed in the leaching process or emitted with waste water.[54]

Source Locations

Standard industrial Classification (SIC) codes for miscellaneous uses of EDC are listed below:

- Photographic equipment and supplies manufacturing - 3861
- Agricultural chemicals manufacturing - 287
- Copper ores mining - l02

VOLATILIZATION FROM WASTE TREATMENT, STORAGE AND DISPOSAL FACILITIES

Considerable potential exists for volatile substances, including EDC, to be emitted from hazardous waste treatment, storage and handling facilities. A study in Callfornia[55] shows that significant quantities of

EDC may be contained in hazardous wastes, which may be expected to volatilize within hours, days, or months after disposal by landspreading, surface impoundment or covered landfill, respectively. Volatilization of EDC and other substances was confirmed in this study by significant ambient air concentrations of EDC over one site. Reference 56 provides general theoretical models for estimating volatile substance emissions from a number of generic kinds of waste handling operations, including surface impoundments, landfills, landfarming (land treatment) operations, wastewater treatment systems, and drum storage/handling process. If such a facility is known to handle EDC, the potential should be considered for some air emissions to occur.

Several studies show that low levels of EDC may be emitted from municipal wastewater treatment plants. In a test at a small municipal treatment plant (handling 40% industrial and 60% municipal sewage), EDC emission rates from the aeration basins were measured at levels ranging from 5 to 10 grams/hour.[57] Tests at a larger municipal treatment plant (handling about 50 percent industrial sewage) show that less than 92 to 184 grams/day of EDC are emitted, primarily from air stripping as part of the activated sludge treatment process. This emission rate was calculated from the EDC content of the influent to the plant, and assuming 50 to 100 percent volatilization as part of the overall treatment process, which is the range of removal observed for other volatiles.[58] Too little data are available to extrapolate these test results to other wastewater treatment plants.

SECTION 5
SOURCE TEST PROCEDURES

Ethylene dichloride emissions can be measured using EPA Reference Method 23, which was proposed in the Federal Register on June 11, 1980.[59] EPA has validated the method for ethylene dichloride in the laboratory60 as well as in the field.[61]

In Method 23, a sample of the exhaust gas to be analyzed is drawn into a Tedlar® or aluminized Mylar® bag as shown in Figure 14. Tedlar® is considered a more reliable bag material than Mylar® for EDC.[61] The bag is placed inside a rigid leak proof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. Sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography (GC) coupled with flame ionizatlon detection (FID). Analysis should be conducted within one day of sample collection. The recommended GC column is 3.05 m by 3.2 mm stainless steel, filled with 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. This column normally provides an adequate resolution of halogenated organics. (Where resolution interferences are encountered, the GC operator should select the column best suited to the analysis.) The column temperature should be set at 100°C. Zero helium or nitrogen should be used as the carrier gas at a flow rate of approximately 20 ml/min.

The peak area corresponding to the retention time of ethylene dichloride is measured and compared to peak areas for a set of standard gas mixtures to determine the ethylene dichloride concentration. The range of the method is 0.1 to 200 ppm; however the upper limit can be extended by extending the calibration range or diluting the sample. The method does not apply when ethylene dichloride is contained in particulate matter.

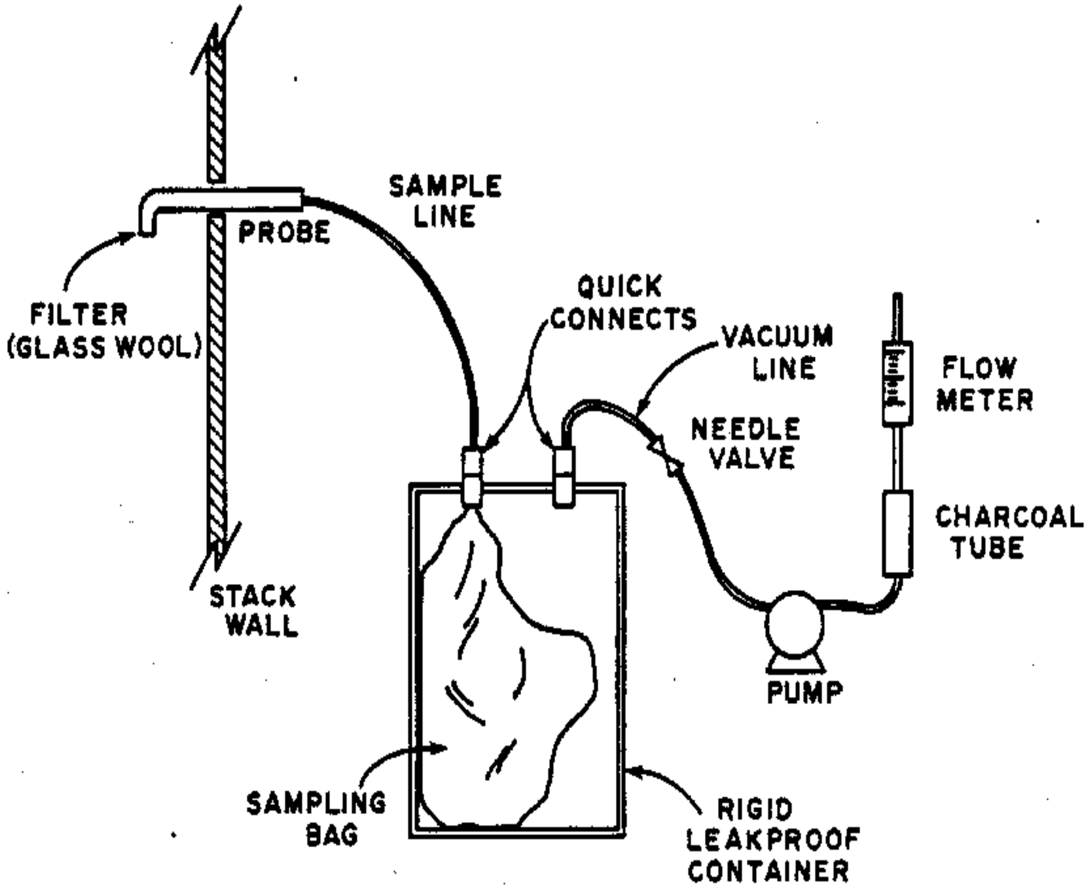


Figure 14. Method 23 sampling train.[59]

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16. ABSTRACT

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

This document presents information on 1) the types of sources that may emit ethylene dichloride, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for ethylene dichloride release into the air from each operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

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