

VINYL CHLORIDE

1. Introduction

Vinyl chloride [75-01-4], $\text{CH}_2=\text{CHCl}$, by virtue of the wide range of application for its polymers in both flexible and rigid forms, is one of the largest dollar-volume commodity chemicals in the United States and is an important item of international commerce. Growth in vinyl chloride production is directly related to demand for its polymers and, on an energy-equivalent basis, rigid poly(vinyl chloride) (PVC) [9002-86-2] is one of the most energy-efficient construction materials available. Initial development of the vinyl chloride industry in the 1930s stemmed from the discovery that, with plasticizers, PVC can be readily processed and converted into a rubbery product (1). However, it was not until after World War II that vinyl chloride production grew rapidly as a result of the increased volume of PVC products for the consumer market.

The early history of vinyl chloride has been documented (2–6). Justus von Liebig at the University of Giessen, Germany, won the distinction of being the first person to synthesize vinyl chloride when, in the 1830s, he reacted the so-called oil of the Dutch chemists, dichloroethane [1300-21-6], with alcoholic potash to make vinyl chloride. Liebig's student, Victor Regnault, confirmed his discovery and was allowed to publish it as sole author in 1835 (7). In 1872, E. Baumann observed that white flakes precipitated from vinyl chloride upon prolonged exposure to sunlight in a sealed tube (8). This material was further investigated in the early 1900s by Ivan Ostromislensky, who named it *Kauprenchlorid* (cauprene chloride), and gave it the empirical formula $(\text{C}_2\text{H}_3\text{Cl})_{16}$ (9). However, vinyl chloride was of little commercial interest until Waldo Semon's work with plasticized PVC for the B. F. Goodrich Company beginning in 1926 (10). Some years earlier, Fritz Klatte had developed the first practical route to vinyl chloride while looking to find uses for acetylene [74-86-2] for Chemische Fabrik Griesheim-Elektron. This process, in which hydrogen chloride [7647-01-0], HCl , is added to acetylene over a mercuric chloride [7487-94-7] catalyst, was patented in 1912 (11). By 1926, Griesheim-Elektron had concluded that the patent held no commercial value and allowed it to lapse. Klatte's process eventually formed the basis of the vinyl chloride industry for many years from its beginnings in the 1930s, but it was ultimately supplanted by a balanced process from ethylene [74-85-1] and chlorine [7782-50-5] in which vinyl chloride is made by pyrolysis of 1,2-dichloroethane [107-06-2] (ethylene dichloride (EDC)).

Vinyl chloride (also known as chloroethylene or chloroethene) is a colorless gas at normal temperature and pressure, but is typically handled as the liquid (bp -13.4°C). However, no human contact with the liquid is permissible. Vinyl chloride is an OSHA-regulated material.

2. Physical Properties

The physical properties of vinyl chloride are listed in Table 1 (12). Vinyl chloride and water [7732-18-5] are nearly immiscible. The equilibrium concentration of vinyl chloride at 1 atm partial pressure in water is 0.276 wt % at 25°C , whereas the solubility of water in vinyl chloride is 0.0983 wt % at 25°C and saturated

pressure (13). Vinyl chloride is soluble in hydrocarbons, oil, alcohol, chlorinated solvents, and most common organic liquids.

3. Reactions

3.1. Polymerization. The most important reaction of vinyl chloride is its polymerization and copolymerization in the presence of a radical-generating initiator.

3.2. Substitution at the Carbon–Chlorine Bond. Vinyl chloride is generally considered inert to nucleophilic replacement compared to other alkyl halides. However, the chlorine atom can be exchanged under nucleophilic conditions in the presence of palladium [7440-05-3], Pd, and certain other metal chlorides and salts. Vinyl alcoholates, esters, and ethers can be readily produced from these reactions.

Use of alcohol as a solvent for carbonylation with reduced Pd catalysts gives vinyl esters. A variety of acrylamides can be made through oxidative addition of carbon monoxide [630-08-0], CO, and various amines to vinyl chloride in the presence of phosphine complexes of Pd or other precious metals as catalyst (14).

Reaction of vinyl chloride with butyllithium [109-72-8] and then with carbon dioxide [124-38-9], CO₂ in diethyl ether [60-29-7] at low temperatures gives high yields of α , β -unsaturated carboxylic acids.

Vinylmagnesium chloride [3536-96-7] (Grignard reagent) can be prepared from vinyl chloride (15) and then used to make a variety of useful end products or intermediates by adding a vinyl anion to organic functional groups (16–22). For instance, the vinylmagnesium compounds can be coupled with cuprous chloride [7758-89-6], CuCl, at -60°C to give 1,3-butadiene [106-99-0], while vinyl ketones and alcohols can be prepared by the addition of vinylmagnesium chloride to organic acids.

Vinyl chloride similarly undergoes Grignard reactions with other organomagnesium halide compounds. For example, cross-coupling with 1- or 2-phenylethylmagnesium bromide [41745-02-2 or 3277-89-2] yields 4- or 3-phenyl-1-butene [768-56-9 or 934-10-1], respectively (23,24), whereas 4-(3-methyl-2-butenyl)styrene [85964-33-6] (*p*-phenylstyrene) is obtained by coupling 4-(3-methyl-2-butenyl)phenylmagnesium chloride [106364-41-4] with vinyl chloride (25).

Vinylolithium [917-57-7] can be formed directly from vinyl chloride by means of a lithium [7439-93-2] dispersion containing 2 wt % sodium [7440-23-5] at $0-10^{\circ}\text{C}$. This compound is a reactive intermediate for the formation of vinyl alcohols from aldehydes, vinyl ketones from organic acids, vinyl sulfides from disulfides, and monosubstituted alkenes from organic halides. It can also be converted to vinylcopper [37616-22-1] or divinylcopper lithium [22903-99-7], which can then be used to introduce a vinyl group stereoselectively into a variety of α , β -unsaturated systems (26), or simply add a vinyl group to other α , β -unsaturated compounds to give γ , δ -unsaturated compounds. Vinylolithium reagents can also be converted to secondary alcohols with trialkylboranes.

Vinyl chloride reacts with sulfides, thiols, alcohols, and oximes in basic media. Reaction with hydrated sodium sulfide [1313-82-2] in a mixture of

dimethyl sulfoxide [67-68-5] (DMSO) and potassium hydroxide [1310-58-3], KOH, yields divinyl sulfide [627-51-0] and sulfur-containing heterocycles (27). Various vinyl sulfides can be obtained by reacting vinyl chloride with thiols in the presence of base (28). Vinyl ethers are produced in similar fashion, from the reaction of vinyl chloride with alcohols in the presence of a strong base (29,30). A variety of pyrroles and indoles have also been prepared by reacting vinyl chloride with different ketoximes or oximes in a mixture of DMSO and KOH (31).

The carbon–chlorine bond can also be activated at high temperatures. Vinyl chloride reacts with alkanethiols, and with dialkyl sulfides and disulfides at 400°C to form vinyl sulfide compounds in low yields (32). Aryl and thienyl vinyl sulfides can be prepared in similar fashion, reacting aryl and thienyl thiols with vinyl chloride in a quartz tube at 380–440°C (33). Thiophene [110-02-1] and its substituted forms can be obtained by heterocyclization of vinyl chloride with hydrogen sulfide [7783-06-4] in the presence of an acetylenic reagent at 500–550°C (34) (see THIOPHENE AND THIOPHENE DERIVATIVES). Reaction of vinyl chloride with germanium tetrachloride [10038-98-9] and trichlorosilane [10025-78-2] in a tubular reactor at 600–700°C gives vinyltrichlorogermane [4109-83-5] in moderate yield (35). Vinyltrichlorosilane [75-94-5] is obtained at yields of up to 77% by reacting vinyl chloride with trichlorosilane at 400–750°C in a tubular reactor (36), while vinylsilanes can be made from mono-, di-, or trisilane [7803-62-5, 1590-87-0, or 7783-26-8] and vinyl chloride in a tubular reactor at 100–650°C (37).

Finally, the reaction of vinyl chloride with hydrogen fluoride [7664-39-3], HF, over a chromia [1308-38-9], Cr₂O₃, on-alumina [1344-28-1], Al₂O₃, catalyst at 380°C yields vinyl fluoride [75-02-5] (38).

3.3. Oxidation. The chlorine atom [22537-15-1]-initiated, gas-phase oxidation of vinyl chloride yields 74% formyl chloride [2565-30-2] and 25% CO at high oxygen [7782-44-7], O₂, to Cl₂ ratios; it is unique among the chloro olefin oxidations because CO is a major initial product and because the reaction proceeds by a nonchain path at high O₂/Cl₂ ratios. The rate of the gas-phase reaction of chlorine atoms with vinyl chloride has been measured (39).

The oxidation of vinyl chloride with oxygen in the gas phase proceeds by a nonradical path which, again, is unique among the chloro olefins. No C₂ carbonyl compounds are made; the main products are formyl chloride, CO, HCl, and formic acid [64-18-6]. Complete oxidation of vinyl chloride with oxygen in the gas phase can be achieved using a cobalt chromite [12016-69-2] catalyst (40). At –15 to –20°C, vinyl chloride reacts with oxygen, with ultraviolet (uv) light initiation, to give a peroxide, reported as [OCH₂CHClO]₂. On heating to 35°C, this peroxide decomposes to formaldehyde [50-00-0], CO, and HCl.

Reaction with triplet oxygen O(³P) atoms [17778-80-2] gives high yields of CO and chloroacetaldehyde [107-20-0], with smaller amounts of acetyl chloride [75-36-5], HCl, methane [74-82-8], and polymer. The rate of the gas-phase reaction of vinyl chloride with O(³P) atoms has also been reported (41).

Oxidation of vinyl chloride with ozone [10028-15-6] in either the liquid or the gas phase gives formic acid and formyl chloride. The ozone reaction with vinyl chloride can be used to remove it from gas streams in vinyl chloride production plants.

Vinyl chloride can be completely oxidized to CO_2 and HCl using potassium permanganate [7722-64-7] in an aqueous solution at pH 10. This reaction can be used for wastewater purification, as can ozonolysis, peroxide oxidation, and uv irradiation (42). The aqueous phase oxidation of vinyl chloride with chlorine yields chloroacetaldehyde (43).

The combustion of vinyl chloride in air at $510\text{--}795^\circ\text{C}$ produces mainly CO_2 and HCl along with CO . A trace of phosgene [75-44-5] also forms.

3.4. Addition. Chlorine adds to vinyl chloride to form 1,1,2-trichloroethane [79-00-5] (44–46). Chlorination can proceed by either an ionic or a radical path. In the liquid phase and in the dark, 1,1,2-trichloroethane forms by an ionic path when a transition-metal catalyst such as ferric chloride [7705-08-0], FeCl_3 , is used. The same product forms in radical reactions up to 250°C . Photochemically initiated chlorination also produces 1,1,2-trichloroethane by a radical path (47). Above 250°C , the chlorination of vinyl chloride gives unsaturated chloroethylenes produced by dehydrochlorination of 1,1,2-trichloroethane. The presence of small amounts of oxygen greatly accelerates the rate of the radical-chain chlorination reaction at temperatures above $250\text{--}300^\circ\text{C}$ (48). Other halogens can be added to vinyl chloride to form similar 1,2-addition products but these reactions have not been thoroughly studied. Vinyl chloride can be halo-fluorinated in the sulfur tetrafluoride [7783-60-0]– HF-Cl_2 system (49).

Hydrogen halide addition to vinyl chloride in general yields the 1,1-adduct (50–52). The reactions of HCl and hydrogen iodide [10034-85-2], HI , with vinyl chloride proceed by an ionic mechanism, while the addition of hydrogen bromide [10035-10-6], HBr , involves a chain reaction in which a bromine atom [10097-32-2] is the chain carrier (52). In the absence of a transition-metal catalyst or anti-oxidants, HBr forms the 1,2-adduct with vinyl chloride (52). HF reacts with vinyl chloride in the presence of stannic chloride [7646-78-8], SnCl_4 , to form 1,1-difluoroethane [75-37-6] (53).

Various vinyl chloride adducts can be formed under acid-catalyzed Friedel-Crafts conditions. Vinyl chloride can add tertiary alkyl halides (54). It can be condensed with ethyl chloride [75-00-3] to yield 1,1,3-trichlorobutane [13279-87-3] and 1,1-dichloroethane [75-34-3] (55). The reaction of 2-chloropropane [75-29-6] with vinyl chloride yields 1,1-dichloro-3-methylbutane [625-66-1] (55). At $0\text{--}5^\circ\text{C}$, vinyl chloride reacts with benzene [71-43-2], resulting in a mixture of 1-chloroethylbenzene [672-65-1] and 1,1-diphenylethane [612-00-0] (56). Reaction with toluene (qv) [108-88-3] leads to 1,1-ditolylethane [29036-13-3], whereas reaction with anisole [100-66-3] (methoxybenzene) gives 1,1-di-*p*-anisylethane [10543-21-2]. Phenol [108-95-2] also reacts to give *p*-vinylphenol [2628-17-3].

Vinyl chloride forms a photo [2+2] cycloadduct with 1-isoquinolone [491-30-5] and its *N*-methyl derivative (57).

Condensation of vinyl chloride with formaldehyde and HCl (Prins reaction) yields 3,3-dichloro-1-propanol [83682-72-8] and 2,3-dichloro-1-propanol [616-23-9]. The 1,1-addition of chloroform [67-66-3] as well as the addition of other polyhalogen compounds to vinyl chloride are catalyzed by transition-metal complexes (58). In the presence of iron pentacarbonyl [13463-40-6], both bromoform [75-25-2], CHBr_3 , and iodoform [75-47-8], CHI_3 , add to vinyl chloride (59,60). Other useful products of vinyl chloride addition reactions include

2,2-difluoro-4-chloro-1,3-dioxolane [162970-83-4] (61), 2-chloro-1-propanol [78-89-7] (62), 2-chloropropionaldehyde [683-50-1] (63), 4-nitrophenyl- β,β -dichloroethyl ketone [31689-13-1] (64), and β,β -dichloroethyl phenyl sulfone [3123-10-2] (65).

Sodium β -chloroethanesulfonate [15484-44-3] can be obtained by reacting vinyl chloride with sodium bisulfite [7631-90-5] (66). Reaction with nitronium tetrafluoroborate [13826-86-3] yields 1-chloro-1-fluoro-2-nitroethane [461-70-1] (67).

Vinyl chloride reacts with ammonium chloride [12125-02-9] and oxygen in the vapor phase at 325°C over a cupric chloride [7447-39-4], CuCl_2 , catalyst to make 1,1,2-trichloroethane and ammonia (68).

Vinyl chloride can be hydrogenated over a 0.5% platinum [7440-06-4], Pt, on alumina catalyst to ethyl chloride and ethane [74-84-0]. This reaction is zero order in vinyl chloride and first order in hydrogen.

3.5. Photochemistry. Vinyl chloride is subject to photodissociation. Photexcitation at 193 nm results in the elimination of HCl molecules and Cl atoms in an approximately 1.1:1 ratio (69). Both vinylidene ($^3\text{B}_2$) [2143-69-3] and acetylene have been observed as photolysis products (70), as have H_2 molecules (71) and H atoms [12385-13-6] (72). HCl and vinylidene appear to be formed via a concerted 1,1 elimination from excited vinyl chloride (70). An adiabatic recoil mechanism seems likely for Cl atom elimination (73). As expected from the relative stabilities of the 1- and 2-chlorovinyl radicals [50663-45-1 and 57095-76-8], H atoms are preferentially produced by detachment from the β carbon (72). Finally, a migration mechanism appears to play a significant role in H_2 elimination (71).

3.6. Pyrolysis. Vinyl chloride is more stable than saturated chloroalkanes to thermal pyrolysis, which is why nearly all vinyl chloride made commercially comes from thermal dehydrochlorination of EDC. When vinyl chloride is heated to 450°C, only small amounts of acetylene form. Little conversion of vinyl chloride occurs, even at 525–575°C, and the main products are chloroprene [126-99-8] and acetylene. The presence of HCl lowers the amount of chloroprene formed.

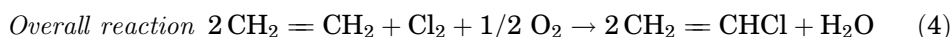
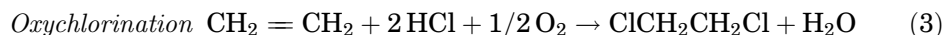
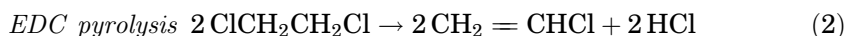
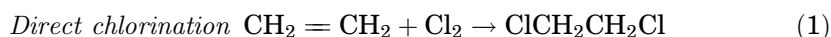
Decomposition of vinyl chloride begins at approximately 550°C, and increases with increasing temperature. Acetylene, HCl, chloroprene, and vinylacetylene [689-97-4] are formed in about 35% total yield at 680°C (74). At higher temperatures, tar and soot formation becomes increasingly important. Vinyl chloride pyrolysis is a free-radical chain process, in which Cl atoms are important carriers. Abstraction of H atoms from vinyl chloride by Cl atoms leads to 2-chlorovinyl and 1-chlorovinyl radicals, respectively. The former lose Cl atoms to form acetylene, while the latter add to vinyl chloride, ultimately resulting in chloroprene. Addition of HCl increases the acetylene–chloroprene product ratio, probably owing to reversal of the reaction leading to the 1-chlorovinyl radical through H atom transfer from HCl (74).

When dry and in contact with metals, vinyl chloride does not decompose below 450°C. However, if water is present, vinyl chloride can corrode iron, steel, and aluminum because of the presence of trace amounts of HCl. This HCl may result from the hydrolysis of the peroxide formed between oxygen and vinyl chloride.

4. Manufacture

Vinyl chloride monomer was first produced commercially in the 1930s from the reaction of HCl with acetylene derived from calcium carbide [75-20-7]. As demand for vinyl chloride increased, more economical feedstocks were sought. After ethylene became plentiful in the early 1950s, commercial processes were developed to produce vinyl chloride from ethylene and chlorine. These processes included direct chlorination of ethylene to form EDC, followed by pyrolysis of EDC to make vinyl chloride. However, because the EDC cracking process also produced HCl as a co-product, the industry did not expand immediately, except in conjunction with acetylene-based technology. The development of ethylene oxychlorination technology in the late 1950s encouraged new growth in the vinyl chloride industry. In this process, ethylene reacts with HCl and oxygen to form EDC. Combining the component processes of direct chlorination, EDC pyrolysis, and oxychlorination provided the so-called balanced process for production of vinyl chloride from ethylene and chlorine, with no net consumption or production of HCl.

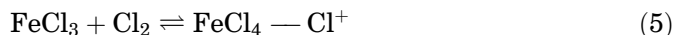
Although a small fraction of the world's vinyl chloride capacity is still based on acetylene or mixed acetylene–ethylene feedstocks, nearly all production is conducted by the balanced process based on ethylene and chlorine (75). The reactions for each of the component processes are shown in equations 1–3 and the overall reaction is given by equation 4:



In a typical balanced plant producing vinyl chloride from EDC, all the HCl produced in EDC pyrolysis is used as the feed for oxychlorination. On this basis, EDC production is about evenly split between direct chlorination and oxychlorination, and there is no net production or consumption of HCl. The three principal operating steps used in the balanced process for ethylene-based vinyl chloride production are shown in the block flow diagram in Figure 1, and a schematic of the overall process for a conventional plant is shown in Figure 2 (76). A typical material balance for this process is given in Table 2.

4.1. Direct Chlorination of Ethylene. Direct chlorination of ethylene is generally conducted in liquid EDC in a bubble column reactor. Ethylene and chlorine dissolve in the liquid phase and combine in a homogeneous catalytic reaction to form EDC. Under typical process conditions, the reaction rate is controlled by mass transfer, with absorption of ethylene as the limiting factor (77). Ferric chloride is a highly selective and efficient catalyst for this reaction, and is widely used commercially (78). Ferric chloride and sodium chloride [7647-14-5] mixtures have also been utilized for the catalyst (79), as have tetrachloroferrate

compounds, eg, ammonium tetrachloroferrate [24411-12-9], NH_4FeCl_4 (80). The reaction most likely proceeds through an electrophilic addition mechanism, in which the catalyst first polarizes chlorine, as shown in equation 5. The polarized chlorine molecule then acts as an electrophilic reagent to attack the double bond of ethylene, thereby facilitating chlorine addition (eq. 6):



The direct chlorination process may be run with a slight excess of either ethylene or chlorine, depending on how effluent gases from the reactor are subsequently processed. For example, the noncondensables could easily be routed to an oxychlorination process in the case of excess ethylene (81). Conversion of the limiting component is essentially 100%, and selectivity to EDC is greater than 99% (78). The main by-product is 1,1,2-trichloroethane, which most likely forms through radical reactions beginning with homolytic dissociation of a small fraction of the chlorine. However, oxygen, which is frequently present as an impurity in chlorine, tends to increase selectivity to EDC by inhibition of free-radical reactions that produce, 1,1,2-trichloroethane. Consequently, oxygen is often added to a level of about 0.5% of the chlorine feed. Amides, eg, *N,N*-dimethylformamide [68-12-2], also increase selectivity to EDC, as do aromatic hydrocarbons and phenols (82).

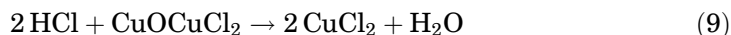
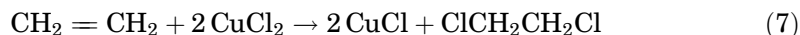
The direct chlorination reaction is very exothermic ($\Delta H = -180 \text{ kJ/mol}$ for eq. 1, Ref. 83) and requires heat removal for temperature control. Early direct chlorination reactors were operated at moderate temperatures of 50–65°C to take advantage of lower by-product formation, and utilized conventional water cooling for heat removal. As energy costs became more significant, various schemes for recovering the heat of reaction were devised. A widely used method involves operating the reactor at the boiling point of EDC, allowing the pure product to vaporize, and then either recovering heat from the condensing vapor, or replacing one or more EDC fractionation column reboilers with the reactor itself (84–86). An alternative method entails operation of the reactor at higher pressure to raise the boiling point of EDC; in this case, the reactor operates without boiling, but at higher temperatures (75–200°C) to allow more efficient heat transfer to some other part of the process (87,88). For reactors equipped with liquid product removal, the EDC is usually treated to remove ferric chloride. The latter, which would lead to rapid fouling of the EDC cracking reactor, can be removed by washing with water or by adsorption on a solid. With dry feedstocks (<10 ppm water) and good temperature control, carbon steel can be used in direct chlorination reactors operating at low temperature and in auxiliary equipment. Higher temperature operation generally requires materials that are more resistant to erosion–corrosion in the reactor, eg, hard alloy cladding below the liquid level and nickel alloy feed spargers.

4.2. Oxychlorination of Ethylene. When compared with direct chlorination, the oxychlorination process is characterized by higher capital investment, higher operating costs, and slightly less pure EDC product. However,

use of the oxychlorination process is dictated by the need to consume the HCl generated in EDC pyrolysis.

In oxychlorination, ethylene reacts with dry HCl and either air or pure oxygen to produce EDC and water. Various commercial oxychlorination processes differ from one another to some extent because they were developed independently by several different vinyl chloride producers (78,83), but in each case the reaction is carried out in the vapor phase in either a fixed- or fluidized-bed reactor containing a modified Deacon catalyst. Unlike the Deacon process for chlorine production, oxychlorination of ethylene occurs readily at temperatures well below those required for HCl oxidation.

Oxychlorination catalysts typically contain cupric chloride as the primary active ingredient, impregnated on a porous support, eg, alumina, silica–alumina [37287-16-4], diatomaceous earth [7631-86-9], etc, and may also contain numerous additives (89–91). Although the detailed catalytic mechanism is not known, CuCl_2 is widely recognized as the active chlorinating agent. The CuCl produced during the ethylene chlorination step is rapidly reconverted to CuCl_2 under reaction conditions, and the presence of some CuCl is thought to be advantageous because it readily complexes with ethylene, bringing it into contact with CuCl_2 long enough for chlorination to occur (78). A very simple representation of this heterogeneous catalytic cycle is given in equation 7–9, and the overall, net reaction is given in equation 3.



Other mechanisms, involving initial formation of ethylene oxide [75-21-8] as the possible rate-limiting step, complexation of CuCl_2 with HCl (92), and Cl_2 as the chlorinating agent (93) have been suggested.

Because commercial oxychlorination processes differ with respect to catalysts in terms of their composition, morphology, and physical properties, with respect to the catalyst contacting method (fluidized- or fixed-bed reactor), and with respect to oxygen source (air or pure oxygen feed), the operating conditions, feed ratios, conversions, and yields also vary, depending on the particular combination used and on the methods employed for secondary recovery of feedstock and product. For any particular combination of reactor type and oxygen source, however, good temperatures control of this highly exothermic reaction ($\Delta H = -239 \text{ kJ/mol}$ for eq. 3, Ref. 83) is essential for efficient production of EDC. Increasing reactor temperatures lead to increased by-product formation, mainly through increased oxidation of ethylene to carbon oxides and increased cracking of EDC. Cracking, ie, dehydrochlorination of EDC, results in the formation of vinyl chloride, and subsequent oxychlorination and cracking steps lead progressively to by-products with higher levels of chlorine substitution. High temperatures ($>300^\circ\text{C}$) can also cause catalyst deactivation through increased sublimation of CuCl_2 .

Fluidized-bed reactors typically are vertical cylindrical vessels equipped with a support grid/feed sparger system for adequate fluidization and feed distribution, internal cooling coils for heat removal, and either external or internal cyclones to minimize catalyst carryover. Fluidization of the catalyst assures intimate contact between feed and product vapors, catalyst, and heat-transfer surfaces, and results in a uniform temperature within the reactor (78). Reaction heat can be removed by the generation of steam within the cooling coils or by some other heat-transfer medium. An operating temperature of 220–245°C and reactor gauge pressures of 150–500 kPa (22–73 psig) are typical for oxychlorination with a fluidized catalyst. Given these operating conditions, fluidized-bed reactors can be constructed with a carbon steel shell and with internal parts made from a corrosion-resistant alloy.

While fluidized-bed oxychlorination reactors are generally well-behaved and operate predictably, under certain (usually upset) conditions, they are subject to a phenomenon known, appropriately, as catalyst stickiness. This can be described as catalyst particle agglomeration, which is characterized by declining fluidization quality and, in severe cases, can result in a slumped or collapsed bed. Oxychlorination catalyst stickiness is brought on by adverse operating conditions that promote the formation of dendritic growths of cupric chloride on the surface of individual catalyst particles, which leads to increasing interparticle interactions and agglomeration. All fluidized-bed oxychlorination catalysts normally exhibit some level of catalyst particle agglomeration/deagglomeration dynamics, and the severity of stickiness depends on catalyst characteristics as well as process operating conditions. Stickiness can be largely avoided by using catalyst formulations that exhibit excellent fluidization characteristics over a wide range of operating conditions (91).

Fixed-bed reactors resemble multitube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of catalyst within the tubes is important to ensure uniform pressure drop, flow, and residence time through each tube. Reaction heat can be removed by the generation of steam on the shell side of the reactor or by some other heat-transfer fluid. However, temperature control is more difficult in a fixed-bed than in a fluidized-bed reactor because localized hot spots tend to develop in the tubes. The tendency to develop hot spots can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that there is low catalyst activity at the inlet, but the activity steadily increases to a maximum at the outlet (78). Another method for minimizing hot spots is to pack the tubes with catalysts having a progressively higher loading of CuCl_2 so as to provide an activity gradient along the length of the tubes. Multiple reactors are also used in fixed bed oxychlorination, primarily to control heat release by staging the air or oxygen feed. Each successive reactor may also contain catalyst with a progressively higher loading of CuCl_2 . These methods of staging the air or oxygen feed and of grading the catalyst activity tend to flatten the temperature profile and allow improved temperature control. Compared with the fluidized-bed process, fixed-bed oxychlorination generally operates at higher temperatures (230–300°C) and gauge pressures (150–1400 kPa (22–203 psig)). Given these operating conditions, a corrosion-resistant alloy is needed for the reactor tubes, and steel tubesheets and reactor

heads need to be clad with nickel, whereas the reactor shell itself can be constructed of carbon steel.

In the air-based oxychlorination process with either a fluidized- or fixed-bed reactor, ethylene and air are fed in slight excess of stoichiometric requirements to ensure high conversion of HCl and to minimize losses of excess ethylene that remains in the vent gas after product condensation. Under these conditions, typical feedstock conversions are 94–99% for ethylene and 98–99.5% for HCl with EDC selectivities of 94–97%. Downstream product recovery involves cooling the reactor exit gases by either direct quench or with a heat exchanger, and condensation of the EDC and water, which are then separated by decantation (see Fig. 2). The remaining gases still contain 1–5 vol % EDC and hence are further processed in a secondary recovery system involving either solvent absorption or a refrigerated condenser. In air-based processes operating at high ethylene conversion, the dilute ethylene remaining in the vent is generally incinerated, but in those operating at lower conversion, various schemes are first used to recover unconverted ethylene, usually by direct chlorination to EDC (94–96).

The use of oxygen instead of air in the oxychlorination process with either a fixed- or fluidized-bed reactor permits operation at lower temperatures and results in improved operating efficiency and product yield (97). Unlike the air-based process, ethylene is generally fed in somewhat larger excess over stoichiometric requirements. The reactor exit gas is cooled, purified from traces of unconverted HCl, separated from EDC and water by condensation, recompressed to the reactor inlet pressure, reheated, and recycled to the oxychlorination reactor. Recycle of the effluent gas permits lower ethylene conversion per pass through the reactor with minimal loss in overall ethylene yield. A small amount of reactor off-gas, typically 2–5 vol %, is continuously purged from the system to prevent accumulation of impurities, eg, carbon oxides, nitrogen, argon, and unreacted hydrocarbons, which either form in the oxychlorination reactor or enter the process as impurities in the feed streams. An important advantage of oxygen-based oxychlorination technology over air-based operation is the drastic reduction in volume of the vent gas discharge. Since nitrogen is no longer present in the reactor feed streams, only a small amount of purge gas is vented. On a volume comparison, the reduced purge gas stream typically amounts to only 2–5% of the vent gas volume for air-based operation. Air-based processes release significant quantities of vent gases to the atmosphere, generally after treatment by incineration and scrubbing. Typically, for every kilogram of EDC produced by oxychlorination, ca 0.7–1.0 kg of vent gas is emitted from the air-based process (see Table 2). Therefore, for an air-based, balanced vinyl chloride plant with a rated capacity of 450,000 metric tons of vinyl chloride per year, the total vent gas volume released to the atmosphere would be 70–100 m³/s (2,450–3,530 ft³/s). However, the vent gas consists mainly of nitrogen, some unconverted oxygen, and small amounts of carbon oxides. Depending on the type of oxychlorination process involved, however, there are differing levels of undesirable impurities, ethylene, and chlorinated hydrocarbons in the oxychlorination vent gas.

Chlorinated by-products of ethylene oxychlorination typically include 1,1,2-trichloroethane; chloral [75-87-6] (trichloroacetaldehyde); trichloroethylene [7901-6]; 1,1-dichloroethane; *cis*- and *trans*-1,2-dichloroethylenes [156-59-2 and 156-60-5]; 1,1-dichloroethylene [75-35-4] (vinylidene chloride); 2-chloroethanol

[107-07-3]; ethyl chloride; vinyl chloride; mono-, di-, tri-, and tetrachloromethanes (methyl chloride [74-87-3], methylene chloride [75-09-2], chloroform, and carbon tetrachloride [56-23-5]); and higher boiling compounds. The production of these compounds should be minimized to lower raw material costs, lessen the task of EDC purification, prevent fouling in the pyrolysis reactor, and minimize by-product handling and disposal. Of particular concern is chloral, because it polymerizes in the presence of strong acids. Chloral must be removed to prevent the formation of solids which can foul and clog operating lines and controls (78).

Oxychlorination reactor feed purity can also contribute to by-product formation, although the problem usually is only with low levels of acetylene which are normally present in HCl from the EDC cracking process. Since any acetylene fed to the oxychlorination reactor will be converted to highly chlorinated C₂ by-products, selective hydrogenation of this acetylene to ethylene and ethane is widely used as a preventive measure (78,98–102).

4.3. Purification of Ethylene Dichloride for Pyrolysis. By-products contained in EDC from the three main processes must be largely removed prior to pyrolysis. These include by-products from direct chlorination and oxychlorination, and in the recovered, unreacted EDC from the cracking process. EDC used for pyrolysis to vinyl chloride must be of high purity, typically greater than 99.5 wt %, because the cracking process is highly susceptible to inhibition and fouling by trace quantities of impurities (78). It must also be dry (less than 10 ppm water) to prevent excessive corrosion downstream. Inadvertent moisture pickup, however, is always possible. In such cases, the corrosion of steel equipment tends to be greatest in reboilers, the bottom section of distillation columns, bubble caps, plates, condensers, water separators, valves, pumps, and fittings.

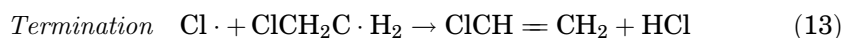
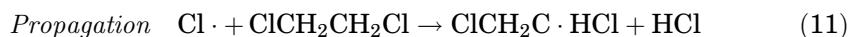
Direct chlorination usually produces EDC with a purity greater than 99.5 wt %, so that, except for removal of the FeCl₃, little further purification is necessary. Ferric chloride can be removed by adsorption of a solid, or the EDC can be distilled from the FeCl₃ in a boiling reactor, as noted above. Alternatively, the FeCl₃ can be removed by washing with water, usually in conjunction with EDC from the oxychlorination process.

EDC from the oxychlorination process is less pure than EDC from direct chlorination and requires purification by distillation. It is usually first washed with water and then with caustic solution to remove chloral and other water-extractable impurities (103). Subsequently, water and low boiling impurities are taken overhead in a first (light ends or heads) distillation column, and finally, pure, dry EDC is taken overhead in a second (heavy ends or product) column (see Fig. 2).

Unreacted EDC recovered from the pyrolysis product stream contains a variety of cracking by-products. A number of these, eg, trichloroethylene, chloroprene, and benzene, are not easily removed by simple distillation and require additional treatment (78). Chloroprene can build up in the light ends column where it can polymerize and cause serious fouling. Benzene boils very close to EDC, as does trichloroethylene, which also forms an azeotrope with EDC. If allowed to accumulate in the recovered EDC, these by-products can inhibit the cracking reaction and increase coking rates. Because they are all unsaturated, they can be converted to higher boiling compounds for easy separation by

subjecting the recovered EDC stream to chlorination prior to distillation (104–107). Chloroprene can also be removed by treatment with HCl and by hydrogenation.

4.4. Ethylene Dichloride Pyrolysis to Vinyl Chloride. Thermal pyrolysis or cracking of EDC to vinyl chloride and HCl occurs as a homogenous, first-order, free-radical chain reaction. The accepted general mechanism involves the four steps shown in equations 10–13:



The overall, net reaction is given in equation 2. Reactions 11 and 12 are the chain propagation steps, because each elementary step consumes one of the two chain carriers and simultaneously produces the other. The net effect of reactions 11 and 12 is continuation of the chain by conversion of EDC to vinyl chloride. Thus, the two chain carriers are chlorine atoms and 1,2-dichloroethyl radicals [23273-86-1]. In general, anything that consumes a chain carrier is an EDC cracking inhibitor, and anything that produces a chain carrier is a promoter. Therefore, any molecular or radical species that consumes a chain carrier without simultaneously producing either 1,2-dichloroethyl radicals or chlorine atoms is an EDC cracking inhibitor, eg, propylene [115-07-1]. The allylic hydrogen atoms of propylene can be easily abstracted by one of the chain carriers, either 1,2-dichloroethyl radicals or chlorine atoms. The resulting allyl radical can then combine with a chlorine atom forming allyl chloride [107-05-1]. Because the same sequence can occur two more times, one molecule of propylene can consume up to six chain carriers. Reaction initiators or accelerators include carbon tetrachloride, chlorine, bromine [7726-95-6], iodine [7553-56-2], or oxygen, although exclusion of oxygen is claimed to result in considerably less fouling on the pyrolysis tube walls. Carbon tetrachloride, a minor by-product of the oxychlorination process, is often controlled in the EDC purification step to allow a small amount to enter the EDC feed as a cracking promoter in the pyrolysis process.

The endothermic cracking of EDC ($\Delta H = 71$ kJ/mol EDC reacted for eq. 2, Ref. 83) is relatively clean at atmospheric pressure and at temperatures of 425–550°C. Commercial pyrolysis units, however, generally operate at gauge pressures of 1.4–3.0 MPa (200–435 psig) and at temperatures of 475–525°C to provide for better heat transfer and reduced equipment size, and to allow separation of HCl from vinyl chloride by fractional distillation at noncryogenic temperatures. EDC conversion per pass through the pyrolysis reactor is normally maintained at 53–63%, with a residence time of 2–30 s. Cracking reaction selectivity to vinyl chloride of >99% can be achieved at these conditions. Increasing cracking severity beyond this level gives progressively smaller increases in EDC conversion, with progressively lower selectivity to vinyl chloride, since some of

the by-products generated during pyrolysis act as cracking inhibitors. Higher conversion also increases pyrolysis tube coking rates and causes problems with downstream product purification. To minimize coke formation, it is necessary to quench or cool the pyrolysis reactor effluent quickly. Substantial yield losses to heavy ends and tars can occur if cooling is done too slowly. Therefore, the hot effluent gases are normally quenched and partially condensed by direct contact with cold EDC in a quench tower. Alternatively, the pyrolysis effluent gases can first be cooled by heat exchange with cold liquid EDC furnace feed in a transfer line exchanger (TLE) prior to quenching in the quench tower. In this case, application of a TLE to preheat and vaporize incoming EDC furnace feed saves energy by decreasing the amount of fuel gas required to fire the cracking furnace and/or steam needed to vaporize the feed.

By-products from EDC pyrolysis typically include acetylene, ethylene, methyl chloride, ethyl chloride, 1,3-butadiene, vinylacetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane [71-55-6], and other chlorinated hydrocarbons (78). Most of these impurities remain with the unconverted EDC, and are subsequently removed in EDC purification as light and heavy ends. The lightest compounds, ethylene and acetylene, are taken off with the HCl and end up in the oxychlorination reactor feed. The acetylene can be selectively hydrogenated to ethylene. The compounds that have boiling points near that of vinyl chloride, ie, methyl chloride and 1,3-butadiene, will codistill with the vinyl chloride product. Chlorine or carbon tetrachloride addition to the pyrolysis reactor feed has been used to suppress methyl chloride formation, whereas 1,3-butadiene, which interferes with PVC polymerization, can be removed by treatment with chlorine or HCl, or by selective hydrogenation.

Although there are minor differences in the HCl–vinyl chloride recovery section from one vinyl chloride producer to another, in general, the quench column effluent is distilled to remove first HCl and then vinyl chloride (see Fig. 2). The vinyl chloride is usually further treated to produce specification product, recovered HCl is sent to the oxychlorination process, and unconverted EDC is purified for removal of light and heavy ends before it is recycled to the cracking furnace. The light and heavy ends are either further processed, disposed of by incineration or other methods, or completely recycled by catalytic oxidation with heat recovery followed by chlorine recovery as EDC (76).

A process to produce VM from a raw product derived by pyrolysis has been reported (108).

4.5. By-Product Disposal. By-product disposal from vinyl chloride manufacturing plants is complicated by the need to process a variety of gaseous, organic liquid, aqueous, and solid streams, while ensuring that no chlorinated organic compounds are inadvertently released. Each class of by-product streams poses its own treatment and disposal challenges.

Gaseous vent streams from the different unit operations may contain traces (or more) of HCl, CO, methane, ethylene, chlorine, and vinyl chloride. These can sometimes be treated chemically, or a specific chemical value can be recovered by scrubbing, sorption, or other method when economically justified. For objectionable components in the vent streams, however, the common treatment method is

either incineration or catalytic combustion, followed by removal of HCl from the effluent gas.

Organic liquid streams include the light and heavy ends from EDC purification (see Fig. 2 and Table 2). The light ends typically consist of ethyl chloride, *cis*- and *trans*-1,2-dichloroethylene, chloroform, and carbon tetrachloride. The heavy ends are mainly composed of 1,1,2-trichloroethane, lesser amounts of tetrachloroethanes, chlorinated butanes, and chlorinated aromatics, and many other chlorinated compounds present at small concentrations. If there is economic justification, these streams can be fractionated to recover specific, useful components, and the remainder subsequently incinerated and scrubbed to remove HCl. An alternative method involves combining all liquid by-product streams and passing them along with air or oxygen-enriched air into a fluidized bed, catalytic oxidation reactor (76). The resulting combustion product stream, consisting essentially of HCl, CO₂, H₂O, O₂, and N₂, is fed directly into an oxychlorination reactor where the HCl content is recovered as EDC. Furthermore, the heat of combustion is recovered as high pressure steam in a manner similar to that in fluidized-bed oxychlorination processes. In addition, there is no direct vent to the atmosphere, and any unconverted chlorinated organic material is recovered in the crude EDC from the oxychlorination process and ultimately recycled back to the catalytic oxidation unit. Minor drawbacks to this process include increased inerts loading and the potential for carryover of entrained oxidation catalyst into the oxychlorination reactor.

Process water streams from vinyl chloride manufacture are typically steam-stripped to remove volatile organics, neutralized, and then treated in an activated sludge system to remove any nonvolatile organics. If fluidized-bed oxychlorination is used, the process wastewater may also contain suspended catalyst fines and dissolved metals. The former can easily be removed by sedimentation, and the latter by precipitation. Depending on the specific catalyst formulation and outfall limitations, tertiary treatment may be needed to reduce dissolved metals to acceptable levels.

Solid by-products include sludge from wastewater treatment, spent catalyst, and coke from the EDC pyrolysis process. These need to be disposed of in an environmentally sound manner, eg, by sludge digestion, incineration, landfill, etc.

5. Technology Trends

The ethylene-based, balanced vinyl chloride process, which accounts for nearly all capacity worldwide, has been practiced by a variety of vinyl chloride producers since the mid-1950s. The technology is mature, so that the probability of significant changes is low. New developments in production technology will likely be based on incremental improvements in raw material and energy efficiency, environmental impact, safety, and process reliability.

More recent trends include widespread implementation of oxygen-based oxychlorination, further development of new catalyst formulations, a broader range of energy recovery applications, a continuing search for ways to improve conversion and minimize by-product formation during EDC pyrolysis, and chlor-

ine source flexibility. In addition, the application of computer model-based process control and optimization is growing as a way to achieve even higher levels of feedstock and energy efficiency and plant process reliability.

Nearly all oxychlorination processes built since 1990 are oxygen-based, and many existing, air-based units are being retrofitted for pure oxygen feed. This is the result of significant advantages of oxygen-over air-based operation, described above. The greatest benefit is drastic reduction (over 95%) in the volume of vent gas discharged by the process, making destruction of any environmentally objectionable compounds in this stream more manageable. Savings in ethylene and chlorine feedstock, incineration, and air compression costs can more than offset the oxygen raw material cost. For existing, air-based plants, the decision whether to convert to oxygen depends on local emission standards, oxygen availability and cost, electrical energy cost, and the viability of alternative, add-on processes for cleaning the vent stream, eg, catalytic oxidation or sorption methods.

New catalyst developments have steadily progressed, especially for ethylene oxychlorination (91,109), so that the remaining potential increases in reactor productivity and feedstock efficiency keep shrinking. Nevertheless, there is still room for further catalyst improvements. Direct chlorination, for example, would benefit from a catalyst that provides increased reaction selectivity to EDC and minimizes by-product formation at the higher temperatures required for boiling reactors. A catalyst that is more resistant to poisoning by the metals content of by-product streams, eg, iron from direct chlorination, sodium from caustic washing, tramp metals from corrosion, etc, would improve the performance of catalytic hydrogenation and oxidation processes.

The search for new EDC cracking promoters and by-product inhibitors (110–113) and for improved feed purification methods is expected to continue. Since current cracking technology limits EDC conversion to 55–65%, considerable energy and cost savings would be realized if conversion could be increased without concurrent loss of EDC to undesirable side reactions and coking. Laser-induced EDC cracking has been studied as a way to promote thermal cracking (114–117). At temperatures comparable to those used in commercial pyrolysis reactors, laser-induced cracking is claimed to increase conversion while decreasing by-product formation. However, commercial application at the current state of development appears unlikely. Periodic furnace decoking is still normally accomplished thermally by controlled air/stream oxidation. However, shot peen and catalytic decoking are two more recent alternative methods aimed at faster turnaround times and less thermal stress on the cracking furnaces.

Tightness of the chlorine market, which was accompanied by rising chlorine prices, sparked interest in alternative sources of chlorine, ie, HCl and EDC, where these are available. Some plants no longer operate in a strictly balanced mode, but instead operate with more than half of their EDC made from oxychlorination (owing to importation of HCl or EDC as a chlorine source, thus bypassing direct chlorination). The ideal situation is one in which the plant can adapt to any feed combination, allowing operation at the optimum mix of feedstocks as determined by minimization of the sum of raw material and operating costs (118–120).

Alternatives to oxychlorination have also been proposed as part of a balanced VCM plant. In the past, many vinyl chloride manufacturers used a balanced ethylene–acetylene process for a brief period prior to the commercialization of oxychlorination technology. Addition of HCl to acetylene was used instead of ethylene oxychlorination to consume the HCl made in EDC pyrolysis. Since the 1950s, the relative costs of ethylene and acetylene have made this route economically unattractive. Another alternative is HCl oxidation to chlorine, which can subsequently be used in direct chlorination (121). Processes recently developed are among the available commercial HCl oxidation technologies (122–125). Each has had very limited industrial application, perhaps because the equilibrium reaction is incomplete and the mixture of HCl, O₂, Cl₂, and water presents very challenging separation, purification, and handling requirements. HCl oxidation does not compare favorably with oxychlorination because it also requires twice the direct chlorination capacity for a balanced vinyl chloride plant. Consequently, it is doubtful that it will ever displace oxychlorination in the production of vinyl chloride by the balanced ethylene process.

If the production of vinyl chloride could be reduced to a single step, such as direct chlorine substitution for hydrogen in ethylene or oxychlorination/cracking of ethylene to vinyl chloride, a major improvement over the traditional balanced process would be realized. The literature is filled with a variety of catalysts and processes for single-step manufacture of vinyl chloride (109,126–128). None has been commercialized because of the high temperatures, corrosive environments, and insufficient reaction selectivities so far encountered. Substitution of lower cost ethane or methane for ethylene in the manufacture of vinyl chloride has also been investigated. The Lummus-Transcat process (129), for instance, proposes a molten oxychlorination catalyst at 450–500°C to react ethane with chlorine to make vinyl chloride directly. However, ethane conversion and selectivity to vinyl chloride are too low (30% and less than 40%, respectively) to make this process competitive. Numerous other catalysts and processes have been patented as well, but none has been commercialized owing to problems with temperature, corrosion, and/or product selectivity (130–134). Because of the potential payback, however, this is a very active area of research.

6. Economic Aspects

Vinyl chloride monomer (VCM) is used primarily in the production of poly(vinyl chloride) (PVC) homopolymer and copolymers. In 2002, 27×10^6 t of vinyl chloride was consumed in manufacturing PVC (135).

Vinyl chloride is a global product and is manufactured in about fifty countries (135). Table 3 gives production data for the U.S. and Canada for 2003 (75).

Consumption of vinyl chloride is expected to increase at an annual rate of 3.5% globally through 2007. The United States growth is expected at 2.8%. The largest growth will occur in Asia.

The market is under pressure from high energy and feedstock costs that impact ethylene dichloride, from which vinyl chloride is made. Stricter water management regulations should favor PVC pipe in the United States. New

resin grades and compounds are driving the use of PVC in other applications where metal, wood, concrete, and glass are used.

7. Specifications

Polymerization-grade vinyl chloride should not contain more than the amounts of impurities listed in Table 4 (136).

8. Environmental Considerations

Since the early 1980s, there has been much debate among environmental activist organizations, industry, and government about the impact of chlorine chemistry on the environment (136,137). One aspect of this debate involves the incidental manufacture and release of trace amounts of hazardous compounds such as polychlorinated dibenzodioxins, dibenzofurans, and biphenyls (PCDDs, PCDFs, and PCBs, respectively, but often referred to collectively as dioxins) during the production of chlorinated compounds like vinyl chloride. Initial concerns were prompted by the acute animal toxicity of 2,3,7,8-tetrachlorodibenzodioxin [1746-01-6] (TCDD) and 2,3,7,8-tetrachlorodibenzofuran [51207-31-9] (TCDF). More recently, the focus has shifted to the reported estrogen mimic capabilities of dioxins (136). In 1994, the EPA released a review draft of its reassessment of the impact of dioxins in the environment on human health, which prompted speculation as to the amount of dioxins that might be attributed to chlorine-based industrial processes (138). The U.S. vinyl industry responded to this document by committing to a voluntary characterization of dioxin levels in its products and in emissions from its facilities to the environment. The results of this study to date support the vinyl industry's position that it is a minor source of dioxins in the environment (139). Furthermore, a recent process model analysis of a vinyl chloride purification distillation unit demonstrated that, owing to the roughly 500°C boiling point difference between vinyl chloride and TCDD, any incidentally manufactured TCDD would be quantitatively removed from the vinyl chloride product (140). In addition, a global benchmark study released by the American Society of Mechanical Engineers found no relationship between the chlorine content of waste and dioxin emissions from combustion processes (141). Reviews of this issue and other environmental considerations related to vinyl chloride production are available (136,137,142).

Because of the toxicity of vinyl chloride, the EPA in 1975 proposed the following emission standards for vinyl chloride manufacture: (1) emissions from all point sources except oxychlorination would be limited to 10 ppm vinyl chloride; (2) emissions from the oxychlorination process would be limited to 0.02 kg vinyl chloride per 100 kg EDC produced by oxychlorination; (3) no preventable relief valve discharges would be allowed; and (4) fugitive emissions would be minimized by enclosing emission sources and collecting all emissions (143). This proposal was subsequently enacted as EPA Regulation 40 CFR 61, Subpart F (144). Compliance testing began in 1978. Additional EPA and state actions were initiated in 1977 to reduce hydrocarbon emissions from vinyl chloride plants in

nonattainment regions. These were aimed primarily at lowering the ethylene content of vent streams from air-based oxychlorination units (78).

Environmental concerns and government regulations have prompted a major increase in the amount of add-on technology used in U.S. vinyl chloride production plants. Primary and redundant incineration facilities for all vinyl chloride point source and collected fugitive emissions are needed to ensure compliance. The incinerators are typically equipped with HCl scrubbing and neutralization or recovery units. Process sewers and sewage collection systems are closed. Larger and/or redundant strippers are used to remove trace organics from wastewater. Dual mechanical seals on pumps and agitators are required. Other common emissions control and reduction measures include vinyl chloride and EDC leak-detection systems and portable monitors, enclosed sampling and analytical systems, and vapor recovery systems for vinyl chloride loading and unloading and equipment cleaning (78).

8.1. Regulation of Vinyl Chloride. In 1974, the U.S. Congress passed the Safe Drinking Water Act. This law requires EPA to determine safe levels of chemicals in drinking water which may not cause health problems. These non-enforceable levels, based solely on possible health risks and exposure, are called Maximum Contaminant Level Goals (MCLG) (145).

The MCLG for vinyl chloride has been set at zero because EPA believes this level of protection would not cause any of the potential health problems described below. Based on this MCLG, EPA has set an enforceable standard called a Maximum Contaminant Level (MCL). MCLs are set as close to the MCLGs as possible, considering the ability of public water systems to detect and remove contaminants using suitable treatment technologies. The MCL has been set at 2 parts per billion (ppb) because EPA believes, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water.

These drinking water standards and the regulations for ensuring these standards are met, are called National Primary Drinking Water Regulations. All public water supplies must abide by these regulations.

Production of vinyl chloride in 1993 was nearly 14 billion lbs. Its major release to the environment would be as emissions and wastewater at poly(vinyl chloride) (PVC) plastics production and manufacturing facilities. Small quantities of vinyl chloride can be released to food since it is used to make many food wrappings and containers.

Vinyl chloride released to soil will either quickly evaporate, be broken down by microbes or may leach to the groundwater. It also rapidly evaporates from water, but does not degrade there. It will not accumulate in aquatic life.

Vinyl Chloride Detection and Removal from Drinking Water. The regulation for vinyl chloride became effective in 1989. Between 1993 and 1995, EPA required water suppliers to collect water samples every three months for one year and analyze them to find out if vinyl chloride is present above 0.5 ppb. If it is present above this level, the system must continue to monitor this contaminant.

Drinking water standards are MCLG: zero, MCL: 0.002 mg/L, or 2 parts per billion.

If contaminant levels are found to be consistently above the MCL, the water supplier must take steps to reduce the amount of vinyl chloride so that it is

consistently below that level. The following treatment methods have been approved by EPA for removing vinyl chloride: Granular activated charcoal in combination with Packed Tower Aeration (145).

If the levels of vinyl chloride exceed the MCL, 2 ppb, the system must notify the public via newspapers, radio, TV and other means. Additional actions, such as providing alternative drinking water supplies, may be required to prevent serious risks to public health.

9. Health and Safety Factors

Vinyl chloride is an OSHA-regulated substance (146). Current OSHA regulations impose a permissible exposure limit (PEL) to vinyl chloride vapors of no more than 1.0 ppm averaged over any 8-h period. Short-term exposure is limited to 5.0 ppm averaged over any 15-min period. Contact with liquid vinyl chloride is prohibited. Monitoring is required at all facilities where vinyl chloride is produced or PVC is processed. OSHA regulations also define an action level of 0.5 ppm, 8-h time-weighted average. Employers must demonstrate that monitoring results show exposure below the action level of 0.5 ppm on subsequent readings taken not less than five working days apart in order to discontinue monitoring. Where concentrations cannot be lowered below the 1.0-ppm PEL, the employer must establish a regulated area with controlled access, a respirator program conforming to paragraph g of the OSHA standard (146), and a written plan to reduce vinyl chloride levels. OSHA regulations require facilities that handle vinyl chloride to develop a medical surveillance program with annual physical examinations and blood serum analyses for all employees exposed at levels above the action level. Surveillance frequency increases to semiannually for these employees when they attain 10 or more years of service in the manufacture of vinyl chloride.

Contact with liquid vinyl chloride can cause frostbite. Chronic exposure to vinyl chloride at concentrations of 100 ppm or more is reported to have produced Raynaud's syndrome, lysis of the distal bones of the fingers, and a fibrosing dermatitis. However, these effects are probably related to continuous intimate contact with the skin. Chronic exposure is also reported to have produced a rare cancer of the liver (angiosarcoma) in a small number of workers after continued exposure for many years to large amounts of vinyl chloride gas (147). Consequently, the vinyl industry worked in conjunction with government regulatory agencies to develop the much more stringent hygiene standards that exist. Toxicology data on vinyl chloride, eg, TC_{Lo} (human), TC_{Lo} (rat), LD_{50} (rat), and threshold limit values, are reported in Reference 148. Vinyl chloride monomer is listed as a cancer-suspect agent by OSHA (146). The American Conference of Governmental Industrial Hygienists (ACGIH) calls it a confirmed human carcinogen, while the National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC) both regard it as a human carcinogen (149).

Vinyl chloride also poses a significant fire and explosion hazard. It has a wide flammability range, from 3.6 to 33.0% by volume in air (150). Large fires of the compound are very difficult to extinguish, while vapors represent a severe

explosion hazard. Vapors are more than twice as dense as air and tend to collect in low lying areas, increasing the risk of fire. Workers entering these low lying areas risk suffocation, which can occur at levels above 18,000 ppm. The mild, sweet odor of vinyl chloride becomes detectable around 260 ppm (151).

Vinyl chloride is generally transported via pipeline, and in railroad tank cars and tanker ships. Containers of vinyl chloride must be labeled “vinyl chloride,” “extremely flammable gas under pressure,” and “cancer-suspect agent” (146). Because hazardous peroxides can form on standing in air, especially in the presence of iron impurities, vinyl chloride should be handled and transported under an inert atmosphere. The presence of peroxide from vinyl chloride and air can initiate polymerization of stored vinyl chloride; however, stabilizer can be added to prevent polymerization. Inhibitors such as hydroquinone [123-31-9] are often added, particularly when shipping long distances in warmer climates.

Vinyl chloride is listed as “ethene, chloro-” on the Toxic Substances Control Act (TSCA) inventory and on the Canadian Domestic Substances List (DSL). It is listed as “chloroethylene” on the European Inventory of Existing Commercial Chemical Substances (EINECS), bearing the identification number 2008 310 (149).

10. Uses

Vinyl chloride has gained worldwide importance because of its industrial use as the precursor to PVC. It is also used in a wide variety of copolymers. The inherent flame-retardant properties, wide range of plasticized compounds, and low cost of polymers from vinyl chloride have made it a major industrial chemical. About 95% of current vinyl chloride production worldwide ends up in polymer or copolymer applications (75,83). Vinyl chloride also serves as a starting material for the synthesis of a variety of industrial compounds, as suggested by the number of reactions in which it can participate, although none of these applications will likely ever come anywhere near PVC in terms of volume. The primary nonpolymeric uses of vinyl chloride are in the manufacture of vinylidene chloride, vinyl stearate and tri- and tetrachloroethylene [127-18-4] (75,83).

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Table 1. Physical Properties of Vinyl Chloride^a

Property	Value
molecular weight	62.4985
melting point (1 atm), K	119.36
boiling point (1 atm), K	259.25
heat capacity at constant pressure, J/(mol·K) ^b	
vapor at 20°C	53.1
liquid at 20°C	84.3
critical temperature, K	432
critical pressure, MPa ^c	5.67
critical volume, cm ³ /mol	179
critical compressibility	0.283
acentric factor	0.100107
dipole moment, C·m	4.84×10^{-30}
enthalpy of fusion (melting point), kJ/mol ^b	4.744
enthalpy of vaporization (298.15 K), kJ/mol ^b	20.11
enthalpy of formation (298.15 K), kJ/mol ^b	28.45
Gibbs energy of formation (298.15 K), kJ/mol ^b	41.95
vapor pressure, kPa ^c	
−30°C	49.3
−20°C	78.4
−10°C	119
0°C	175
viscosity, mPa·s	
−40°C	0.345
−30°C	0.305
−20°C	0.272
−10°C	0.244
explosive limits in air, vol %	
lower limit	3.6
upper limit	33
autoignition temperature, K	745

^aRef. 12.^bTo convert J to cal, divide by 4.184.^cTo convert MPa to psi, multiply by 145.

Components, kg	Raw materials	Interme- diates	By- products	Aqueous streams	Vent streams			Product
					Direct chlorination ^a	Oxychlori- nation	Distillation columns	
C ₂ H ₄	0.4656				0.0025			
Cl ₂	0.5871				0.0001		0.0001	
N ₂	0.5782					0.5779	0.0003	
O ₂	0.1537					0.0214		
CO ₂	0.0003					0.0116		
CO						0.0032		
ClCH ₂ CH ₂ Cl		1.6370 ^b	0.0029		0.0016	0.0017	0.0045	
HCl		0.6036						
H ₂ O	0.0171		0.1438	0.1196		0.0413		
NaOH				0.0008				
NaCl				0.0014				
lights			0.0029		0.0003	0.0025		
heavies			0.0023					
CH ₂ =CHCl			0.0008		0.0001	0.0012	0.0024	1.0000
Total, kg/kg vinyl chloride	1.8020	2.2406	0.1527	0.1218	0.0046	0.6608	0.0073	1.0000

^aInerts present in chlorine feed are emitted in this vent stream.

^bRepresents EDC necessary for a stoichiometric balance, including that converted to by-products, but no recycled EDC.

Table 3. U.S. and Canadian Producers of Vinyl Chloride and Their Capacities^a

Producer	Location	Capacity, $\times 10^3$ t
<i>United States</i>		
Dow Chemical	Oyster Creek Freeport, Tex.	1225
Dow Chemical	Plaquemine, La.	680
Formosa Plastics	Baton Rouge, La.	445
Formosa Plastics	Point Comfort, Tex.	560
Geismar Vinyls	Geismar, La. (idle)	295
Georgia Gulf	Lake Charles, La.	454
Georgia Gulf	Plaquemine, La.	726
OxyMar	Ingleside, Tex.	1043
Oxy Vinyls	Deer Park, Tex.	590
Oxy Vinyls	LaPorte, Tex.	1088
PHH Monomers	Lake Charles, La.	590
Westlake Monomers	Calvert City, Ky.	544
<i>U.S. Total</i>		<i>8240</i>
<i>Canada</i>		
Dow Chemical	Fort Saskatchewan, Alberta	544
<i>Canada Total</i>		<i>544</i>
<i>Total</i>		<i>8784</i>

^aRef. 75.

Table 4. Typical Impurity Levels in Monomer Grade Vinyl Chloride^a

Impurity	Maximum level, ppm
acetylene	0.5–2.0
acidity, as HCl, by wt	0.1–1.0
acetaldehyde	0.4–1.0
alkalinity, as NaOH, by wt	0.25
1,3-butadiene	8–12
ethyl chloride	35
EDC	10
iron, as Fe, by wt	0.15–0.4
methyl chloride	60–75
vinyl acetylene	10
water	100
nonvolatiles	25–50
total C ₄ unsaturates	40
oxygen in vapor space after loading	200–1,000
vinyl chloride, wt %	99.96–99.98 ^b

^aRef. 136.^bMinimum vinyl chloride content.

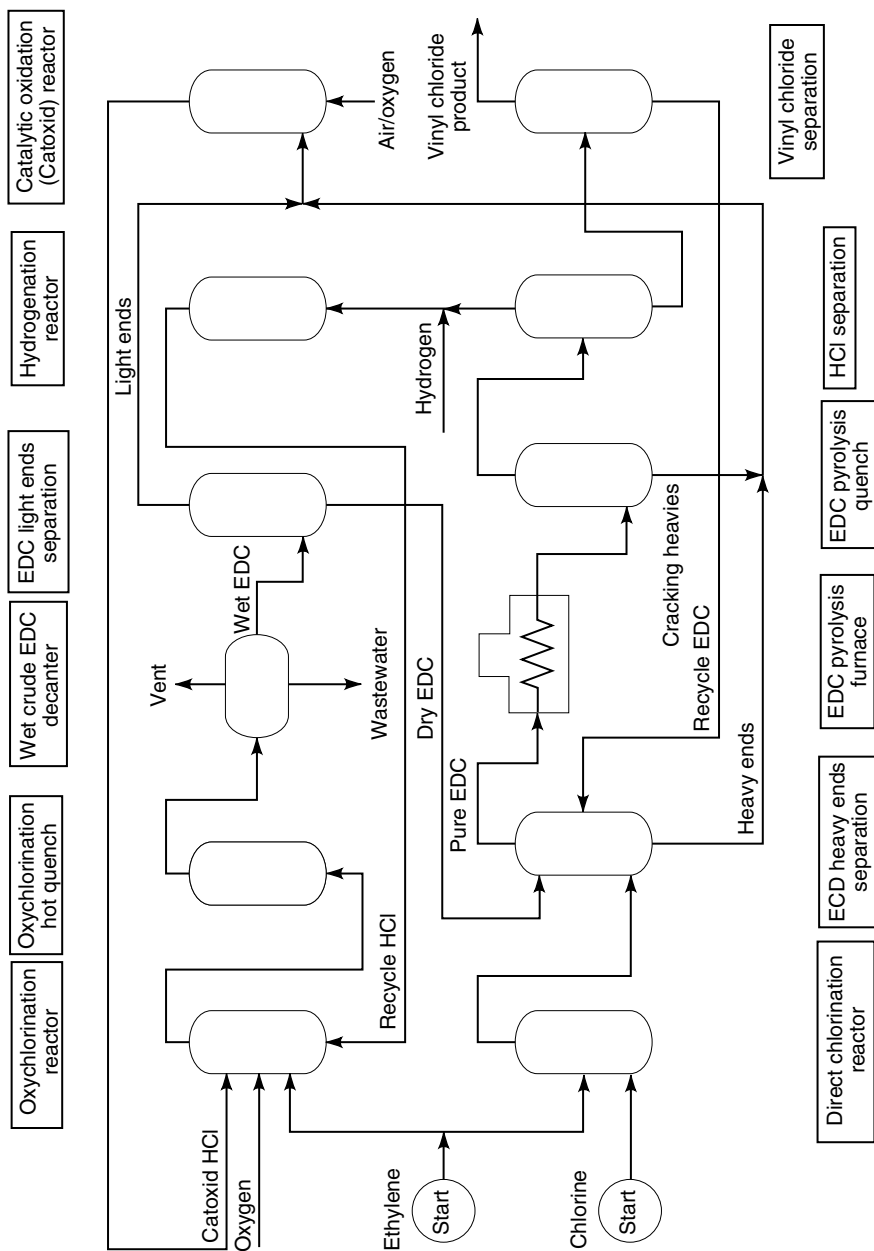


Fig. 2. Typical (Geon) balanced vinyl chloride process with oxygen-based oxychlorination (76).