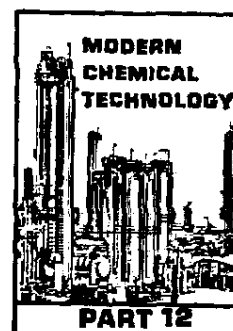


Vinyl Chloride Processes



Conversion of acetylene by hydrochlorination to vinyl chloride or that of ethylene by vapor-phase or liquid-phase chlorination to dichloroethane, followed by pyrolysis to vinyl chloride, are fundamental reactions for its manufacture by different processes or their combinations.

LYLE F. ALBRIGHT, *Purdue University*

Large-scale production of vinyl chloride in the U.S. reflects important process developments of the last few years. To understand this growth, we will consider in this article the current information for these developments. In later articles of this series, we will continue the discussion on vinyl chloride production and also review that for polyvinyl chloride.

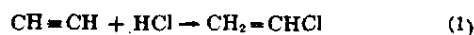
Several combinations of chemical reactions are used in commercial units in order to obtain the best over-all economics. Reactants for these operations include: (a) acetylene and/or ethylene, and (b) hydrogen chloride and/or chlorine. Vinyl chloride is now produced for as low as 5¢/lb., or even less in some of the newer processes.

Relatively small plants for vinyl chloride probably cannot compete economically with newer and larger units. It is thought to be only a matter of time before smaller plants are shut down or enlarged. The trend in the U.S., in particular, has been to large units, some of which have capacities greater than 300 million lb./yr.^{6, 9} Announcement has just been made by B. F. Goodrich Co. that its plant of over 500 million lb./yr. will be expanded to 1 billion lb./yr. by 1968.

Decreased cost and new developments in polymerization of vinyl chloride are expected to reduce significantly the production cost of polyvinyl chloride polymers.

General Chemistry of the Reaction

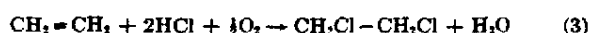
Vinyl chloride is produced from acetylene and hydrogen chloride in the presence of a catalyst as follows:



When ethylene is the starting hydrocarbon, it is

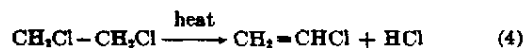
To meet the author, see *Chem. Eng.*, Feb. 13, 1967, p. 164.

chlorinated or oxychlorinated to produce 1,2-dichloroethane by the following catalytic reactions:



Reaction (2), the chlorination reaction, is practiced commercially in both the vapor phase and the liquid phase. Each method will be discussed in this article.

Pyrolysis of dichloroethane produces both vinyl chloride and hydrogen chloride:



Hydrogen chloride from Reaction (4) can be used as the reactant in Reaction (1) or (3). All of the above four reactions occur with relatively few side reactions, i.e., they have high yields.

Attempts have been made to produce vinyl chloride from ethylene by substitutive chlorination of ethylene as follows:

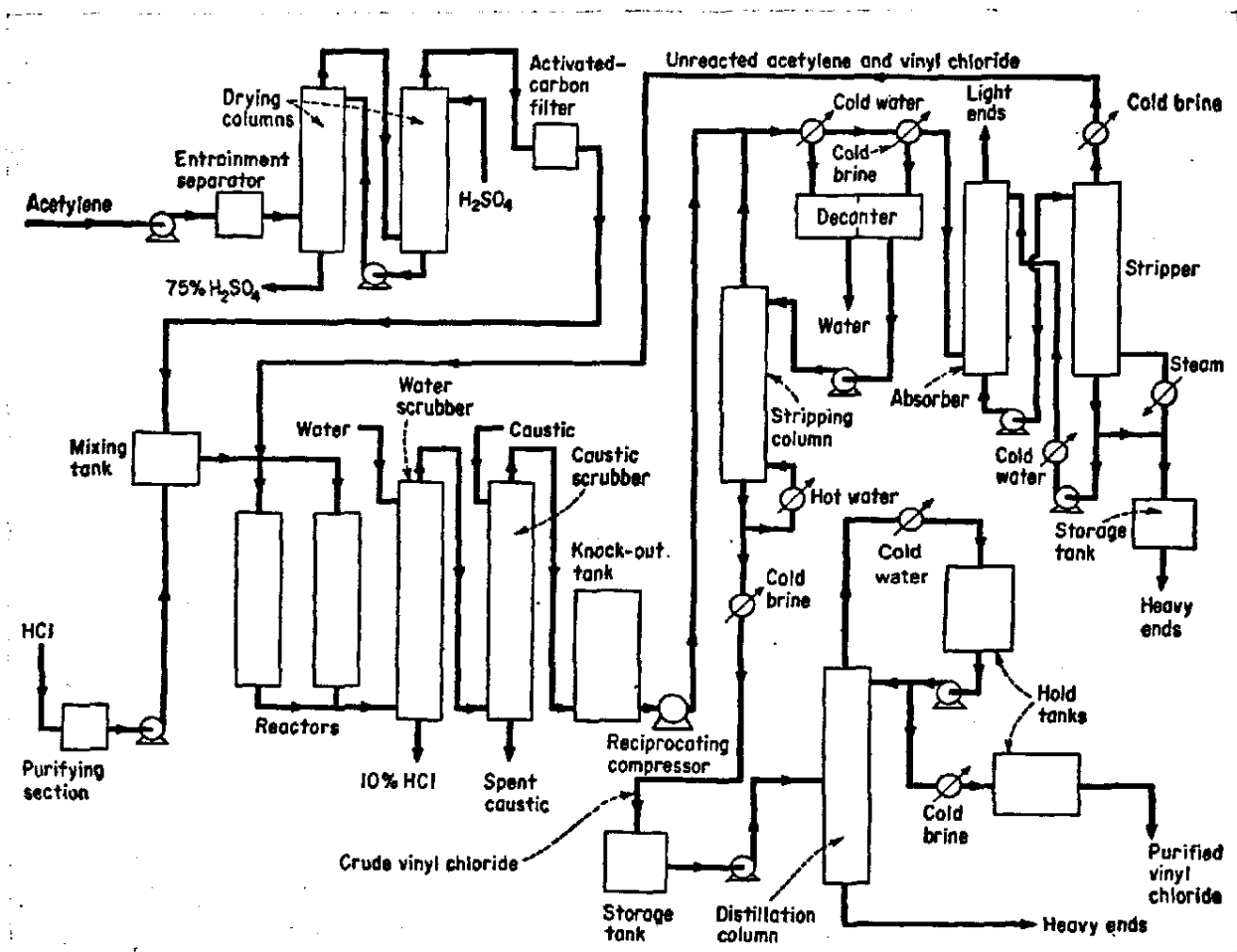


However, yields for such a reaction have been too low for commercial adaptation. Some industrial representatives believe that such a process may yet be developed.

Production of vinyl chloride from acetylene [Reaction (1)] has been the principal method until very recently. The flowsheet for such a plant is shown in Fig. 1, and it will be considered in detail later in this article.

Other commercial methods of producing vinyl chloride involve two or more of the above reactions. One example involves the chlorination of ethylene [Reaction (2)] as a first step, followed by a pyrolysis step [Reaction (4)]. About half of the chlorine ends up in the vinyl chloride, and about half produces hydrogen chloride. Companies that have a large captive use for

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HYDROCHLORINATION of pure acetylene is one commercial route for vinyl chloride production—Fig. 1

hydrogen chloride may find this two-step method of making vinyl chloride attractive.

A balanced process that uses essentially equal moles of relatively pure ethylene and acetylene has been used by several companies. In this process, there is a combination of Reactions (2), (4) and (1). All (or essentially all) of the chlorine eventually ends up in vinyl chloride because the hydrogen chloride from Reaction (4) is used in Reaction (1).

Relatively new and somewhat similar balanced processes have been developed by the Societe Belge de L'Azote (S.B.A.),^{4, 5} and by Kureha Chemical Industry Co., Ltd. of Japan.^{18, 20} In these processes, a hydrocarbon feedstream that contains essentially equal moles of acetylene and ethylene (produced by pyrolysis of naphtha) is reacted first with hydrogen chloride to remove essentially all of the acetylene. The remainder of the hydrocarbon stream that contains ethylene is now reacted with chlorine. The resulting dichloroethane is separated and then pyrolyzed. This method is relatively unique compared to several previous balanced processes in that no attempt is made to use pure

ethylene or acetylene. In other words, the acetylene and ethylene in the effluent stream from the naphtha pyrolysis do not have to be separated. Such a separation step is relatively expensive.

Several processes have recently been developed in which one of the chemical steps is oxychlorination of ethylene. The first step in such a process is the chlorination of ethylene. The resulting dichloroethane is then pyrolyzed to produce vinyl chloride and hydrogen chloride. The hydrogen chloride is then used for oxychlorination.

Hydrochlorination of Acetylene

Fig. 1 is the flowsheet for a commercial process for producing vinyl chloride from relatively pure acetylene. Care must be taken in handling pure acetylene because it can detonate under some conditions. General safety procedures include:^{7, 19}

1. Avoidance of alloys or solders containing copper, silver or mercury.
2. Preference for relatively small-diameter piping

or tubing. Sizes up to 6 in. I.D. have been used at relatively low pressures with suitable flame or flash arresters installed in the line.

3. Compression by means of centrifugal, liquid-sealed compressors has been successful.

When hydrocarbon streams (such as the effluent stream from a naphtha cracker) contain only a small fraction of acetylene, less stringent safety precautions are necessary.

Vinyl chloride must also be handled with care. In 1964, a large plant for the polymerization of vinyl chloride was almost completely destroyed as a result of a leak in which vinyl chloride escaped and formed a mixture with air and detonated.⁸

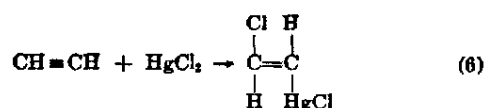
Production of Acetylene

Up to several years ago, production of vinyl chloride accounted for 30% of all acetylene manufactured in this country. Hence the general economics of acetylene manufacture are important relative to the future of vinyl chloride production. Based on predictions for the next five years, it is unlikely that new acetylene plants will be built in the U.S. unless a substantially cheaper acetylene is made.¹⁰

Within the last few years, new acetylene plants have been built using hydrocarbons as the feed-stock^{12, 16, 17, 19, 22} rather than the older processes using calcium carbide. Acetylene from these hydrocarbon processes is thought to be considerably cheaper than that from carbide processes. Claims, based on research information, have been made that acetylene can be produced from 3 to 5¢/lb.²³ However, at least two companies using hydrocarbon processes have experienced considerable difficulties and expenses in reaching design capacities and yields. Present cost may, in many if not all units, be as high as 7 to 8¢/lb. In 1965, about 53% of the acetylene produced in this country was still by the carbide process, and the remainder from various hydrocarbon processes.

Mechanism of Hydrochlorination

Mercuric chloride is the usual catalyst for the hydrochlorination reaction. It is thought to react with acetylene to form the intermediate compound, *trans*-2-chlorovinylmercuric chloride:^{22, 26}



This compound is attacked at the C-Hg bond by hydrogen chloride to form vinyl chloride and to regenerate the mercuric chloride. As indicated by Reaction (6), acetylene is chemisorbed by the catalyst. Vinyl chloride and possibly also hydrogen chloride are also strongly adsorbed on the catalyst.³⁰ The controlling chemical step is probably the surface reaction between adsorbed reactants. At startup, hydrogen chloride should enter the catalyst bed first, and then the acetylene flow should be started slowly.²⁰

Mercuric chloride is, as a rule, impregnated on activated-carbon pellets. Transfer of the acetylene and hydrogen chloride to the catalyst surface, and of vinyl chloride away from the surface, are necessary steps in the over-all process. The surface available in the carbon pellets affects the resistance to transfer of the materials to and from the catalyst surface. One or more of these transfer steps is partly controlling in terms of the kinetics of the over-all reaction.

Feed Purification

A commercial process for the production of 30 million lb./yr. of vinyl chloride will now be described. Fig. 1 indicates the flowsheet.[†] Acetylene at about 1.5 atm. absolute pressure is first compressed to 2 atm. with a Nash compressor that uses water as the sealing medium. Acetylene is then purified by passing it through an entrainment separator that contains refrigerated water. The temperature of the acetylene is lowered to 15 C., and considerable water is condensed and removed from the gas. A rotary, positive-displacement meter measures the gas to within 0.7%.

Next the acetylene is scrubbed in two columns with sulfuric acid to complete the drying. The first scrubber uses relatively dilute acid, and is 2-ft.-dia. by 24 ft. high. The steel tower is lined with acid brick. The second tower uses a more concentrated acid, and is 1.67-ft.-dia. by 22 ft. high. Each column is packed with 2-in. Raschig rings.

The acid in each column is recycled many times until its strength has dropped sufficiently. It is then replaced with fresh, strong acid. An external heat exchanger maintains the temperature of the recycle acid at 20 to 30 C. [This part of the process is not shown in Fig. 1.] Acetylene from the second scrubber is then passed through an activated-carbon filter to remove traces of catalyst poisons such as sulfides. The filter is 3-ft.-dia. by 7 ft. high. A second filter is provided as a standby for use after the first filter has been depleted.

The purifying section for HCl eliminates undesired impurities such as water, chlorine or chlorinated organic materials that may be present from previous chlorinations. Refrigerated condensers are sometimes used. The HCl is then compressed to about 2.25 atm. absolute by using a reciprocating compressor. The HCl at 70 C. is then passed through a separator tank to remove any entrained liquid. An automatic ratio controller maintains the desired molar ratio of acetylene to HCl. A ratio of about 1:1 is normal but slight variations are sometimes maintained. The HCl and acetylene streams are mixed in a mix tank.

Reactors Are Shell-and-Tube Exchangers

Five reactors are used, but only two are shown in Fig. 1. The five reactors are arranged: two in parallel,

[†] Details on this particular plant were presented by General Tire and Rubber Co. at a seminar sponsored by AIChE at Akron, Ohio on Oct. 16, 1964. R. R. Mattiko and P. R. Sayre were responsible for presentation of the material on vinyl chloride synthesis at this seminar.

followed by two more in parallel, and then the last one. Each reactor is essentially a shell-and-tube heat exchanger that contains 200 tubes, each 2-in. I.D. by 16 ft. long. The steel tubes are packed with activated-carbon pellets impregnated to a weight of about 10% mercuric chloride. The reaction is highly exothermic (about 24,500 cal./gm.-mole of vinyl chloride formed at reaction conditions). A heat-transfer fluid on the shellside maintains the desired temperatures.

The temperature used in the reactor varies from about 90 to 140 C., and depends on age and condition of the catalyst. Lower temperatures are used with fresh catalyst. At higher temperatures, mercuric chloride begins to sublime. There is evidence that the mercuric chloride sublimes from the hotter inlet of the reactor (where most of the reaction occurs), and then recondenses near the cooler outlet. As a result, the locations where the highest rates of reaction occur vary as the catalyst is exhausted.²⁹ The suggestion has been made that the life of the catalyst can be increased if the direction of flow to each reactor is occasionally reversed, but it is not known if such a technique is used commercially. In such a case, the mercuric chloride would tend to "move" from one end of the reactor tube to the other, and vice versa. Maintaining the catalyst at temperatures less than 120 C. gives little or no sublimation loss.¹ At such temperatures, the amount of vinyl chloride produced per pound of catalyst consumed is much greater than it is at higher temperatures.

As indicated above, temperatures of the catalyst in the tubes vary vertically. Temperatures also vary radially because of the cooling fluid on the shellside of the tubes. The temperature and rate at which the cooling fluid is pumped through the shellside of the reactor affects the temperature gradients in the reactor. Reliable information on catalyst life has not been published, but each batch of catalyst is estimated to last about half a year, assuming catalyst poisons are minimized in the feedstreams.

Reactor pressure is maintained at 1.5 to 1.6 atm. absolute. (Some processors perhaps operate at lower pressures.²⁰) Higher pressures are not used for at least two reasons:

- a. Increased dangers involved with higher-pressure acetylene.
- b. Increased rates of reaction cause increased problems in local hot spots, and hence affect the temperature control of the catalyst.

Oil is used as the cooling fluid for the process described here, but presumably other heat-transfer liquids would work satisfactorily. Several years ago, a heat exchanger using water cooled the oil, but now an air-cooled heat exchanger is used. At startup, the oil is heated with steam in order to raise the catalyst to reaction temperatures.

About 98 to 99% conversions of each reactant occur in the reactor. Essentially all of the product is vinyl chloride, but trace amounts of trichloroethylene, dichloroethylene, and aldehydes are also present. In addition, a small amount of unreacted acetylene and HCl are contained in the product stream. A continuous

infrared on-stream analyzer monitors composition of the HCl in the exit gases. Kinetic information concerning the hydrochlorination reaction has been presented by Wesselhoft and others.³⁰ Their predicted rates of reaction are less than those in the commercial unit. The differences are probably due to variations in catalyst activity.

Stripping Section

Exit gases from the reactor are fed directly into the bottom of the water scrubber that is packed with 2-in. Raschig rings and that is built of brick-lined steel. The cooling water (absorbent) is recirculated several times countercurrent to the gases, but this feature is not shown in Fig. 1. The exit solution from the scrubber contains from 3 to 10% HCl. As the concentration increases, a higher percentage of HCl is carried over to the caustic scrubber, also packed with Raschig rings. The gases leave the scrubber essentially free of HCl and flow through a suction knock-out tank to remove entrained liquids. The gases are next compressed to about 7 atm. absolute.

Recovery Section

The gases at 7 atm. are partially condensed by normal cooling water and then cold brine. This pressure was chosen in order to obtain the desired amount of condensation with normal cooling water. Most of the vinyl chloride, water and chlorinated hydrocarbon by-products condense. A decanter separates the water layer from the organic layer that is fed to a stripping column. This column contains 20 bubble-cap trays and is 27 ft. high. The bottom of the column is maintained at 46 C., using hot water in the reboiler of the stripper. Hot water is used instead of steam in order to obtain lower surface temperatures and hence minimize decomposition of vinyl chloride or of a relatively unstable byproduct. The bottom product of the stripper is crude vinyl chloride, which after cooling with brine is fed to a storage tank. The top gaseous product of the stripper is combined with the exit gas stream from the knock-out tank. Mild steel is used for construction of the stripper section.

Acetylene Recovery

The uncondensed materials from the brine cooler are primarily acetylene, vinyl chloride and inert gases. These are fed into the bottom of the absorber. Trichloroethylene, a byproduct of the process, is used as the solvent in the absorber and stripper. The absorber operates at about 4 atm. absolute and 30 C., and the stripper at about 90 C. (in the reboiler) and 2.25 atm. Both columns are packed with 1-in. saddles. The vent gases from the absorber contain 90% inerts, and the remainder is primarily acetylene.

The gas stream from the stripper is cooled with brine to condense most of the trichloroethylene. Uncondensed gas contains 40% vinyl chloride plus 20% acetylene, which represents nearly all of the unreacted

acetylene. These gases, recycled to the reactors, also contain small amounts of chlorinated hydrocarbons, primarily trichloroethylene. As additional trichloroethylene (and other chlorinated byproducts) are recovered, they are fed to the heavy-end storage tank.

Refining Section

Chlorinated organic materials and aldehydes are removed from the vinyl chloride in a distillation column. This column contains 30 bubble-cap trays and is 48 ft. high. It is operated at 4.0 to 4.5 atm. absolute so that the relatively pure vinyl chloride overhead stream can be condensed at 35 C. with normal cooling water. Feed to this column enters at the twentieth tray from the bottom. The top trays and that portion of the equipment contacting vinyl chloride are built from stainless steel in order to minimize iron contamination of the vinyl chloride. Hot water is used as the heating fluid in the reboiler of this column in order to minimize surface temperatures in the reboiler, and hence minimize decomposition of vinyl chloride. The bottom product from the column is discarded.

For every 2,000 lb. (32 lb.-moles) of vinyl chloride produced, the following are required: 1,183 lb. (32.5 lb.-moles) HCl, and 877 lb. (33.7 lb.-moles) of acetylene. Heavy ends produced are 23 lb. (0.18 lb.-mole if they are assumed to be pure trichloroethylene)

Other Hydrochlorination Processes

Nair²¹ has recently described an unspecified European plant, which produces about 5 million lb./yr. of vinyl chloride. The hydrochlorination reactor contains about 1,000 tubes, each 5-cm. dia. and 3 m. long, and each is packed with catalyst. Calculations indicate that the rate of production for a given bulk volume of the catalyst is only about one-quarter to one-third that in the General Tire process.

A hydrochlorination reaction is also part of several balanced processes. In the S.B.A. or Kureha processes, the hydrocarbon feedstream is relatively dilute in regard to acetylene—9.1% was reported for the Kureha process.¹³ In this latter process, the partial pressure of acetylene was less than 0.6 atm. Hence the total pressure in the reactor was less than 6.6 atm. Temperatures for the reactor were specified as 120 to 180 C.

The Kureha process is well instrumented and is computer controlled.²⁹ Acetylene content of the feedstream to the hydrochlorination unit is continuously measured by a stream analyzer.¹³ Flow of hydrogen chloride is metered in order to provide slightly less than the stoichiometric amount. The excess acetylene is specified as less than 1% according to one reference,²⁹ but is somewhat greater according to another.¹³ Yields of product are 95 to 98% based on the acetylene in the feedstream, and more than 99% based on hydrogen chloride.

The design for the hydrochlorination reactor of the Kureha process is similar to that previously discussed.¹³ Temperature control with a dilute acetylene feedstream is considerably easier than with essentially

pure acetylene. As a result, at least one of the following modifications seems possible:

1. Larger diameter tubes for the packed catalyst bed.
2. Higher gas temperatures since diluents in the gas stream will minimize local hot spots on the solid catalyst. Gas temperatures will in general be more uniform throughout the catalyst bed.

Somewhat longer reactor tubes and lower space velocities may be required to obtain essentially complete reaction with the more-dilute acetylene streams.

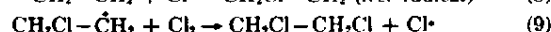
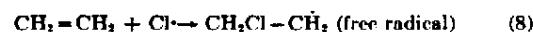
The catalyst used in the Kureha process¹³ is a "mercuric chloride catalyst," and is probably similar to those used with pure acetylene. Although specific details about the catalyst are not reported, the amount of mercuric chloride added and the type of support used may be somewhat different. Reactions with ethylene, carbon oxides, hydrogen and other gases in the feedstream (from the naphtha cracker) are "hardly observed." Although fewer details of the reactor design are available for the S.B.A. process, presumably it is similar to that of the Kureha process.

Vapor-Phase Chlorination of Ethylene

Ethylene is chlorinated in the vapor phase by a free-radical chain mechanism at temperatures from about 90 to 130 C. The initiating step of the over-all reaction is probably the rate-controlling one, and is:



Propagation steps are:

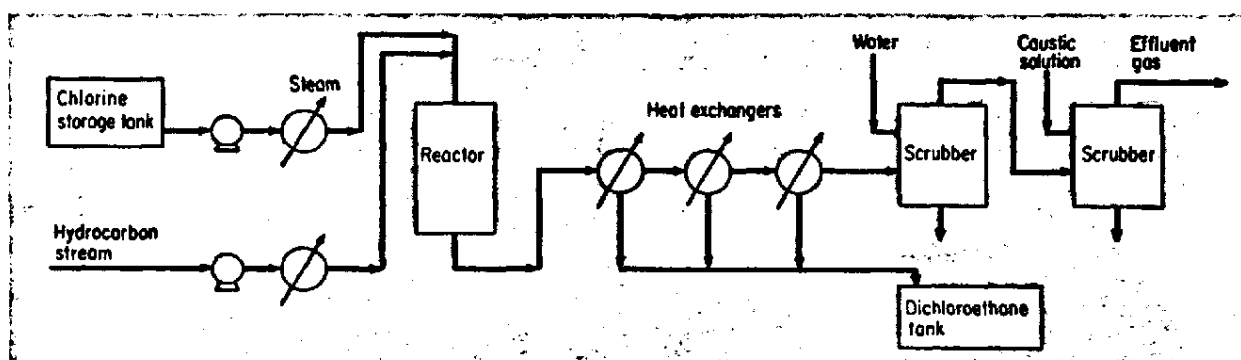


The free-radical chains terminate when two free radicals combine, or when free radicals collide and react at the reactor wall.

The walls of the reactor and/or the catalyst such as iron (probably an iron chloride formed *in situ*) or calcium chloride have a pronounced effect on the over-all reaction.^{11,18,24,27} These materials are involved in the initiation step [Reaction (7)], and may be considered as catalysts.

Surface temperatures in the reactor are therefore important. Semenov²⁵ and others have indicated that the walls of the reactor frequently act both to initiate and to terminate the free-radical chains. Further research is needed, however, to characterize the role of the reactor. Preliminary results of such a project now in progress at Purdue University clearly indicate that the role of the reactor walls is often highly complicated and significant. In many cases, failure to develop simple kinetic equations for the chlorination reaction is not surprising, although several past investigators did not seem to understand this fact.

In addition to type of surface, the amount of surface is also important. The role of the surface is complicated especially if it is porous or rough; hence the controlling factors may be both mass transfer and heat transfer to it. Rust and Vaughn²⁴ found that the rate of chlorination is directly proportional to the chlorine concentration, and to the square of the ethylene con-



VAPOR-PHASE CHLORINATION of ethylene in a dilute hydrocarbon stream produces dichloroethane—Fig. 2

centration in the gas phase. However, the kinetics of the reaction were increased by increased surface.

A pressure of about 7 to 10 atm. is probably used to obtain almost complete condensation and recovery of dichloroethane—using water as coolant. Temperature control may be a problem since the reaction is highly exothermic (about 39 kilocal./g.-mole of product). A large excess of one reactant or an inert gas is generally used for this reason. If only relatively pure ethylene and chlorine react, excess ethylene would be used since excess chlorine would promote undesired side reactions and the formation of over-chlorinated products.

Mixing the chlorine and ethylene is an important step. Equipment for combining the two gas streams should be designed to provide quick and intimate mixing so as to minimize local concentration gradients of the reactants. The temperature of each stream would also have to be carefully controlled; otherwise a runaway, or even explosive, mixture might occur during the mixing step. When excess ethylene is used, it must be recovered and recycled for economical operation.

When the hydrocarbon stream contains ethylene in rather low concentrations as in the S.B.A. process,^{4,5} the temperature can no doubt be controlled without using large, excess amounts of ethylene. There are already adequate inert gases present in the feedstream. A slight excess of ethylene is normally provided to minimize the amount of unreacted chlorine in the process.

Commercial Vapor-Phase Chlorination

Fig. 2 is the flowsheet for the vapor-phase chlorination of ethylene in a dilute hydrocarbon stream such as the S.B.A. process. Liquid chlorine from a storage tank is pumped to a heat exchanger where it is vaporized and heated to perhaps 80 to 90 C. The hydrocarbon feed stream is also adjusted to a similar temperature in a heat exchanger. The two streams are combined at the inlet of the reactor.

In one case, these reactors were apparently heat exchangers, and the catalyst was packed inside the tubes. Steel fins inside the tubes may be used to pro-

vide sufficient surface to generate catalyst for the reaction. Such a finned surface would also provide good heat transfer, and promote turbulence in the fluids. The fins may be coated in some cases with calcium chloride or lead chloride.¹⁴ As a result, reaction rates as high, or higher, than 0.3 lb.-mole/(hr.) (cu.ft.) of dichloroethane seem probable with temperatures of about 125 C.

Selectivity to the desired product of at least 93%, based on ethylene, is possible; but the selectivities decrease with increased temperature.²⁷ The reactors are cooled with water, and pressure must be sufficiently low to allow complete vaporization of all products and reactants. The pressures depend on the amount of inerts in the feedstream.

Exhaust gases from the chlorination reactors are cooled in two or more heat exchangers in series to about -20 C. in order to condense dichloroethane. Uncondensed gases are contacted in two scrubbers: first with water, and then with caustic, to remove small amounts of unreacted chlorine. The remaining gases are probably used as fuel.

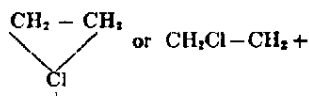
The condensed product is stored in a tank, and the liquid is primarily 1,2-dichloroethane plus small amounts of polychlorinated materials formed by additive and substitutive reactions of chlorine. Ethyl chloride is sometimes present. Dichloropropenes or dichloropropanes will be present if propylene or propane were present in the feedstreams. Generally special attempts are made to eliminate or minimize C₃ hydrocarbons in the feed because their chlorinated products are difficult to separate by distillation from 1,2-dichloroethane. The combined condensed product from the chlorinators is fractionated to produce essentially pure 1,2-dichloroethane that is later cracked to produce vinyl chloride and HCl.

Liquid-Phase Chlorination of Ethylene

Liquid-phase chlorinations occur at essentially ambient temperatures, from about 20 C. or higher, up to perhaps 70 C. In the Kureha process, temperatures from about 50 to 70 C. are indicated,¹³ but temperature control is not critical.²⁹ Pressures in the latter process

are from 4 to 5 atm., and the chlorine and ethylene feedstreams are bubbled through the liquid that is mainly 1,2-dichloroethane.

The mechanism for the liquid-phase chlorination reaction is less well understood than that for the vapor phase. In the polar liquid solution, the reaction is thought to be partly polar (or ionic) in nature. Chlorine atoms presumably add one at a time to produce a half-chlorinated intermediate such as:



This intermediate reacts with Cl^- or Cl_2 to form the desired product. There is some evidence that part of the chlorination reactions are free radical in nature.

Catalyst for liquid-phase reactions are metal chlorides such as iron chloride. They are dissolved in small quantities in liquid 1,2-dichloroethane. These metal chlorides complex with the ethylene and likely provide chlorine ions for the reaction. The reactor walls often serve as additional catalytic sites for the reaction.

The actual chlorination is thought to occur in the liquid phase. Hence ethylene and chlorine must be transferred from the gas phase and dissolved in the liquid. The following analysis is then applicable to each reactant, specified here as R .[†]

$$\left[\begin{array}{c} \text{Net transfer} \\ \text{of } R \text{ from gas} \\ \text{to liquid phase} \end{array} \right] = \left[\begin{array}{c} \text{Net reaction} \\ \text{of } R \text{ in the} \\ \text{liquid phase} \end{array} \right] + \left[\begin{array}{c} \text{Accumulation} \\ \text{of } R \text{ in} \\ \text{liquid phase} \end{array} \right] \quad (10)$$

For a differential volume dV of the reactor:

$$[k_g A (C_R^* - C_R)] dV = k [f(C_R, C_{\text{other}})] dV + \left[\frac{dC_R}{dt} \right] dV \quad (11)$$

Eq. (11) can be integrated over the entire volume V . At steady-state conditions in the reactor, the accumulation term is zero. The chlorination reactions can be assumed to be irreversible at reaction conditions; hence only the forward reaction has to be considered. In Eq. (11), the exact form of the kinetic equation is unknown, but it is proportional to some function of the concentrations of various materials in the liquid phase.

Eq. (11), or its integrated form, is most useful for indicating the effect of various operating variables on both the transfer of components between phases and the kinetics of the reactions in the liquid phase.

1. Temperature affects the forward rate constant k for the chlorination reaction, and indirectly the dissolved concentrations in the liquid of each reactant C_R plus any other compound such as the product C_{other} . The equilibrium concentration at reaction conditions of the reactant C_R^* also varies with temperature. The surface tension and viscosity of the liquid change with temperature, and as a result the mass-transfer coefficient from the gas to the liquid $k_g A$ also changes. The interfacial area A likely varies significantly with temperature as the gas bubbles upward through the liquid, or as mechanical agitation is applied.

[†] Similar analyses have been made for aromatic nitrations and for the alkylation of isobutane. See *Chem. Eng.*, Apr. 25, 1966, pp. 169-172; July 4, 1966, pp. 119-126.

2. Agitation or the type of bubbling affects $k_g A$, and hence indirectly C_R .

3. Total pressure of the system and composition of the reactant gases affect C_R^* .

4. Composition of the liquid phase affects factors that control mass-transfer resistances.

High dissolved ratios of ethylene to chlorine are desired in order to minimize formation of byproducts, which are mainly trichloro and other polychlorinated ethanes.^{2,14} A better understanding of the reaction would be possible if the solubilities of the reactants in the liquid phase were known. In most cases, the actual solubility C_R is probably much lower than the equilibrium solubility C_R^* —i.e., mass-transfer resistances are partially controlling.

Commercial Liquid-Phase Chlorination

Liquid-phase chlorinations are used in the processes of Shell Development Co.¹⁵ and Kureha Chemical Industry Co.^{13,26} There may be significant differences in the liquid-phase processes but the following features probably apply to all.

The product (1,2-dichloroethane) is used as the solvent in which ethylene and chlorine are dissolved. A catalyst such as a small amount of ferric chloride is dissolved in the solvent, and rapid chlorination occurs in the liquid phase. In the Kureha process, about 0.96 to 0.98 moles of chlorine are introduced per mole of ethylene. The ethylene is chlorinated rapidly at 4 to 5 atm. and at 50 to 70 C. At such conditions, about 99% of the chlorine reacts to form the desired product whereas 95 to 98% of the ethylene reacts. Side reactions are negligible. In processes using essentially pure ethylene, a fairly large excess of ethylene is used in some cases, and unreacted ethylene is recovered and recycled.

The conversions in the Kureha process are affected to some extent by the hydrocarbon-gas stream used, which is the product stream from a cracking furnace containing several components such as hydrogen, carbon monoxide, carbon dioxide, methane and others. All of these components are considered to be inert relative to the chlorination reaction. These inert gases act as stripping agents as they pass upward through the reactor. Similar conversions can be obtained, however, in those processes in which relatively pure ethylene is the hydrocarbon feed.

Other factors affecting the reaction are:

1. Methods of contacting the liquid phase with gaseous ethylene and chlorine.

2. Agitation at or near the entrance points for the ethylene and chlorine would help to minimize high local concentrations of reactants if a pool of liquid solvent were used. Bubbling the feed gases into the solvent would cause some mixing of it, but would not necessarily provide adequate shear at the entrance points.

3. Recirculation, either internal or external, of the gases may be necessary in some cases.

Nair²¹ describes a commercial chlorination reactor that is 1-m. dia. and 6 m. high. This reactor is packed

with iron ceramic rings. Ethylene is introduced into the bottom of the reactor and bubbles upward through the liquid and around the Raschig rings. Three exit lines are provided near the top of the reactor. The lower of these is used to recirculate liquid (mainly 1,2-dichloroethane) through an external heat exchanger. Normal cooling water is used in this exchanger to maintain recycle liquid at essentially 40 C. Chlorine gas is introduced into the recycle liquid just before it re-enters the reactor. The second of the exit lines at the top of the reactor is for crude dichloroethane product, and the top line is for exhaust gases that may include any inert gases introduced into the system.

The iron packing in the reactor serves two purposes. First, it maximizes the heat- and mass-transfer surfaces between the gas and liquid. Second, it acts to produce iron chlorides that dissolve to some extent in the liquid, and are catalysts for the reaction. Production capacity of this reactor was not specified, but it is probably a small unit. A high local concentration of chlorine in contact with the product is probably undesired. The method for introducing chlorine to this reactor does not seem to be the ideal one.

Apparently some chlorination reactors contain pools of liquid solvent through which ethylene and chlorine are bubbled. A mechanical agitator is probably used to decrease mass-transfer resistances. Back-mixing might be a problem in such a reactor. To minimize back-mixing and to obtain higher conversions, two or more liquid-phase reactors could be provided in series. Counterflow of the liquid relative to the gas is a possibility, and it could be achieved using a tower column that is packed, or contains plates.

Liquid-phase chlorination has been used for processes in which ethylene enters in both dilute and concentrated streams. The liquid-phase process would appear to have several advantages as compared to gas-phase ones:

a. Better use of the heat of chlorination. Reactant streams can be introduced into the reactor relatively cold. A pilot-plant investigation indicated that heat of reaction can be used to vaporize dichloroethane.³ With this technique, little or no iron chloride catalyst is carried over, and purification steps for the product are simplified.

b. Better temperature control of reactor. Large excess of liquid, good agitation of the liquid, and excellent heat transfer between gas and liquid should be sufficient to maintain isothermal conditions in the reactor.

c. Increased safety because chlorine and ethylene are not premixed.

d. Large excesses of ethylene are not needed nor is an inert gas in order to maintain adequate temperature control. This advantage would be particularly valuable when essentially pure ethylene and chlorine are used as reactants.

Based on rather sketchy literature descriptions, the reactor for a liquid-phase process is simple in design and operation. Corrosion is not a problem if precautions are made to exclude water from the system.³ Both

the capital and operating costs for the liquid-phase process are probably relatively low.

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Key Concepts for This Article

Active (A)	Passive (P)	Input/Feedstock (I)	Output/Product (2)
Reviewing Processes*		Acetylene*	Vinyl chloride*
Vinyl chloride*		Ethylene*	Ethylene
Hydrochlorination*		Chlorine*	dichloride*
Chlorination*		Hydrogen chloride, anhydrous*	
Vapor phase*			
Liquid phase*			

(Words in bold are role indicators; numbers correspond to EJC-AIChE system except for Role 8 modification. Asterisks mark key concepts suggested for indexing. Others are added to improve reading as an abstract. Indexing is described in *Chem. Eng.*, Oct. 11, 1965, p. 187; or you may order Key Concept reprint, 50¢, using Reader Service Postcard.)