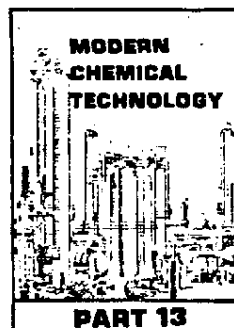


Manufacture of Vinyl Chloride



Oxychlorination of ethylene in packed-bed, fluidized-bed or liquid-phase reactors produces dichloroethane followed by pyrolysis to vinyl chloride.

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Drastic reductions in the cost of making vinyl chloride have occurred in the last few years. Some modern plants have total production costs of 5¢/lb., or even less. To appreciate the importance of these changes, we will review the techniques for making vinyl chloride that incorporate: (1) oxychlorination of ethylene, (2) pyrolysis of dichloroethane, and (3) balanced processes that contain several chemical steps. In most cases, the preferred route for future plants will be in balanced processes of large capacities.

Oxychlorination of Ethylene

The recent development of oxychlorination processes for producing 1,2-dichloroethane from ethylene, hydrogen chloride, and oxygen (or air) is of considerable commercial importance. The over-all reaction is:



Hydrogen chloride, frequently a byproduct from other operations is thus of use, and the resulting dichloroethane is pyrolyzed to vinyl chloride.

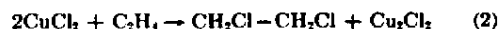
Large oxychlorination plants for dichloroethane have been built in the U.S. and numerous other countries within the last few years.^{5,6,8} In addition, several oxychlorination plants are now reportedly under construction or expansion.

Several modifications of the oxychlorination process have already been made. These include differences in the ratio of reactants, in catalysts, and in the method of contacting the reactants with the catalyst. In some processes, oxychlorination and chlorination occur in a single reactor.

Mechanism of Oxychlorination

Oxychlorination is applicable to numerous hydrocarbons such as methane, ethane and light hydrocarbons.^{6,7} However, our discussion will be limited to oxychlorination of ethylene for the production of 1,2-dichloroethane. Copper chloride (a modified Deacon

process catalyst) seems to be universally used. The support material for solid catalysts is of considerable importance and is the subject of numerous patents. The basic chemistry^{10-13, 17, 25} of the process is:



A cupric content of approximately 20%, or greater, is needed in the catalyst in order to obtain a chlorination reaction at temperatures of 250 C., or greater. Potassium chloride or other alkali metal chloride is generally added to the catalyst. Fontana¹² has shown that melting points of mixtures of potassium chloride, cupric chloride and cuprous chloride are as low as 150 C., whereas the melting point of the eutectic mixture of cupric and cuprous chlorides is 375 C. At operating conditions, most (if not all) oxychlorination catalysts apparently contain a liquid phase—probably partly adsorbed on the surface. The molar ratio of Cu:K ions in the catalyst must be greater than 0.5:1 in order to obtain a significant reaction. This ratio is probably related to the melting point of the mixture at reactor temperatures.

Oxygen adsorption in the catalyst is of importance. The rate of adsorption increases significantly as cupric oxide content increases. Actually, cupric oxide may tend to precipitate from the "melt" on the surface. When potassium chloride is replaced with sodium, calcium or lead chloride, the rates of oxygen adsorption decrease. The solid cupric oxide reacts with hydrogen chloride to regenerate the cupric chloride.

Transfer of ethylene, oxygen and HCl to the catalyst surface is also important. Although sufficient data are not available to determine with certainty which step in the oxychlorination process is rate controlling, adsorption (or absorption) of oxygen may be. Such a step seems to be rate controlling for oxychlorination of methane,¹³ but oxychlorination of ethylene may involve a different mechanism than that for light paraffins.¹¹

Temperature has an important effect on the follow-

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

ing features of the over-all oxychlorination process: (a) true kinetics of the reactions, (b) melting point and viscosity of the surface chloride salts, and (c) solubilities or adsorptions of reactants on the surface.

Alumina, silica or other porous materials are apparently preferred supports for the chlorides when solid catalysts are used. These materials form complexes to some extent with the chlorides and may reduce their volatility.³³ In some cases, significant amounts of the chloride salts have been lost from the catalyst by volatilization. Hence, catalyst activity is decreased. Size and porosity of the support is of considerable importance relative to the over-all performance of the catalyst,⁹ but little reliable information is available.

Temperature Control Is Critical

The over-all oxychlorination reaction is highly exothermic. Since heat is released at the surface of the catalyst, temperature control is often a critical factor with solid catalysts. Using diluent gases in the reaction mixture is one important method of minimizing hot spots on the catalyst surface. Air or aqueous solutions of HCl have sometimes been used because the diluent (inert nitrogen, or steam, respectively) helps maintain good temperature control. Vulcan Materials Co.³⁰ has indicated that relatively pure ethylene feed is required. Other sources indicate that relatively impure ethylene is satisfactory in some processes operating at somewhat different conditions—especially when the impurities, including paraffins, are relatively inert. These impurities would aid in temperature control. Commercial reactors have been built that provide sufficient heat-transfer capacity so that relatively pure ethylene, HCl and oxygen can be used. In most commercial units, air is probably used instead of pure oxygen.

In order to improve the thermal conductivity of the packed catalyst bed, materials such as graphite, silicon carbide and nickel have been used as diluents for the granular catalyst. Hot spots in the packed catalyst are most critical near the feed of the bed. Whether such diluents are used commercially is not known. If used, they are perhaps only in the inlet portion of the bed. Probably, the chloride salts slowly volatilize and migrate away from the inlet as the bed is used. Reversing direction of flow in the reactor might occasionally be beneficial.

Oxygen as compared with air does provide advantages of faster reaction rates and higher conversions for a given reactor, assuming that adequate temperature can be maintained. It provides a higher driving force for adsorption (or absorption) on the solid catalyst. Relatively pure oxygen also simplifies the recovery portion of the process. Careful economic evaluation is required in order to determine whether oxygen or air is to be used.

Operating Conditions for Oxychlorination

The exact operating conditions used in commercial reactors are not publicized, but wide variations are

probable, depending on the catalyst and feed. The approximate range of conditions for a solid catalyst is discussed below.

Temperatures of 250 to 350 C. seem common, but lower ones have been reported in patents. Shell²⁰ has patented a catalyst containing rare earths, and a silica gel having an unusually large surface area (200 sq. m./g.). This catalyst is reported to be very active at about 250 C. Presumably, catalysts that operate at such temperatures would have a longer life than those operated at much higher temperatures because volatilization and subsequent loss of catalyst is probably the main reason for catalyst deactivation.

Pressures are normally specified as being from about 1 to 10 atm., and will depend to some extent on whether the solid catalyst is fluidized or used as a packed bed. Since fluidization depends to a large extent on the volume of gas, lower pressures seem more probable for fluidized-bed operation. Higher pressures are likely with packed beds of catalyst, and they facilitate condensation and recovery of the product streams. When large quantities of inerts are present, higher pressures will generally be used in order to obtain comparable partial pressures of reactants.

Feedstreams normally have ratios of ethylene, hydrogen chloride and oxygen in essentially the stoichiometric ratio of 1:2:0.5. Slight excesses of any one of the three reactants are possible. Excess HCl will result in some HCl in the product. Upon condensation, an aqueous solution of HCl will be obtained. Some companies can use or sell such an aqueous solution, whereas other companies would have trouble in disposing of it. These latter firms will probably use a slight excess of ethylene in order to obtain almost complete conversion of HCl on each pass. With a fluidized-bed system, air will likely be used instead of oxygen because of the increased gas volumes obtainable.

Conversions and Yields obtained commercially have not been publicized. Conversions of 95%, or higher, are probable with essentially stoichiometric ratios of reactants. Over-all yields of 1,2-dichloroethane are thought to be about 95%, or possibly slightly higher, based on the entering ethylene and HCl. Some losses are caused by incomplete reaction and incomplete recovery of unreacted feeds. Byproducts include 1,1,2-trichloroethane, ethyl chloride and other polychloroethanes. Hexachloroethane is produced in small quantities when solid catalysts are used. This compound is highly undesirable in the pyrolysis portion of the vinyl chloride process and, further, is difficult to remove in the distillation part of the process.

The M. W. Kellogg Co.²² claims that its process—using an aqueous copper chloride catalyst—gives yields and selectivities of 96 and 98% based on the ethylene and HCl, respectively. It further claims that insignificant amounts of hexachloroethane are produced. B. F. Goodrich⁸ indicates that it had included in its commercial plant a separate distillation unit to remove byproduct chlorinated hydrocarbons. The amount of byproduct actually produced is so low that this unit will not be incorporated in any future plant. Both

the Kellogg process and the Goodrich process (using fluidized beds) probably have good temperature control, which is thought to be very important for minimizing byproducts.

Oxygenated organic compounds and carbon oxides are produced in relatively small quantities (2 to 5%) in most oxychlorination processes. Such compounds are too small in quantity to be recovered. They must be separated from the dichloroethane product because otherwise they would interfere with the pyrolysis operation.

Little quantitative information has been published on factors affecting conversions and yields. Increased conversions are obtained with higher temperatures, higher partial pressures of reactants, and lower space velocities (i.e., longer residence time in the reactor). Higher yields seem to be caused by better temperature control and lower temperatures. Dichloroethane seems to suppress conversions perhaps even more than thermodynamic factors. Considerably more information is needed before the factors affecting conversions and yields can be completely understood.

Packed-Bed Reactors

Several commercial processes use reactors that are essentially shell-and-tube heat exchangers in which the catalyst is packed in the tubes. Temperature inside the tubes is controlled by a cooling fluid on the shell-side of the exchanger. Water has been used as the cooling fluid in at least one case; and 150-psig. steam was generated.¹⁰ Tubes with internal diameters of 2 in., or less, seem to be used in many units.²⁸ Other variables that help to maintain good temperature control include space velocities of gases, presence of diluents or inerts in the gas stream, and dilution of solid catalyst with inert granular solids.

With good temperature control, the catalyst will last up to about one year.²⁰ Since chloride catalysts are relatively volatile, some cupric chloride is sometimes added as a vapor to the reactant feed;²⁰ but the method of adding it may not be easy. When this method is used, the temperature profile in the reactor remains essentially unchanged as a fraction of time. Otherwise, the catalyst migrates toward the exit of the reactor tube, and there is then a slow variation in the reactor temperatures as a function of catalyst life.

Dimensions of commercial reactors have not been publicized, but reactor tubes that are about 1.5 in. I.D. and 20 ft. long seem quite reasonable. Corrosion may be a problem because of dissolved hydrogen chloride in the catalyst that is probably partly molten. The hot-gas phase containing hydrogen chloride should not be especially corrosive. During shutdown, it would seem desirable to exhaust all hydrogen chloride and water from the system in order to minimize corrosion problems. Such problems may also occur during startup. Nickel has been indicated in many patents as the material of construction for the tubes. Both stainless and plain steel tubes have been used in some experimental arrangements with apparently satisfactory results. Nickel or high-quality stainless steel is

probably used in most tubes in order to obtain high-purity product.

Reliable kinetic data for the reactions apparently have not yet been published, and design of a reactor is impossible without such information. In the Vulcan patent,²⁸ rates of production of 1,2-dichloroethane were found to be as high as 0.5 lb.-mole/(hr.) (cu.ft. catalyst bed). Obviously this rate depends on operating conditions and type of catalyst.

Fluidized-Bed Reactors

A fluidized-bed reactor is used by B. F. Goodrich Chemical Co.,^{8, 10} and possibly by others. Such a reactor has the advantage of maintaining quite uniform temperatures throughout, but it promotes back mixing. Relatively cool gaseous feeds are introduced to the reactor and contacted with the fluidized hot catalyst particles. The exothermic heat of reaction provides the sensible heat for raising the reactant gases to the desired reaction temperature.

Because mixing is effective, composition of the gas phase in the reactor is quite similar to that in the product stream. The kinetics of the reactions are relatively low because of the rather low concentrations of reactants. Sometimes a fluidized-bed reactor is operated at only an intermediate conversion level, and a followup reactor is used. Several fluidized-bed reactors may be connected in series. One example is to install these beds in a single column, with the required number of distribution plates in the column to separate the various compartments. Temperature control when partial conversion has been obtained should not be particularly critical. A packed-bed reactor could be used as the second reactor, if desired.

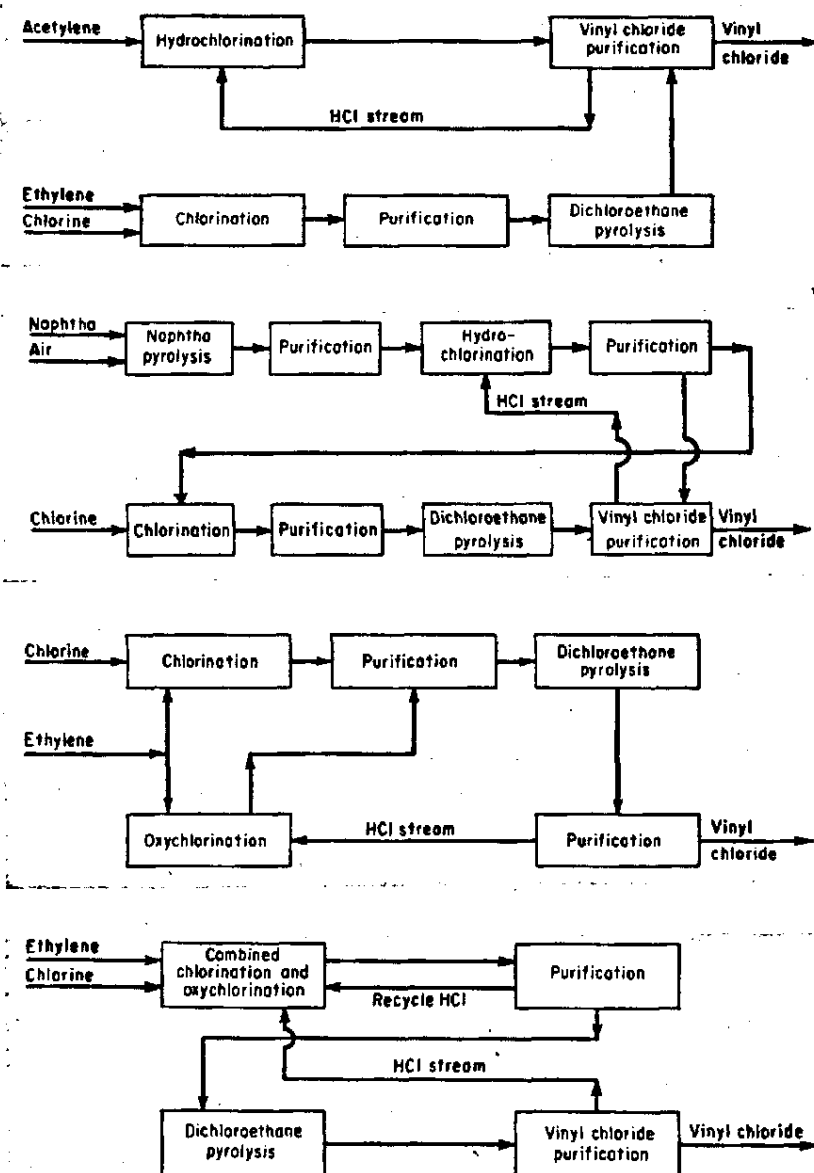
Catalyst particles in the fluidized bed will erode and fragment with time. Makeup catalyst will be occasionally needed to replace the fines carried over with the product. Since the surface of the catalyst is probably semiliquid, some agglomeration or sticking of catalyst particles may occur. Fines may tend to gradually plug the pores of the large particles. To obtain reliable design and kinetic data, a rather large pilot plant is probably needed. Scaleup techniques for a fluidized bed are not yet well understood.

Liquid-Phase Reactor

The oxychlorination process developed by M. W. Kellogg Co. uses an aqueous solution of cupric chloride in the reactor.^{14, 18} The reactant gases (HCl, C₂H₄, and air) are contacted with the solution. Operating conditions for a commercial unit appear to be approximately as follows: temperature, 170 to 185 C.; pressure, 225 to 275 psig.; and concentrations of cupric chloride in the solutions, up to 7 molar. Kinetics of the reaction are first order with respect to cupric chloride concentration. Pilot-plant runs have been made in which about 2.0 to 4.0 g.-moles of product were obtained per liter of unexpanded solution per hour.

Mechanically agitating the solution as the gases

Balanced processes for vinyl chloride manufacture



PROCESS I is a combination of the chemical steps that involve hydrochlorination of acetylene, chlorination of ethylene, and the subsequent pyrolysis of 1,2-dichloroethane.

PROCESS II is similar to Process I except that ethylene and acetylene are present in a dilute stream, obtained by high-temperature pyrolysis of naphtha or other hydrocarbons.

PROCESS III is typical of an operation that involves the oxychlorination of ethylene, chlorination of ethylene, and pyrolysis of 1,2-dichloroethane.

PROCESS IV represents a modification of Process III in that both chlorination and oxychlorination reactions occur in the same reactor.

bubble upward has been found most satisfactory in pilot-plant experiments. As a result, temperature gradients are all but eliminated in this reactor.

Temperature control of this highly exothermic reaction is easy since some of the water vaporizes and no cooling surfaces are required. A heat-exchange surface could be provided inside the reactor. Relatively cool feedstreams can be introduced into sparging rings (or other bubbling devices) inside the reactor. The sparging rings should be designed so that the gases are quickly and intimately dispersed into the liquid phase in order to minimize high local concen-

trations of any reactant. The heat of oxychlorination brings the reactants to the reaction temperature.

A packed-column reactor should also be effective with aqueous-phase solutions. Such a reactor is similar to that described by Nair²⁴ for the chlorination of ethylene. In this reactor, liquid is recycled in order to provide external temperature control. Liquid flows and gas flows through the reactor are cocurrent, and the gases bubble upward through the liquid and past the packing. Countercurrent flow in the column is also possible. If plates are installed inside the column, cooling devices may be provided between them.

The reaction undoubtedly occurs in the liquid phase. As a result, the reactants must dissolve, or at least contact the liquid surface. Agitation due to the bubbling action of the gases through the liquid, or due to a mechanical agitator, creates a large interfacial area between liquid and gas, and hence decreases mass-transfer resistances. Transfer of oxygen is the controlling step in some cases.

The Kellogg reaction system has the big advantage because oxychlorination and chlorination of ethylene can be done in the same reactor. Regardless of the ratio of hydrogen chloride to chlorine, dichloroethane is formed in high yields and relatively high conversions. (The importance of this will be considered later.) In addition, aqueous solutions of hydrogen chloride can be used as feedstreams. Such solutions cannot be used with some oxychlorination catalysts.

Pyrolysis of 1,2-Dichloroethane

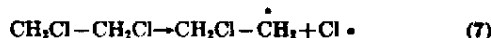
Noncatalytic and catalytic processes are used for the pyrolysis of 1,2-dichloroethane. Noncatalytic processes have been announced by B. F. Goodrich Chemical Co. for its relatively new plant,^{8, 23} by Kureha Chemical Co.,^{15, 32} and by Shell Development Co.¹⁹ However, the S.B.A. process uses a catalytic pyrolysis unit.³

Chemistry of Pyrolysis

The pyrolysis reaction involves a free-radical chain mechanism^{2, 21} in which a free radical of chlorine starts the chain:



These two propagation steps are thought to occur primarily, if not exclusively, in the gas phase. The initiation step for the above chain has not been established with certainty, but there is some evidence that part of the initiation occurs at the wall of the reactor—even for the so-called noncatalytic type of pyrolysis. When a catalyst is used, initiation apparently occurs at the catalyst, possibly as follows:



Chlorine and oxygen promote the pyrolysis reaction. Presumably, chlorine molecules decompose to produce chlorine free-radicals, and oxygen abstracts a hydrogen atom from 1,2-dichloroethane molecules to form the dichloroethyl radicals. However, chlorine and oxygen also form byproducts, and these compounds are probably not used commercially.

Since wall reactions occur, the wall temperature is important.³² High wall temperatures that may occur for large heat fluxes through the tubewalls are detrimental because they promote side-reactions. In unpacked tubular reactors, both tube diameter and flow rates in the tubes are important relative to wall temperatures. As carbonaceous materials are deposited

on the tube walls, heat transfer through the walls becomes less efficient. The importance of the metal surface as compared to the carbonaceous deposits in terms of the initiation chemistry is not known. In any event, as carbonaceous deposits increase, higher wall temperatures will be required in order to maintain adequate heat transfer.

Noncatalytic Pyrolysis

B. F. Goodrich Chemical Co. has indicated that it uses the patented process of H. Krehler, which is assigned to Hoechst.²³ In this process, 1,2-dichloroethane is passed through unpacked tubes at temperatures from 450 to 650 C., for fractions of a second up to several seconds. Residence times in the reactor increase at lower operating temperatures. Pressures vary from about 20 atm. up to perhaps 35 atm. Conversions of dichloroethane are maintained at about 50% per pass because yields of vinyl chloride decrease at higher conversions.

Advantages claimed for the high pressures in this process include:

1. Higher yields to vinyl chloride with fewer by-products, especially carbon. In the patent, yields from 95% to 98% are specified. Goodrich indicates that they actually get yields of 99%.¹⁶

2. Easier and hence better separation of the product. The entire product stream can be liquefied at about 0 C. at a pressure of 25 atm. Distillation can be used to separate the product stream into relatively pure components.

3. Higher production, in that about 120 to 150 kg./ (hr.) (l. of reactor space) of dichloroethane can be converted into vinyl chloride [i.e., 7,500 to 9,200 lb./ (hr.) (cu.ft.)].

The patent²³ indicates that the reactor tube should "advantageously have a small diameter" in order to avoid becoming clogged with soot. A small-diameter tube decreases wall temperature of the reactor. Since the amount of vinyl chloride produced for a given reactor volume is high, a significant amount of heat must be transferred. The patent discloses that internal diameter of the reactor tubes was 6 mm., or 0.238 in. Goodrich indicated that it scaled up the pyrolysis unit.⁸ Undoubtedly careful control of the wall temperature, in addition to the bulk-gas temperature, was an important consideration.

In a commercial unit, tube diameters of at least one inch can probably be used. The following values for reactor tubes were calculated for a 500-million-lb./yr. vinyl chloride unit, assuming linear scaleup. Number of tubes is sixty, each 1 in. dia. and 40 ft. long. Average flow velocity in each tube would be about 40 to 70 ft./sec. Hence, a relatively high Reynolds number and high heat-transfer coefficient would be expected relative to those for the laboratory unit.

Some of the carbon and tars formed during pyrolysis remain in the reactor. Hence, the reactor must be cleaned at periodic intervals. Reliable information is not available concerning the length of time that a commercial unit can be operated between cleanings. About

Reactants per pound of vinyl chloride—Table I

	Process I	Process II
Acetylene	0.21 lb.	
Ethylene	0.23 lb.	0.48–0.50 lb.
Chlorine	0.59 lb.	0.67–0.68 lb.
Total cost of reactants	4.07¢	3.70¢

1,300 hr. was reported for a laboratory unit.¹⁶ Probably as long a period is possible for a commercial unit. Steam is probably not used to remove carbon by means of a shift reaction because of the low temperatures used in the process. Instead oxygen, or air, is likely used to burn out the carbonaceous material. Possibly some metal oxides are formed on the reactor walls during the burnout. Such metal oxides are known to have undesired "catalytic" effects on some pyrolysis reactions. Research at Purdue is now being directed to methods for preventing or minimizing oxide effects.

In the Goodrich process, the gases from the reactor pass through a quench condenser in which cold 1,2-dichloroethane is sprayed into the gases in order to obtain partial condensation of the product. The Krehler patent²³ discloses that the gases were cooled to 50 C. at about 25 atm. Most of the carbon and tars in the product stream would probably drop out in this condenser. The mixture of condensed liquid and uncondensed gases is fed to a distillation column that is operated with a bottom temperature of 170 C. and a top one of about 0 C., according to the patent. Top product is hydrogen chloride, and the bottom liquid is a mixture primarily of vinyl chloride and 1,2-dichloroethane. A second distillation column (operated at 8 atm., according to the patent) separates this mixture. Although the simplified flowsheet¹⁹ of the Goodrich process does not show additional columns, such columns would be needed to separate byproducts.

In the Kureha process, 1,2-dichloroethane is vaporized and fed as superheated vapor to the pyrolysis reactors. Radiant burners fed with off-gas provide heat to the cracker coil.³² Pyrolysis occurs at about 7 atm. and 450 to 550 C., to give a conversion rate of 60% per pass.¹⁵ Yield of vinyl chloride is 96%.

Catalytic Processes

The S.B.A. process uses a catalyst for cracking 1,2-dichloroethane. Braconier⁴ claims that "all secondary reactions and, more particularly, the decomposition into carbon black" are avoided. Details for this process are not known, but based on patents issued to S.B.A.^{27, 28} some type of carbon is apparently the catalyst. This catalyst is described as "de-ashed active" carbon that is packed into the reactor tubes. Operating variables for the process are thought to be in these ranges: temperature, 400 to 450 C.; pressure, 8 to 10 atm.; conversion per pass, 60 to 70%. At these relatively low temperatures, selectivities to vinyl chloride

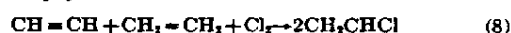
of 99%, or greater, are obtained. In a packed tubular reactor, there are obviously temperature gradients both radially and axially.

Wacker-Chemie³¹ has reported on a carbon catalyst whose activity is such that temperatures as low as 200 to 350 C. can be used. Carbon formation becomes a problem at temperatures approaching 450 C. This temperature seems to be the upper limit for carbon-catalyzed pyrolysis. Up to one year's operation can be obtained from such catalysts when used in a packed bed. During this period, the temperature for pyrolysis is slowly raised in order to maintain the desired level of conversion. Once the catalyst is deactivated, presumably because of carbon and tar formation, it has to be replaced.

Balanced Processes

In this article and in an earlier one,¹ mention was made of balanced (or integrated) processes for producing vinyl chloride. To obtain high yields of the reactants, several chemical steps are incorporated in the over-all process. Four balanced processes are shown by block diagrams in the illustrations on p. 226; all parts of these diagrams have been previously discussed.

Process I represents a technique that has been popular for many years. The over-all reaction is:



A flowsheet for Process II has been described in rather general terms by S.B.A.^{3, 4} and by Kureha^{15, 32} personnel. Details of the process have also been discussed in the earlier article.¹

Information and flowsheets for several variations of Process III have been reported in this series, or in the literature.^{5, 6, 8, 10, 19, 30} The over-all reaction is:



Process IV combines chlorination and oxychlorination in the same reactor, such as in the process of the M. W. Kellogg Co.^{14, 18} Also shown is a recycle stream of hydrogen chloride from the purification section. Such a recycle stream would be obtained if incomplete conversion of hydrogen chloride occurred in the reactor. Usually this stream is an aqueous solution.

Edwards and Weaver¹⁰ have compared both the capital and production costs for three types of vinyl chloride plants. For a 200-million-lb./yr. plant, they estimated the following capital and startup costs for each:

Edwards and Weaver process (a Process III type)	\$6,400,000
Acetylene plus HCl process	4,590,000
Ethylene plus chlorine process, but without oxychlorination	5,460,000

Although the capital costs were greater, the total production costs per pound of vinyl chloride were significantly less by the Edwards and Weaver process than by the other processes. Cost of reactants in the three processes is over 70% of the total production cost.

Table I indicates the amounts of reactants required