

Vinyl chloride monomer... What you should know

This survey of the VCM (vinyl chloride monomer) industry commercial developments chemistry commercial processes and new developments indicates that VCM can remain competitive with rising crude costs

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DEVELOPMENT OF THE VINYL chloride monomer (VCM) industry has been closely interrelated with the polyvinyl chloride (PVC) industry. Effectively 96 percent of the VCM production goes into the manufacture of PVC. Therefore technological advances in one area have significant impacts upon the other producing a domino effect. This in conjunction with increasingly tighter environmental regulations has insured a continuing evolu-

tion of VCM technology. It is timely to review the state of the art.

INDUSTRY PROFILE

The commercial significance of vinyl chloride monomer (VCM) can be highlighted by the statistical ranking of the 19th largest chemical commodity in the United States. Turning our view upstream we realize the significance VCM plays in wedding the petrochemical and chloroalkali industries. Fig 1 schematically depicts the US market integration surrounding VCM. Pondering the posture individual companies present to the market (Table 1) one can muse as to the motivational forces behind their respective business strategies.

It holds that if 96 percent of the VCM demand in this country is derived from PVC then VCM's future is inescapably tied to that of PVC's. Within the scope of known unknowns one basic fact attests to its longevity. On an energy equivalent basis PVC is one of the most energy efficient construction materials available (Table 2). This follows even after weighing the socioeconomics of health and environment.

Looking at the two principal components of the PVC

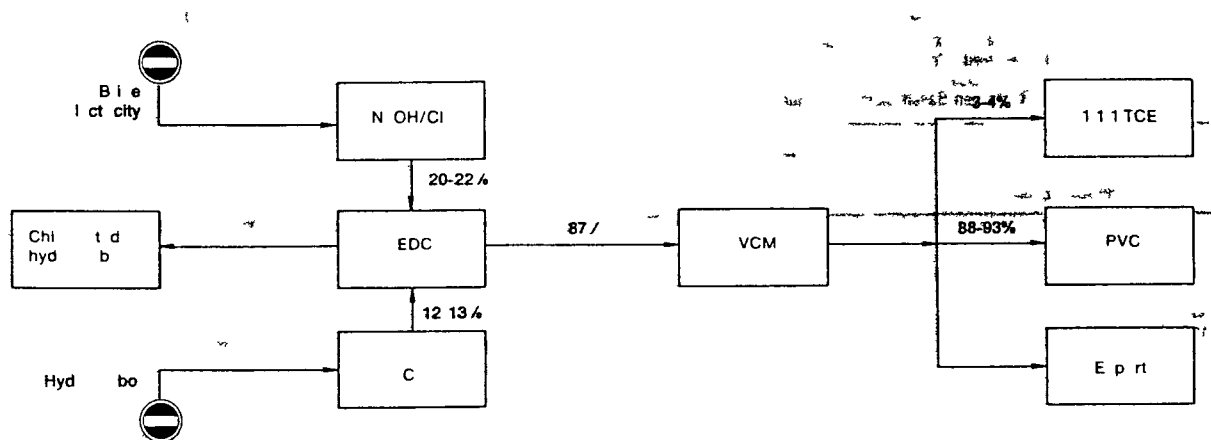


Fig 1—Shows the US market integration surrounding vinyl chloride industry

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market flexible or plasticized products of which fabric for automobile interiors and electrical wiring insulation are examples and rigid products including sewer and water pipes electrical conduits and shoe soles we find the rigid aggregate growing at 9 percent per year as opposed to the flexible area which is increasing at a rate of approximately 5 percent. Within the past few years the rigid aggregate has surpassed the size of the flexible market which can be witnessed by the creeping seasonal response the VCM industry has to construction the major end use outlet for rigid products.

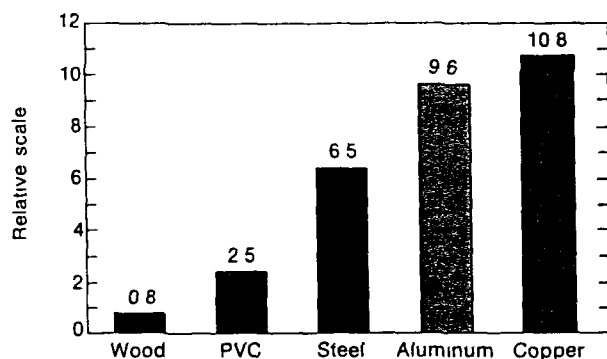


Fig 2—Relative energy content of various construction materials

TABLE 1—Nameplate capacities (MM pounds)

	PVC	VCM	Ethylene	Chlorine
Borden	550	300	None	None
Conoco	550	700	650	None
Diamond	None	1 000	None	2 500
Dow	None	2 250	4 800	8 400
Ethyl	175	300	None	500
B F Goodrich	1 100	1 100	350	250
ICI	None	300	None	300
Monochem	None	300	None	None
PPG	None	900	None	2 900
Shell	None	1 540	2 700	200
Stauffer	420	170	None	780

TABLE 2—Commercial types of VCM technology

- I High Purity Acetylene Feedstock
- II Dilute or Mixed Gas Feedstock
- III Balanced Ethylene Feedstock
- A Air Based Oxychlorination
- B Oxygen Based Oxychlorination

Developer/Licensor	Technology	
	Basic	Oxychlorination
Dow	III	A
Ethyl ICI Solvay	III	A
B F Goodrich	III	AB
Kureha	II	—
Mitsui Toatsu	III	B
Monsanto	III	AB
PPG	III	B
Rhone Poulenc	III	A
Stauffer	III	AB
Tokuyama Soda	III	A
Toyo Soda	III	A
Hoechst	I	—
ICI	I	—

Over the course of the past ten years VCM has become a major item of international commerce with the United States the architect of this business. But in 1975 and 1977 eight percent of the VCM produced was carried offshore making it third only to styrene monomer and toluene in the generation of trade dollars by a chemical commodity. This factor has tended to fill in the alleys in demand brought about by construction. More significantly it has permitted the VCM industry to consistently operate near capacity levels by exporting domestic surpluses into the world arena. Looking at the global VCM market we view forces at work changing the disposition of trade. Beginning within the past five years Europe as a whole has swung from a net importer to exporter of VCM. With ten billion pounds of VCM capacity integrated to where there is less than 15 percent more cheaply derived PVC demand producers are now challenging U.S. material for a share of the remaining world exports.

Japan whose five billion pound VCM industry was built to serve the whole of the Asian South Pacific market first in PVC and then later in VCM has witnessed a major influx of U.S. and now European monomer producers into their domain.

The present situation in the U.S. is manifested by cheaper feedstocks versus energy and an undervalued currency that together are able to offset logistical costs and remain competitive in the consuming markets. Eventually merging energy parity and emission cost pass throughs will leave U.S. VCM no more competitive than that of any other nation. We conclude therefore that exports will continue as developing third world markets seek to establish a plastics industry in advance of petrochemicals. Conversely the major market imbalances of the past have gone by the wayside and market growth will come from the domestic sector. Fig 3 depicts the longer term outlook for VCM. In making our projections we assume that the growing capital commitment required to make VCM will not force PVC to become uncompetitive with alternative products. Secondly we foresee no major technological innovation on the horizon that could radically alter the economics of production. We do see however technological improvements of degree that directionally level out the inflationary trend of plant construction. Within the U.S. we project a 700 to 1 000 MM lb per year grass roots plant will be required every two years to meet demand. It is within the scope of this time frame that innovation will be tested.

COMMERCIAL DEVELOPMENT

VCM was first produced commercially in the early 1900s via reaction of HCl and acetylene derived from calcium carbide. VCM usage in the manufacture of synthetic rubber accelerated dramatically during and after World War II. This increased demand prompted searches for more economical hydrocarbon feedstocks. Acetylene was recovered from refining steps and new technology was developed to produce acetylene specifically from hydrocarbon cracking.

Ethylene became plentiful in the early 1950s. Direct chlorination processes to produce 1,2-dichloroethane (EDC) from chlorine and ethylene were developed in

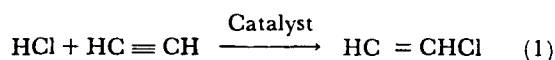
conjunction with EDC cracking technology to yield VCM. This process yielded byproduct HCl and did not proliferate immediately except in conjunction with acetylene based technology which needed HCl to produce VCM.

In the U.S. ethylene production from abundant supplies of low cost LPG began to predominate. In Europe ethylene prices also continued to drop though not to the same degree since higher priced naphtha and gas oil were the primary feedstocks. Therefore while European producers continued to use acetylene based VCM technology American companies moved rapidly to ethylene based technology. With the startup in 1958 of the first large scale oxychlorination process to yield EDC from HCl and ethylene a new era in VCM technology began. This balanced process allowed production of VCM from two commodity chemicals chlorine and ethylene without voluminous byproduct HCl.

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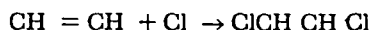
Large scale production of vinyl chloride was first done by addition of hydrogen chloride to acetylene.

Hydrochlorination of acetylene

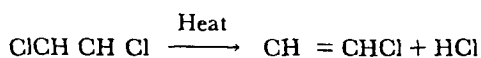


However much lower costs for production of ethylene than acetylene and the discovery that 1,2-dichloroethane (EDC) thermally decomposes to vinyl chloride in excellent yield led to the following reaction sequence as the predominant manufacturing method for VCM.

Direct chlorination of ethylene



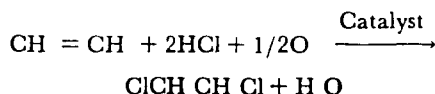
EDC cracking to VCM



This method was especially advantageous for those producers having a use for the HCl byproduct particularly so if acetylene were available since then a balanced VCM process with no coproducts could be operated.

Later the discovery that oxychlorination technology could be applied to ethylene to give 1,2-dichloroethane in high selectivity now allowed a completely balanced process based only on ethylene and chlorine as feedstocks.

Oxychlorination of ethylene



At present about 92 percent of the vinyl chloride produced in the United States is from plants that use the balanced process based on ethylene via chlorination, oxychlorination and thermal cracking of EDC. These three separate steps are described in greater detail below. Additionally the hydrochlorination of acetylene is also discussed below since plants using this chemistry are still

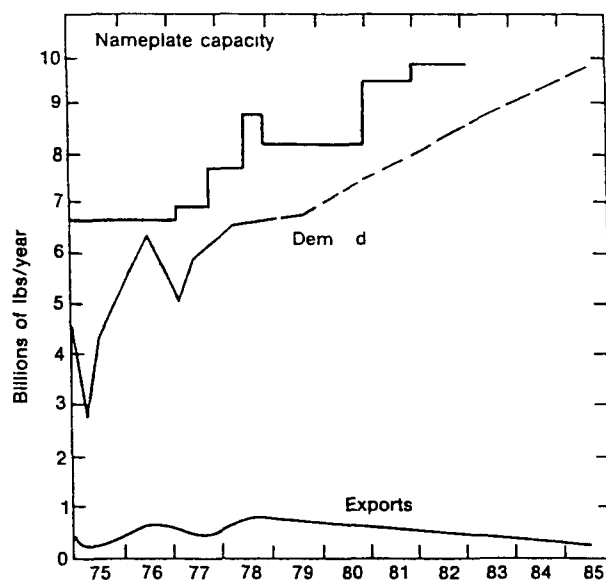


Fig 3—US vinyl chloride nameplate capacity versus demand

in operation. Moreover some recent crude oil cracking technology may narrow the cost gap between acetylene and ethylene with consequent revival of interest in VCM from acetylene. Some chemistry on direct preparation of VCM from ethane is also briefly outlined.

Direct chlorination of ethylene Direct chlorination of ethylene to 1,2-dichloroethane is almost always conducted in a liquid phase reactor by intimately mixing ethylene and chlorine in liquid EDC. Ferric chloride, a highly efficient and selective catalyst for this reaction is normally used in commercial processes. Amides such as *N,N*-dimethylformamide have been reported to increase PVC selectivity. Oxygen frequently present as an impurity in chlorine likewise increases EDC selectivity in direct chlorination of ethylene by inhibition of free radical reactions that give 1,1,2-trichloroethane.

Direct chlorination reactions may be run rich in either ethylene or chlorine depending on the methods available to the plant for handling offgases from this reactor. Conversion of the lean component is usually 100 percent and selectivity to EDC is greater than 99 percent.

1,2-Dichloroethane as it comes from the direct chlorination reactor is frequently of sufficient purity for cracking except that it may contain ferric chloride which would lead to rapid fouling of the cracking reactor. To avoid expensive purification of this already pure EDC one may remove FeCl₃ by adsorption on activated carbon or other solids. Alternately one may operate the direct chlorinator at the boiling point of EDC taking pure EDC overhead and using the heat of reaction to supply the heat for vaporization.

Oxychlorination of ethylene to EDC Ethylene oxychlorination is normally conducted at temperatures of 225–325 °C and at pressures of one to 15 atmospheres. Catalysts for this reaction almost always contain copper chloride and sodium or potassium chloride deposited on alumina or other suitable support. The detailed mech-

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anism of the catalyst's activity is not known but it is recognized that cuprous chloride is the active chlorinating agent. The cuprous chloride produced is rapidly reconverted to CuCl under the reaction conditions but the presence of some cuprous chloride is thought to be advantageous because it complexes with ethylene bringing it into contact with CuCl for a long enough time for chlorination to occur. The sodium or potassium chloride serves to increase EDC selectivity mostly by inhibiting formation of ethyl chloride. Other catalyst components such as rare earth metal chlorides, sulfate salts, ferric chloride and numerous other additives have been described in the patent literature.

Good temperature control of the highly exothermic oxy reaction is a key element in successful production of 1,2-dichloroethane. Temperatures higher than about 325°C lead to increased byproduct formation mostly through increased dehydrochlorination of EDC to vinyl chloride followed by additional oxychlorination to give products having high levels of chlorine substitution. High temperatures also increase the amount of ethylene burned to carbon monoxide and carbon dioxide. Of equal importance, high temperatures deactivate the catalyst by highly accelerated coking and consequent powdering of the catalyst units and by increased sublimation of copper chloride away from the catalyst.

Temperature control in fluidized bed reactors is maintained by the excellent intermixing of the catalyst particles and by use of internal cooling surfaces. Temperature control in fixed bed reactors is more difficult since hot spots tend to develop. To keep the hot spot temperature below 325°C yet get maximum utilization from the reactor, it is common practice to pack the reactor tubes with active catalyst and inert diluent mixtures in proportions of each so adjusted as to have low catalyst activity at the inlet, steadily increasing to maximum activity at the outlet. This grading of the catalyst activity flattens the temperature profile allowing for good temperature control with high productivity. For example, one patent indicates the use of four zones with 93 percent, 85 percent, 40 percent and 0 percent respectively of the active catalyst pellets replaced by inert graphite. As an alternate to using inert materials in the catalyst bed, catalysts each with higher levels of CuCl and consequently of increasing reactivity are sometimes used.

Fluid bed oxychlorination of ethylene operated under good control results in 94-97 percent ethylene conversion, 95-97 percent HCl conversion and EDC selectivities in the range of 94-96 percent. Fixed bed oxychlorinations are normally run with excess ethylene relative to HCl, resulting in 93-97 percent ethylene conversion, 94-95 percent HCl conversions and EDC selectivities of 93-95 percent. These data do not include recovery of excess ethylene in subsequent reaction steps. Excess ethylene in vent gases from oxychlorination is normally converted to EDC by direct chlorination with chlorine although if oxygen is used rather than air, the excess ethylene may be recycled directly back to oxychlorination.

Byproducts of ethylene oxychlorination are vinyl chloride, ethyl chloride, 1,1-dichloroethane, vinylidene chloride, cis and trans 1,2-dichloroethylenes, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral and high boiling compounds. All of these byproducts present problems in one way or another such that their production needs to be minimized to lower raw material costs, to lessen the difficulties of preparing pure EDC and to prevent fouling in the cracking reactor. Chloral, in particular, needs to be removed since it polymerizes readily in strong acids to give solids which clog and foul operating lines and controls.

One must also take care to see that the feeds to oxychlorination are pure. Normally the only problem is with low levels (0.1 to 0.5 percent) of acetylene present in the HCl from cracking of EDC. Acetylene in the feed leads to the formation of considerable highly chlorinated byproducts and tars. Selective hydrogenation of this acetylene to ethylene and ethane is practiced by many companies.

Oxychlorination with oxygen instead of air. Use of oxygen instead of air for ethylene oxychlorination has received much attention. The outstanding benefits from using oxygen are avoidance of expensive facilities to recover EDC, ethylene and other chemicals from the large nitrogen vent gas stream, a large reduction in the quantity of offgases that will probably need to be incinerated, and the ability to use ethylene as a diluent for oxychlorination, a procedure said to improve heat transfer in tubular reactors.

Purification of EDC for cracking. Great care must be taken to ensure that EDC used for cracking to vinyl chloride is of high purity, normally greater than 99.5 percent, since cracking is exceedingly susceptible to inhibition and fouling by trace amounts of impurities. Additionally, the EDC must be bone dry to prevent excessive corrosion downstream of the cracker. For these purposes, one must consider removal from EDC of byproducts from three sources: EDC from direct chlorination, EDC from oxychlorination, and EDC recovered from the cracking step (see below).

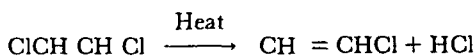
EDC from direct chlorination is usually quite pure, greater than 99.5 percent, and except for the FeCl₃ present, it needs little further purification. As mentioned previously, ferric chloride may be removed by adsorption on a solid or the EDC may be distilled away from FeCl₃ in a boiling reactor. Alternatively, the ferric chloride may be removed by washing with water, usually in conjunction with oxy-EDC.

1,2-Dichloroethane from oxychlorination contains a variety of impurities as listed previously. EDC from this source is usually washed with water and then with caustic solution to remove chloral and other water extractable impurities. Low boiling impurities and water are taken overhead in a first (light ends) distillation column and then pure, dry EDC is taken overhead in a second (heavy ends) column.

EDC recovered from the cracking step contains an

appreciable number of impurities of which chloroprene and trichloroethylene are not readily removable by distillation necessitating the use of other treatments. Chloroprene is not altered by chemical treatment concentrates in the light ends column where it can polymerize to solid or rubbery materials which seriously foul and upset this column. Trichloroethylene forms an azeotrope with EDC boiling very close to EDC. If it is not removed in some way it accumulates in the EDC leading to reduced cracking rates and increased fouling. Both impurities may be removed by subjecting the recycle EDC stream to chlorination prior to distillation. Treatments with HCl and by hydrogenation have also been patented as methods for removal of chloroprene.

Cracking of 1,2-dichloroethane to vinyl chloride At temperatures in the range of 425-550°C and near atmospheric pressure EDC undergoes clean thermal dehydrochlorination (cracking) to yield vinyl chloride and hydrogen chloride.



The mechanism of this reaction has been extensively investigated and shown to involve a sequence of free radical intermediates.

Use of pressure up to 25 to 30 atmospheres during cracking at temperatures of 500-550°C provides better heat transfer, reduced equipment size and easier separation of HCl from the product by fractional distillation. EDC conversion levels are normally maintained in the range of 50 to 60 percent at residence times of 2 to 30 seconds with selectivities of VCM ranging from 96 to 99 percent. Some byproducts generated during cracking act as inhibitors to the free radical sequence so that increasing severity leads to smaller and smaller increases in EDC conversion with correspondingly increasing levels of byproducts. Various materials such as chlorine, bromine or oxygen have been shown to be initiators for EDC cracking.⁸ Recently however, exclusion of oxygen is claimed to result in considerable reduction of fouling on the cracker tube walls. A rather spectacular claim has been made that use of nitromethane as an initiator provides EDC conversion levels of up to 92.5 percent at 480°C. An important processing requirement in EDC cracking is rapid cooling or quenching of the reaction mixture. If cooling is done too slowly substantial yield losses to heavy ends and tars result.

Byproducts from the cracking reaction include acetylene, ethylene, methyl chloride, butadiene, vinyl acetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and other compounds. Most of these impurities remain in the unconverted EDC fraction and are removed when this stream is distilled. Ethylene and acetylene codistill with the HCl and are thus routed back to oxychlorination (after optional hydrogenation of the acetylene to ethylene). Methyl chloride and butadiene more or less codistill with the vinyl chloride depending on the efficiency of the VCM fractional distillation system. Addition of chlorine or carbon tetrachloride to the cracker feed is claimed to suppress methyl chloride formation. Removal of butadiene, a contaminant which can interfere with polymerization of VCM, has been

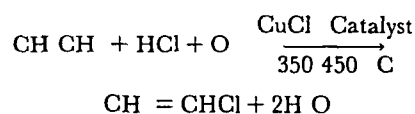
done by treatment with chlorine, anhydrous HCl or selective hydrogenation.

HCl addition to acetylene Recent development of a new crude oil cracking process using very high temperature steam (2000°C) as a heat transfer fluid produces substantial yield of acetylene along with ethylene. Under some economic and geographic conditions the use of this cracking process may be advantageous and may thereby provide acetylene for vinyl chloride production.

Typical conditions of hydrogen chloride addition to acetylene are total pressures on the order of five to 15 atmospheres, temperatures of 150 to 180°C and use of a mercuric chloride on carbon catalyst.⁸ With stoichiometric quantities of reactants, essentially 100 percent conversion is observed with VCM selectivities on the order of 98 percent. It is notable that ethylene does not react under these conditions, thereby allowing the use of mixed ethylene/acetylene streams as feeds. Ethylene is easily recovered from the vinyl chloride product by fractional distillation. It is then chlorinated to yield 1,2-dichloroethane.

Other catalysts have been shown to be effective for addition of HCl to acetylene, but HgCl₂ is vastly superior. However, in addition to the general toxicity problems involved in working with mercury-containing substances, HgCl₂ has appreciable volatility under the above reaction conditions leading to a need for considerable care and control in operation of the reactor. In fixed bed operations, HgCl₂ vaporizes from the hot spot of the reactor, condenses at cooler locations downstream and results in continuous movement of the hot spot downstream with eventual loss of catalytic activity. This loss is minimized by periodic reversal of flow through the reactor.

Ethane-based vinyl chloride processes A number of patents dealing with chemistry for conversion of ethane to EDC and/or VCM have been published in recent years.⁹ Most of these reactions involve high temperature oxychlorinations such as



However, these processes suffer from a number of disadvantages, the most important of which includes low selectivities, low conversions and difficult operating conditions such as CuCl sublimation.

One reaction system based on ethane, called the TRANSCAT process, has been developed on a large pilot plant scale but is not yet in commercial practice. The chemistry of this process is a complex series of reactions generally involving chlorination, dehydrochlorination and oxychlorination. A mixture of ethane, ethylene, ethyl chloride, chlorine and HCl are fed to a melt of cupric oxychloride and potassium chloride, yielding vinyl chloride, water and cuprous chloride as the main products. The cuprous chloride/potassium chloride product is taken to an oxidation reactor where the cupric oxychloride is regenerated by treatment with air. Vinyl chloride is separated from the organic product and purified.

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fied by fractional distillation. Removal of about 0.4 per cent butane plus butenes present in the main VCM cut represents a very difficult separation. Ethyl chloride and ethylene can be recycled into the feed. Chlorine values in the chlorinated byproducts can be recovered by incineration and then feeding these gases to the cuprous chloride oxidative regenerator reactor.

Disposal of byproducts Disposal of byproducts presents special problems for vinyl chloride manufacturing plants since a variety of gaseous organic liquid and aqueous streams must be handled each with its own particular problems.

Vent gas streams from various units may contain small amounts of HCl, chlorine, ethylene, vinyl chloride, methane and carbon monoxide. These streams may sometimes be treated by scrubbing, chemical treatment, sorption or other methods to recover some chemicals when economically justified. Otherwise, the common cleanup technique is either incineration or catalytic combustion followed by recovery of HCl from the vent gases.

Two organic byproduct streams are produced. The light ends contain mainly ethyl chloride, *cis* and *trans* 1,2-dichloroethylene, chloroform and carbon tetrachloride. The heavy ends or tars contain mostly 1,1,2-trichloroethane, lesser concentrations of tetrachloroethanes, chlorinated butanes, chlorinated aromatics and a large number of other compounds present in small amounts. These streams are normally fractionated to recover useful components; the others are incinerated to recover chlorine values either as aqueous or anhydrous HCl.

Process water streams are steam stripped to remove volatile organics, followed by neutralization and then treatment in an activated sludge system to remove non-volatile organics in the water.

COMMERCIAL PROCESSES

Broadly speaking, there are three types of VCM processes in commercial use today. These are categorized as acetylene, ethylene or mixed gas based on feedstock requirement. Within the ethylene type plants, further classification is desirable to distinguish the type of oxychlorination technology used, i.e., oxygen versus air feedstock (see Table 2). Over 90 percent of the world's listed 35 billion lb per year VCM capacity currently is based upon the balanced ethylene feedstock route. Of this, just under 90 percent uses air-based oxychlorination. However, of the projected worldwide plant startups for the period 1979-1981, approximately 30 percent of the 7.7 billion lbs per year VCM will be derived from oxygen-based oxychlorination. Other existing producers will undoubtedly be evaluating the conversion of present air-based plants to the use of oxygen during this time frame.

Table 3 presents a summary of the technology sources in use today. It is thought that the technology currently licensed by ICI and Solvay is similar to the process normally attributed to Ethyl. Therefore, all are listed under Ethyl's technology. It is interesting to note that several plants exist where the oxychlorination process

TABLE 3—Current VCM technology sources

Technology Source	Existing		Planned (1979-1981)	
	Plants	VCM MM Lbs/Yr	Plant	VCM MM Lbs/Yr
1 B F Goodrich	18	5 840	4	2 160
2 Hoechst/BFG	11	4 290	2	580
3 Stauffer/BFG	5	2 360	—	—
4 Stauffer	19	6 390	2	350
5 Ethyl Solvay ICI	14	5 000	1	260
6 Dow	7	3 040	3	1 050
7 PPG	5	1 700	3	1 780
8 Rhone Poulenc	5	1 330	1	500
9 Monsanto	4	1 110	1	250
10 Toyo Soda	3	400	1	330
11 Tokuyama Soda	2	660	—	—
12 Mitsui Toatsu	3	610	1	90
13 Kureha	2	410	—	—
14 Miscellaneous	10	2 400	1	330
	107	35 540	20	7 680

Oxychlorination process provided by BFG

of one licensor. B F Goodrich has been combined with direct chlorination and VCM technologies of others, i.e., Hoechst and Stauffer. Table 4 presents a tabulation of worldwide VCM producers. This summary was prepared from scores of literature sources, some of which were contradictory. However, the authors have exercised their best judgment in the absence of specific information from the listed licensors.

The reader is referred to Leonard, Gomi, or Sittig⁵ for details of the acetylene and mixed gas routes to VCM. The technology discussion herein will be limited to the balanced ethylene feedstock route used overwhelmingly today.

Although each of the major technology licensors has many patents, none has complete coverage of each step of his process. As a result, the sequence and type of operating steps tend to be very similar from process to process. The basic differences stem from the oxychlorination technology and the types of impurities appearing in the crude EDC. The licensor therefore provides process know-how primarily as opposed to patent position. As a result, published literature by major licensors is understandably very sparse and highly simplified, with certain exceptions.

TYPICAL VCM PROCESS

The typical VCM process combines direct and oxychlorination (oxy) processes to provide 1,2-dichloroethane (EDC) feedstock for the EDC pyrolysis unit (see Fig. 4).

The direct chlorination process relative to oxy is characterized by low capital investment, low operating costs and high purity product. However, HCl generated from the EDC pyrolysis unit dictates the use of an oxy unit. With the current pyrolysis yield of approximately 0.55 mol VCM per mol EDC fed, and the HCl yield of 1 mol per mol VCM, the oxy unit size is set at approximately 0.5 mol EDC per mol of VCM desired. This sets the direct chlorination unit size at approximately 0.5 mol EDC per mol VCM.

The combined EDC streams are caustic treated to re-

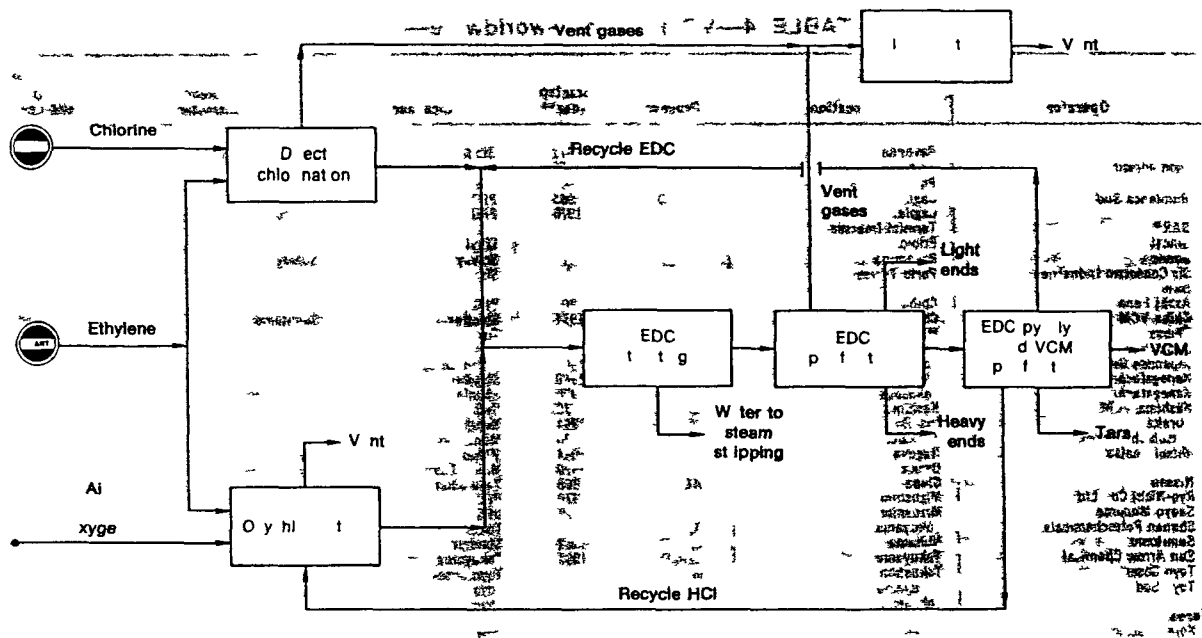


Fig 4—Typical vinyl chloride monomer block/flow diagram

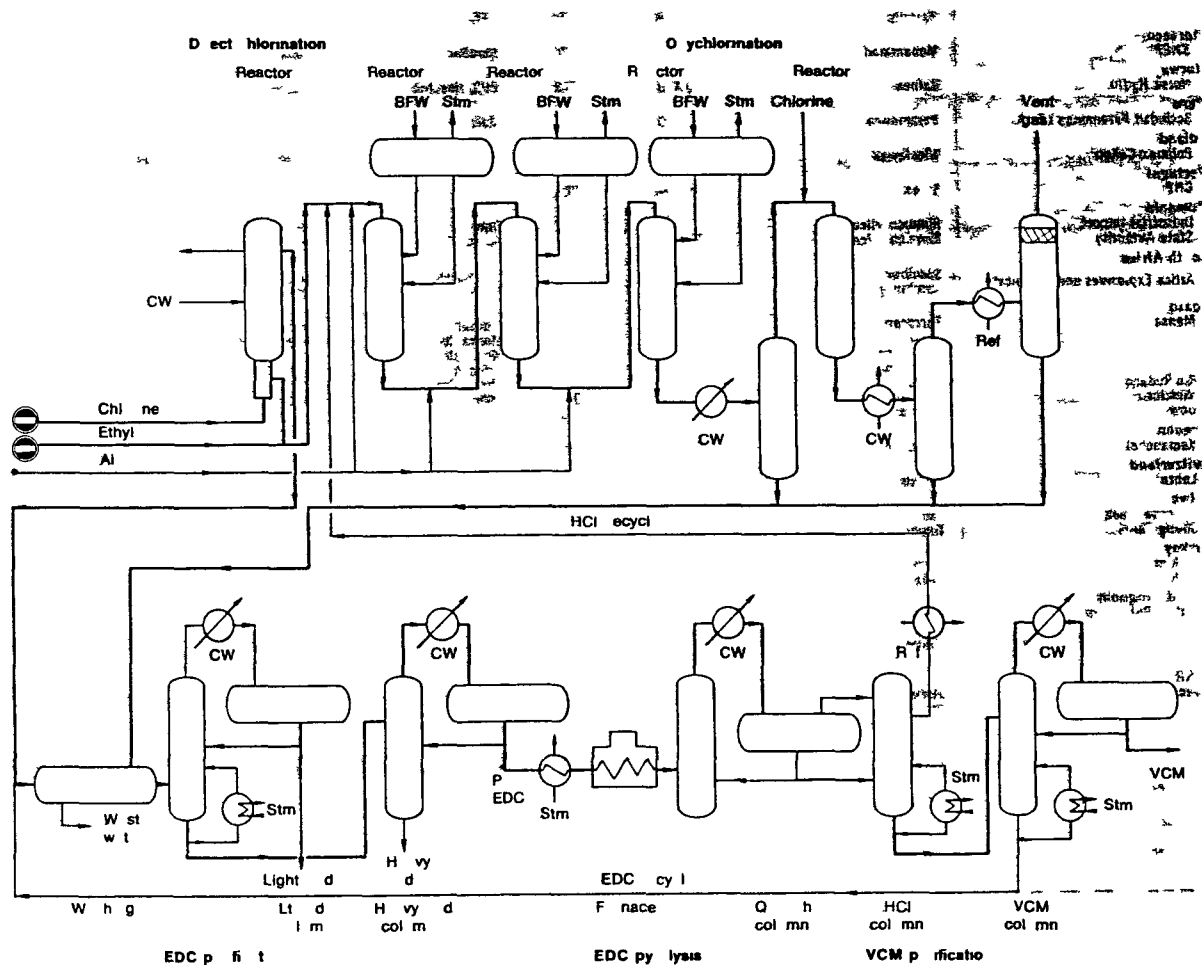


Fig 5—Schematic of the Stauffer vinyl chloride monomer process

TABLE 4—VCM plants—worldwide—(cont d)

Op t	L cat	P oc	Sta t p Y	L	E g C t t /	VCM C ty MM Lb /Y
Italy						
A	R na	A / /	1971	St ff	F t Wh i	165
M d so	d	M/A/O	1969	BFG		400
R m S d	P rt M gh	M/A/O	1970	BFG		400
SARP	C gl	E / / D	1965	PPG	Opt S i	350
S i t	T m l m	E/A/O	1976	PPG	E t co	350
S i C sorz i d t	P i			Ethyl	S i y	(110)
J p	R y m			S i y	E t co	290
Asah P	P rt T			S		110
Ch b VCM	Ch b	AE / / D	1967	PPG		310
Ch so	Ch b	E/A/B	1971	Sta ff	S m t m	99
D k K g k	M m t			T y Sod	H t h	350
J p Ge	Ch b			D k K g k		220
K g l h	T k k	M / / D	1967	J p se Geo		(330)
K g f h	T k sag	E/A/B	1969	St uff	S m t m	257
K h m VCM	T k sag	E/A/B	1970	St uff	K g l h	331
K h	K h m	E/A/B	1970	BFG		770
M t b h M sa t	N h k	M / / D	1964	K h	Ch yod	265
M t T t	Y k k h	AE/A/	1970	M sa t		130
N	N g y	AE/A/O	1964	M t T t	T y E g g	130
Ry N h C Ltd	Osak	E/A/B	1970	M ts T tsu	T y E g g	130
S y M m	Ch b	AE/A/O	1968	T y Sod	H t h	73
Sh P t h m i	M h m	E/A/B	1970	BFG		440
S m t m	M h m	AE/A/O	1970	BFG		238
S A Ch m i	Tok y m	A / /		T k y m S d		440
T y G se	N h m	E/A/B	1968	St ff		180
T y S d	T k y m	E/A/O	1967	T k y m Sod		220
	T k h m	M / / D		T y G se		88
	T k y m C ty	E/A/B	1966	T y Sod	H t h	110
	Y k k h			T y S d		220
K	Yeo-S		(1979)	D	Fl / D l m	(330)
K P f	Uisa			D	P oco	132
L by						
GNOI	Ab K mm h		(1980)	BFG Hoe h t	F Uhd S i g t t	(136)
M						
P m	P j t	E/A/B		M sa t	L mm	155
	P ja t	E/A/B	1978	BFG	B l t	440
M oc						
SNEP	M h mm d		1976	Sta ff	K b	59
N w y						
N k Hyd	R i	E/A/B	1978	BFG Hoe h t	B dg	660
P						
Soc d d P m g LTDA	P m g	E/A/O		V ica		17
P i d						
P i m C k p	Wloci k	E/O/B	(1979)	PPG	P t ocarb D y P g	(450)
P t g i						
CNP	S	P i d	(1981)			(330)
R m i						
I d t l l m p t	R m Vice			D	Klock	88
St t A th ty	R m Vi	E/O/B		M ts T t	T y E g g	350
S th Af ica						
Af ca E pl d Ch i	S solb g	E / / D	1968	ICI S i y	H mph & G l g	50
	S solb g	A / /	1978	T	C wf d R l	440
Sp						
M t	T g			M sa t	L mm	176 330
	T g			M sa t	M Kee CTIP	(250)
	T g			M sa t		530
	T g			M sa to	M K CTIP	220
R R d	H i		(1980)	Rh ne-P g l		(500)
Y l	M t i	E/A/B	1970	S i y	M K CTIP	265
D	H i		(1981)	D		(770)
Sw d						
K m b i	St g d	E/A/B	1967	Sta ff	L g	180
S itz i d						
L nz	L id	A / /				44
T w						
F m sa Pl t	K h g	E/A/B	1973	St ff		530
Ch g T (?)	T f	E/O/B/		M t T t		(530)
T k y						
P tk m	Y m i m t			S i y	H mph y d G l g	119
P tk m	Al g l m	E / / D	(1981)	ICI S i y	CTIP	(257)
U it d K g d m						
B t h P i l m	B gl B y W l	AE/A/O	1971	BFG		573
ICI	H l h se			S i y	C F B	
	R	A / /		S i y	C F B	
USSR						
T hm h m p t	Dj j k			Rh P g l	Sp hm	66
	G k	E/A/B	1970	Sta ff	Sp hm	73
	G k			Rh P g l	Sp hm	68
	K l h	E/A/B/	1974	BFG H h t	F Uhd	550
	V l g g d	EA / / D		K h	Ch y d	145
	Z m	E/A/B	(1979)	BFG H h t	F Uhd	(595)
V						
P t pl	El T bl	E/A/B	1977	BFG		110
Y g l						
Ok K m l d	Sk pj			Rh P g l		110
H m j k l d	P	E/A/B	(1979)	St ff	F t Wh i	(220)
D / i	KRK		(1981)	D		(440)

I f m t i b l t d i m m y i () I f t d t y p t th h d th b t j d g m t
P th d t th pl t th gh t b (g g d / t t t g d h t h d p t l t t

L g d
Hyd b F d t k / O y B / P oc
(E)thyl (A) (B) l d
(A) tyl (O) yg (O) y t
(M) d G (D) t

VINYL CHLORIDE MONOMER

TABLE 4—VCM plants—worldwide

Op t	L cat	P	Sta t p Y	Li	E gl C tr / tor	VCM C p lty MM Lb /Y
U t d St t	B t R g L	E/A/B	1968	BFG		
ICI Am	L k Ch l L	E/A/B	1968	St ff		300
D oc Ch m l	F p t T			D	R M P so	700
D w	Oy t C k T	E/A/O	1969	D		200
	Pl q m n e L		1978	Dow		700
Ethyl C p	B t R g L			Ethyl		1 150
	H t T			Ethyl		300
B F G od h	C l t C t K t ky	E/A/O	1964	BFG		1050
M h m	G m L	A/ /				300
PPG	L k Ch l L	E/O/B	1960	PPG	F d B & D	400
	L k Ch l L	E/O/B	(1980)	PPG	R M P so	(1 000)
Sh ll Ch m l	G y ll P rt R	E/O/B	1971	PPG	FI	500
	D P k T	E/A/B	1972	St ff	R M P so	840
St ff	N l	E/A/B	1972	St ff	R M P so	700
B d Ch m l	L g B h C li	E/A/B	1957	Sta ff	C F B	175
G g P f	G m L	E/A/B		Sta ff	R M P so	(330)
D m d Sh m k	Pl q m L	E/O/B	(1980)	PPG	B w d Root	(1 000)
Alg i	Dee P k T	E/A/B	1978	St ff BFG	L mm B dge B & R t	1 000
S t h						
A g t	Sk kd	E/O/B	(1979)	M t T ts	T y E g g	(88)
D Q m						
El t oc l	B h Bl nc			D	Ch m co	110
	C pt B m d	E/A/B		ICI		73
	B h Bl			BFG	B dg	287
A t l				ICI		?
I nz	B t ry	A/ /D				
B lgi m	A	E/A/B	1967	Stauff	BASF	240
BASF	F ly d i	E/A/B	1972	BFG	B dg	(1 100)
L b h m	J ppe S	E/A/B	1976	Hoech t BFG	B dg	440
Lmb g (LVM)		E/A/B	1968	Ethyl	S i y	440
						550
S i	El l	E/A/B	1972	S i y ICI	M K CTIP	220
B	B h Bl nc			BFG	B dg	(286)
C p m	C m		(1979)	BFG	B dg /P m	(330)
M m V l						
P t q C m	B g D y	E/O/B	(1979)	PPG	T h p/TPL	(330)
B l g						
T h mpl kt	S O t			D		?
C d	F t S k th		(1979)	D		(660)
Sh g	V Q b	E/A/B	1967	BFG	B dg	126
Chll	Sh w g Q b	A/A/O	1969	BFG		126
P t q m						
D /ENAP	C pc			D w	F h E g ee g	35
Chl	C pc					35
T h lmp t C p	P k g	E/A/O	1978	B F Good h	F Uhd	176
C lmb		E/A/B	1973	St ff		
P t q m C lmb						
C h i k	N t	E/A/B	1972	St ff	R M P so Voet Alp	265
Ch m p t l	N ky Sl k	M/ /D	1972	BFG Hoe h t	F Uhd	240
Ch m k dy W P k						
F l d	P		1971	S i y	CTIP	88
P k m Oy						
F	G i ll					
AKZO	L H					
Ch m	Otlm h m					
EMC/DSM						
D f		E/A/B	1967	St ff BFG Hoe h t		440
Rh P i	L	M/ /D		Rh P gi	Rh P gi	795
	St A b	E/A/B	1970	Rh P gi		291
	St F		1965	BFG Hoe h t		440
	T	E/A/B		S i y Ethyl	S i y	440
	F S M	E/A/B	(1980)	BFG	B dg	(440)
S i						
PCUK/Sh ll Ch m	S hk p		(1979)	H h t	F Uhd	(440)
E t G m y						
I d t A l g lmp t						
W t G m y						
Al	W h lm h					(660)
HI	M l	AE/ /D		H l		700-770
BASF	L dw gh	AE/ /D		St uff		160-320
S i y	Rh b g	E/A/B	1973	S i y	S i y	440
Dy m l N b l	L l d r f	E/A/O	1966	St ff BFG	C F B	130
H h t	G d f	E/A/O	1972	BFG Hoe h t	Uhd	375
	K psa k	EA/A/O	1963	BFG H h t	B dg Uhd	220
	Vi g					(440)
K p k AG	K psa k			BFG	B dg Uhd	220
	K psa k			BFG	B dg K psa k	330
W k	B gh	E/A/O	1971	St ff /St H	R M P	176</

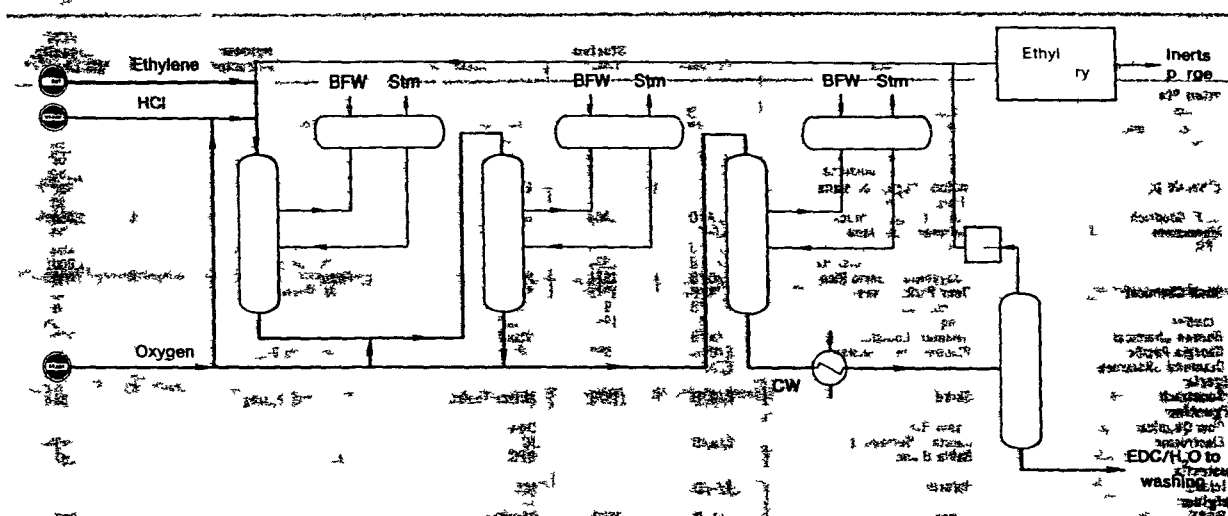


Fig 6—Modifications used in the Stauffer oxygen based oxychlorination process

move HCl and certain chlorinated byproducts which otherwise would hinder fractionation or pyrolysis. The clean EDC is subjected to distillation steps in which water and other light components are removed as well as heavy components typically labeled tars. The dry product EDC generally of 99.5 percent or greater purity is thermally cracked to yield HCl and VCM in an EDC carrier stream. Further distillation equipment separates EDC and HCl for recycle and yields product VCM for final treating.

The typical VCM plant includes VCM treating, offgas treating, light ends/tars handling and waste treating facilities. It will also include incineration units for reclaiming waste chlorinated hydrocarbons from offgas or liquid streams.

Stauffer technology In the Stauffer direct chlorination process (see Fig 5) ethylene and chlorine are reacted in the liquid phase and under controlled conditions to yield a crude product which analyzes 99.7 percent EDC. The reactor product is then combined with the crude oxy EDC, washed and distilled to remove water, light ends and heavy ends.

Pure EDC is preheated in the economizer of the pyrolysis furnace and then vaporized with steam. EDC vapor is then heated to dissociation temperature in the furnace tubes to yield a mixture of vinyl chloride and hydrogen chloride. Conditions are controlled to maintain EDC conversion at 50 to 55 percent. Following a quench and condensation step, HCl, VCM, and uncracked EDC are separated by distillation. Hydrogen chloride gas is sent to the oxy section. Unreacted EDC is recycled to purification.

The oxy section combines recycle HCl with fresh ethylene and air in tubular fixed bed catalytic reactors. The ethylene and air are fed in excess of stoichiometric requirements to assure high HCl conversion. Reaction

heat is removed by generation of steam on the shell side of each reactor. The final reactor effluent is cooled to condense EDC and the offgas is contacted/reacted with chlorine to recover ethylene as additional EDC. The offgas stream is cooled versus cooling water and refrigeration to further condense EDC before exiting the process. Residual ethylene concentration in the vent gas is reportedly as low as 10 ppm.

Stauffer also offers an oxygen based oxy process (Fig 6) in which the main reactor offgas following condensation of EDC is compressed and recycled to the first oxy reactor. An excess of ethylene is used to maximize HCl conversion and minimize byproducts. A small slipstream from the ethylene rich recycle is purged to an ethylene recovery unit for control of inerts.

Ethyl integrated VCM process Gaseous chlorine and ethylene are introduced into a direct chlorination reactor in which they combine to form EDC. The very high purity EDC product can be sent directly to (or after degassing can bypass) the EDC purification system (see Fig 7).

Air and gaseous ethylene and HCl are introduced into an oxychlorination reactor in which EDC is produced at an elevated pressure and temperature in the presence of a fluidized catalyst. The reaction products are neutralized and partially condensed to recover EDC which is first sent to a drying column and then to the EDC purification system. A portion of the vent gas consisting primarily of nitrogen and carbon dioxide is recycled to the reactor for added safety.

The purified EDC stream which contains recycled EDC as well as the EDC from direct and oxychlorination is vaporized and introduced into a furnace. At least half of the EDC stream is cracked to HCl and VCM. The reaction products are cooled rapidly, partially condensed, and then sent to the VCM purification system.

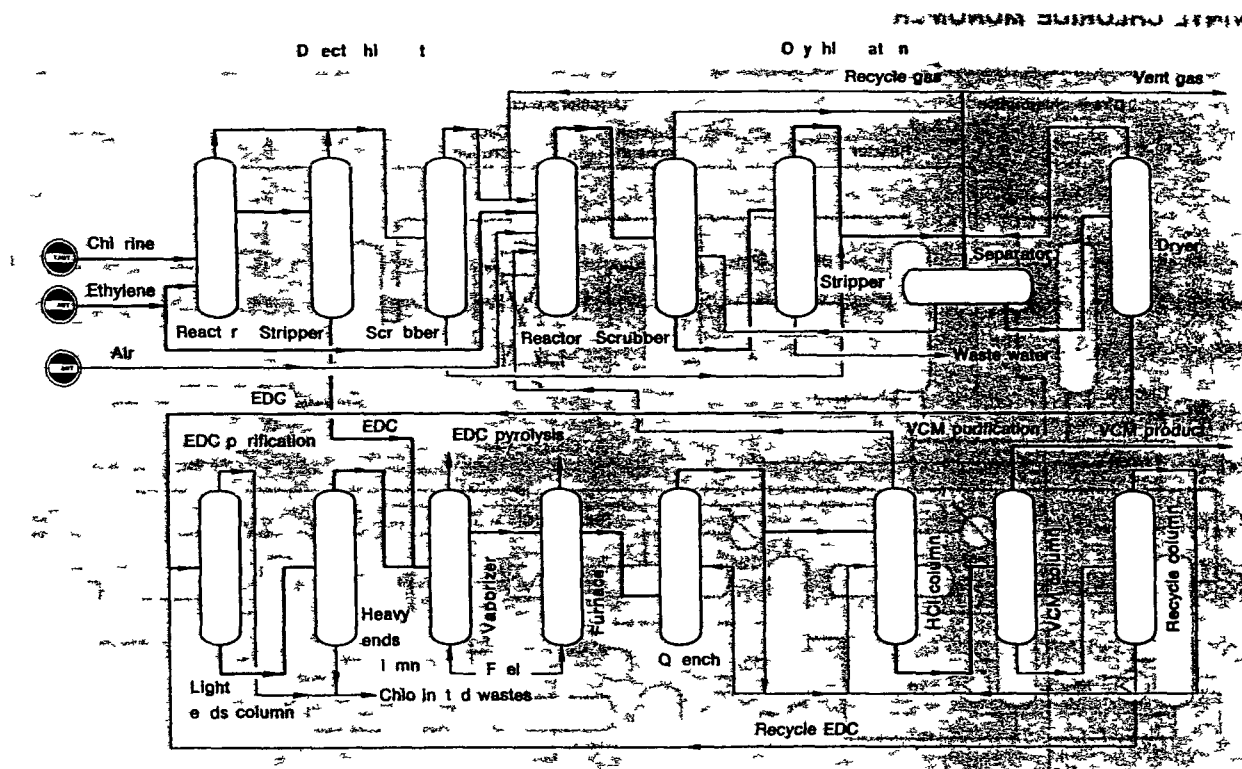


Fig 7—Ethyl Corp's integrated vinyl chloride monomer process

HCl and VCM are separated by fractional distillation from the unconverted EDC and small amounts of byproducts. The EDC containing the byproducts is recycled to the EDC purification system.

Mitsui Toatsu Chemicals technology The MTC technology utilizes a boiling liquid process for the direct chlorination reaction. Reaction heat is dissipated with the gaseous EDC exit stream which is condensed externally and sent to purification.

The oxychlorination process is characterized by the use of oxygen feedstock and a fluidized bed reactor. The reactor effluent gases are quenched with circulating EDC followed by caustic neutralization. The neutralized gas is cooled to condense EDC and water. Uncondensed gases, primarily ethylene, are recycled back to the oxy reactor. A small stream is vented from the recycle gas to allow purging of inerts. EDC liquid is phase separated from water and dehydrated before joining the EDC streams in the purification system.

A conventional EDC purification system splits crude EDC into light ends, heavy residue, and pure EDC. The latter is cracked to yield VCM, which is purified in a manner similar to that described in the Stauffer technology (see Fig 8).

PPG technology The EDC production technology appears very similar to that described for Mitsui Toatsu, particularly in the use of oxygen feedstock and fluidized bed reaction for oxychlorination. However, PPG does not indicate use of a dehydrator to dry crude oxy EDC prior

to purification. Also, PPG uses three rather than two towers to obtain the HCl/VCM/EDC separation.

B F Goodrich technology Goodrich direct chlorination uses conventional water-cooled technology similar to that shown for Stauffer. The air-based fluidized bed oxychlorination technology is similar to that shown for Ethyl. Goodrich also utilizes an absorber-stripper system on the oxy vent gas stream to minimize hydrocarbon losses. Goodrich, in conjunction with Badger Inc., offers complete technology for waste treating of VCM plant effluent streams.

Toyo Soda technology This technology appears very similar to that offered by Stauffer. The principal differences are in the use of an absorber-stripper on the oxy vent gas effluent (as with Goodrich) and the dehydration of crude EDC prior to purification. As with other oxychlorination processes, steam generation is used to remove reaction heat.

Phone Poulenc technology Rhone Poulenc offers two processes, Chloe I and Chloe II. The former is of a special nature to yield concurrently significant quantities of other chlorinated hydrocarbons such as trichloroethylene and trichloroethane. The Chloe II process is true VCM technology using air-based fluidized bed oxychlorination in combination with boiling liquid direct chlorination.

Monsanto technology This process appears very similar to that offered by Stauffer.

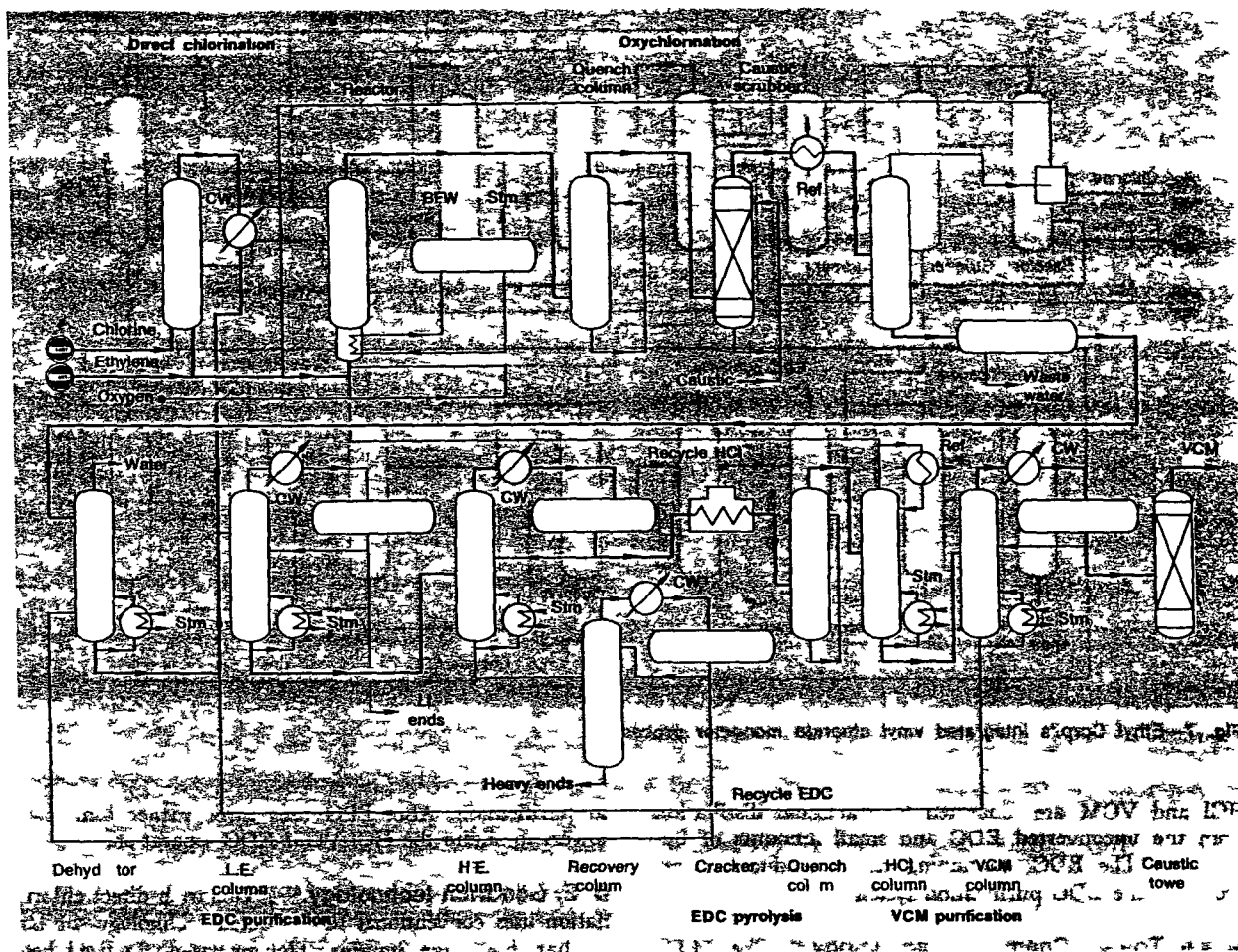


Fig 8—Mitsui Toatsu uses these modifications in their vinyl chloride monomer process

Dow technology Dow's technology has not been publicized. It has been used only by Dow and its foreign affiliates.

NEW DEVELOPMENTS

Although it is believed that several VCM producers currently use boiling liquid reactors for direct chlorination, Stauffer has developed a unique application of this concept. Their approach, High Temperature Chlorination, in effect uses the reactor as a reboiler for the conventional EDC purification system (see Fig 9). Purified EDC is withdrawn as a side stream from the tower, and any light components formed are removed overhead. Normal feed to the tower consists of treated EDC from oxy and recycle. Small amounts of the normal heavy ends or tars are purged from the base of the reactor. This application eliminates approximately 100,000 lbs per hour of 150 psig steam consumption for a one billion lb per year VCM plant. A similar energy savings is achieved in reduction of cooling water usage relative to a conventional reactor and light ends tower. B F Goodrich also offers a boiling liquid process in which the heat of reaction

is utilized to purify all EDC processed in the purification train.

Increased activity by EPA (U.S. Environmental Protection Agency) and state agencies in regulating hydro

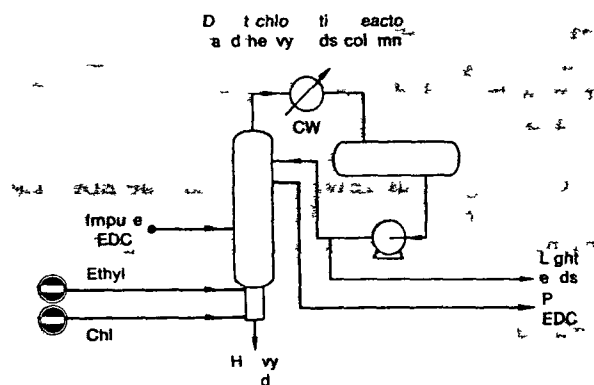


Fig 9—Stauffer high temperature chlorination and ethylene dichloride purification schematic

carbon emissions are likely to stimulate further new developments particularly in oxychlorination processes. These will range from development of new oxygen based technology to various add on systems for cleaning up oxy vent gas. The latter may include catalytic oxidation, incineration (of oxygen based oxy vent gas), solvent absorption, combined refrigeration and absorption techniques and/or other combinations. Several companies not active as VCM producers are involved in developing these add on systems.

It is expected that companies will continue to devote considerable effort to the development of cracking promoters and inhibitors of side reactions in pyrolysis chemistry. Current cracking practices limit EDC conversion to 50-60 percent. Considerable energy and cost savings could be achieved through increased conversion levels without concurrent losses of EDC to undesirable side reactions.

EPA regulations EPA's Standard Support and Environmental Impact Statement, Emission Standard for Vinyl Chloride, presented the following regulations:

- Emissions from all point sources except oxychlorination would be reduced to 10 ppm VCM by volume.
- Emissions from the oxychlorination reactor would be reduced to 0.02 lb VCM per 100 lbs EDC product from the oxy process.
- Preventable relief valve discharges would not be permitted.
- Fugitive emissions would be minimized by requiring enclosure of the emission sources and collection of the emissions.

EPA estimated typical VCM plant emissions in 1974 as follows:

Source	Lbs /VCM/ 100 Lbs VCM
Fugitive	0.1215
EDC Finishing Column	0.05
VCM Finishing Column	0.24
Oxy Process	0.0364
Process Water	0.0007
Total	0.4479

The regulations were predicated upon reduction of such emissions by 94 percent using best available technology. Compliance testing of these installations was begun in the last quarter of 1978.

Additional EPA and state actions were initiated in mid 1977 to reduce hydrocarbon emissions from VCM plants in non attainment regions, i.e. much of the Gulf Coast. EDC production is reported to account for 28 percent of the hydrocarbon emissions in the southern Louisiana and East Texas AQCRs. These actions were directed primarily against oxychlorination vent gas from air based units. The amount of hydrocarbon reduction sought varies from region to region. No published guidelines are currently available to reference.

The net effect of these various regulations has been to increase substantially the scope of add on technology in VCM plants such as:

Installation of primary and redundant incineration facilities for VCM point (ex oxy) source and collected fugitive emissions.

- Installation of HCl scrubbing and neutralization or recovery units in conjunction with the incinerators.
- Installation of closed process sewers, collection systems and larger or redundant waste water strippers.
- Replacement of single mechanical seals on pumps and agitators with double mechanical seals. (In some cases conventional pumps were replaced with canned or magnetic drive pumps).
- Leak detection systems and portable monitors.
- Enclosed sampling and analytical systems.
- Vapor recovery systems for VCM loading/unloading and equipment cleaning.

The EPA report estimated a maximum capital impact of \$0.8 to \$1.9 MM (1975 dollars) for a model 700 MM lb per year VCM plant. Recent cost estimates indicate the true impact for these items is nearer \$15 MM based on 1978 dollars. Addition of hydrocarbon compliance (proposed regulations) may add another \$2.5 MM.

EPA also has proposed further reductions in VCM emissions. Under consideration at present are regulations which will reduce allowable emissions from 10 ppm to 5 ppm for all point sources including oxy vent gas. EPA further plans to prohibit emission increases within 8 kilometers of an existing source due to construction of a new emission source. This will effectively prevent expansion of existing facilities or construction of new plants in the vicinity of existing plants. The proposed oxy vent gas regulation will also dictate substantial capital expenditures for add on facilities and possibly the conversion of air based to oxygen based plants to facilitate incineration of tail gases.

ECONOMICS

Table 5 presents a 1981 manufacturing cost buildup for a typical 700 MM lb per year grass roots VCM plant. Raw materials total 12 cents per lb VCM or 54 percent of the required FOB plant selling price. Capital related costs amount to 6.8 cents per lb VCM or 32 percent. Utilities are only 6.7 percent of the total VCM cost. In perspective, the 1972-1973 reported VCM selling price was only 4.5 cents per lb. By 1981 the capital related unit costs alone will exceed this by 50 percent.

The obvious major factor in VCM pricing is raw materials cost. Although chlorine price is expected to double between 1973 and 1981, the impact of ethylene price will be even greater (three cents per lb versus 17 cents per lb). The real culprit of course is crude oil cost. During the late 1960s and early 1970s plants using inexpensive LNG feedstocks were significant contributors to the low cost U.S. ethylene supply picture. The energy crisis rapidly reversed the low cost feedstock trend. LNG scarcity

dictated construction of naphtha and/or gas oil crackers for present and future ethylene production. This tied VCM prices irreversibly to crude oil prices through ethylene fuel and power (particularly via its impact on chlorine).

Th thor g f lly k owl dg trib b A B S ryker J
f Sta ff d H Wall f Eth l and permissi by th mp nies
us th frm p ese d h espe p ocesses

U.S. E nm tal P Ag cy R p N EPA-450/2 75-009
Rrch t gl P k NC (1975)
Lch HS (Mnsan Chmcal Co) US Pa 3 338 982 (1967)
BFG odr h C British P 1 233 238 (1971)
Campbell R G (S ff Chmcal C) US P 4 000 205 (1976)
B d D (t U C bd) US P t 2 929 852 (1960)
D F L d C lcg B (Soc Ital R) US P
3 911 036 (1975)
T U (t L mm C) US P 3 917 727 (1975)
Ktz B D d Om lia A (All d Chmcal C) US P
3 941 568 (1976)
Vlan Ma ls B h p 980 983 (1965)
V A wrp AE H prj g J W S benz R G d K g T L
(to B F Goodrich) US P 3 488 398 (1970)
Se FT (Sta ffer Chmcal C) US P 4 046 822 (197)
S uff Chmcal C B tush Pa t 1 230 607 (1971)
B F Good ch Co B l g m p 680 413 (1966)
K H (M T Chm l) J p P 46-43367 (1971)
18 Miya chu K (M tsu Toats Chmcal) Brn h P l 189 815
(1970)
28 Tak hash T (M ts T Chmcal) J p P 45 32406
(1970)
M T ts Chmcal J p P t 46-33010 (1971)
19 PPG I d F ch P 2 080 666 (1971)
M A P (PPG I dus res) B h P 1 220 394 (1971)
20 Abl om J R C (D w Chmcal C) US P 3 966 304
(1976)
S rin J C d C J R (Rh P og l) US P 3 935 286
(1976)

CHARLES M STARKS is d ect f ex
plorat ry esearch Continental Oil Co
Ponca City Okla Dr Starks received
h BS fr m the Un v sity of Okla
h ma and his PhD f m Massachus tts
Institute f Te hn lo gy



	Lb /Lb VCM	£/U t	C t £/Lb/ VCM	%
R M te l				
Chl	0 64	5 6	3 53	16 2
Ethyl ne	0 49	17 1	8 45	38 8
C taly t d h m cal			0 39	1 8
Ubl ti			1 42	6 5
T tai bi			13 79	63 3
Lab			1 18	5 4
M sc ll ne			0 98	4 5
T tal fied			2 16	9 9
T tal m f t t g t			15 95	73 2
C p tal h g d d p t			5 85	26 8
S fl g p ce FOB pi nt			21 79	100 0

8 sas
1 700 MM P d/Y B l d VCM P l t
2 1981 Start p
3 G ss Root l tm t \$140 MM
4 Lght nd h y d nc l d ov d HCl sold m tu d t b k
5 Fft p t DCF l f t t t t h g l dp ft
6 U t l g l f d t t pe fct prt l se so t h lgy

Small y E W Kurtz B E d Bandy p dhy y B (All d Cl m cal C rp) U S P 4 060 460 (1977)
K psack C B ush P 1 266 676 (1972)
S l y t c i F h P 1 602 522 (1971)
K l i A G (Knap k C) U S P 3 484 493 (1969)
J lin A G (ICl) B ush P 956,618 (1964)
F oelch W (H tch) G m P 2 217 694 (1973)
Y g D H R J Ch m Soc 148 (1949)
Y g D P (B P Chem l L d) U S P 3 896 182 (1975)
M t Ch m cal J d J P 42 22921 (1967)
B F G odrich, B h P 938 824 (1963)
K p sa k C U S P 3 476 955 (1969)
M sa Ch m cal Co Br n B Pa en 1 168 329 (1969)
K g H J (M Ch m cal Co) U S P 3 125 607 (1964)
G us E M (M Ch m cal C) U S P en 3 142 709 (1964)
McD ld D W (M Ch m cal C) U S P 3 125 608 (1964)
G m S Eighth World P l um C g ss P oc ding 4, 371 (1971)
K h a Ch m cal l d tr Britash P 977 578 (1964) Br n h P 1 068 793 (1967)
D H d M d M J S Ch m l d (L d) 69 75 (1950) P F d W dl h P H l Ch m A 32 783 (1949)
G d R D d Sta ks C M (Co Ch m al O l C) U S P 4 046 823 (1977)
K ck M A (Sta ff Ch m cal C) U S P 3 987 118 (1976)
W J (P Ch m l R arch l) U S P 3 551 506 (1970)
K t z B Sm lley E W S m m rm W E d V A J R (All d Ch m cal C) U S P 3 987 119 (1976)
G d T H d d K m m l H F (Ow Ill l) U S P 4 042 639 (1972)
R l H (Lumm C) U S P 3 796 641 (1974)
R l H (L mm Co) U S P 3 557 229 (1971)
R l H (Lumm C) U S P 3 937 744 (1976)
S M C (Lumm C) U S P 3 949 010 (1976)
J sa U (L mm C) U S P 3 963 584 (1976)
T U (L mm Co) U S P 3 992 460 (1976)
R l H (L mm C) U S P 3 935 288 (1976)
J sa U (L mm C) U S P 3 985 816 (1976)
Min J D Ch m E g P g 69 (8) 71 (1973)
L d E D V y l d D M m (P t 3) J h W i y c S I New Y k 1971
S M V y l Ch l rd d P V C M f Noy D C p 1978
G m S J p N w V y l Ch l rd P (K h) Hyd b P g V l 43 N 11 N mbe 1964
R w g M d / V y l P oc Has W d Ra g f By P od t (Rh P ogil) Ch m al E g V l 78 N 24 Oc 18 1971
R b J d B A Rh P g l N w P d S l f b M f ur f V y l Ch l rd M m d Ch l d S l f m E h l 164 h A C S N l M g N w Y k A g 27 S p l 1972
B kl y J A P oc Fl w Sh /V y l Chlor d Dr Ch l t d Oxy hl Ch m al E g g V l 73 N 24 N 21 1966
P r v t C m m ca f m A B S yk J S ff Ch m cal C N 29 1978
R h P P Ai Oxyg f VCM H yd b P n g M ch 1976 pp 85 89
P C m m ca on f m H H W ll E hyl C rp N 28 1978
V y l Ch l d Hyd b P g N 1975
EPA-450/3-73-006-C V l 3 N mb 1974
F d R g u J 2 1977
EPA 600/2 76-053 M h 1976
K K D v id P l V y l Ch l d H w Wh Who-F Hyd b P g F b ry 1973
V y l Ch l de-M su T tsu Ch m ls Hyd b P g No mbe 1971
V l Ch l d -PPG l d l Hyd b P g N m b 1975
V y l Ch l de-B F Good h Ch m cal C Hyd b P g N mb 1975
V y l Ch l de-Rh m P l SA Hyd b P g N mbe 1975
V y l Ch l de-(M sa C) Hyd b P g N mb 1975
P m m ca from J S B B F G d r h Ch m cal C l 5 1979