ties were calculated from the data obtained in runs 89 and 90 using an expected yield of 95.4%. The quantity of wash toluene was not increased proportionately, because the amount used in the laboratory preparation was excessive. About 60% of the diphenylmercury in the toluene can be obtained with each crystallization by cooling the solution to 27° C. The quantity of toluene in the mixture in each case is just enough so that the crystal slurry can be handled.

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Synthesis of Ethylene Chlorohydrin

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Ethylene chlorohydrin has been made for many years, but the secretiveness that has surrounded the process has allowed little specific information to appear in the literature. A study has been made of the effect of several of the process variables on the yields and a comparison made with results from recycle and single column operation. Low temperature operation is undesirable because of extensive formation of by-products. High mole ratios of ethylene to chlorine favor high yields of ethylene chlorohydrin, but the yield decreases as charge rates increase for a given reactor. Physical observations and data indicate that the recycle-type reactor has advantages over the single column reactor in terms of both yield and smoothness of operation. Process variables which must be considered in reactor design are stressed, as well as conditions and method of operation.

NUMEROUS processes have been developed for the synthesis of ethylene chlorohydrin. A few of the methods border upon the bizarre; many more are of academic interest only. The most important methods, from an industrial viewpoint, involve the interaction of ethylene with hypochlorous acid formed by the solution of chlorine in water. One of the principal uses of ethylene chlorohydrin is in the production of ethylene oxide which in turn is an intermediate in the synthesis of ethylene glycol and a host of other compounds, including acrylonitrile, ethanolamines, ethers for hydraulic fluids, and polysulfide rubber polymers.

While considerable interest has recently been directed to the catalytic oxidation of ethylene to ethylene oxide, ethylene chlorohydrin will remain an important chemical intermediate for many years. During the industrial expansion after World War II, many firms turned to the production of ethylene glycol through a process that has been practiced in the United States in one form or another since 1922. As pointed out by Sherwood (*11*), the process for the manufacture of ethylene glycol via ethylene chlorohydrin is particularly remarkable for the secretiveness that has surrounded its operation. There is a considerable volume of patent information but only a rather limited number of reports of laboratory investigations, which deal for the most part with studies of small scale batch preparations.

Wurtz (*16*) first prepared ethylene chlorohydrin from ethylene glycol in 1859 by reacting glycol and hydrochloric acid. Four years later Carius (*2*) reported the more direct synthesis by the addition of hypochlorous acid to ethylene, and this has become the basic reaction upon which most industrial processes are founded. In 1919 Gomberg (*6*) described the synthesis of ethylene chlorohydrin from ethylene and chlorine passed into water. Sherwood (*11*), McClellan (*7*), and Curme and Johnston (*3*) have described the chlorohydrin process for the production of ethylene glycol, and Murray (*8*) and Shilov *et al.* (*12–14*) have described some of the more recent investigations of the synthesis of ethylene chlorohydrin.

When chlorine dissolves in water it forms hydrochloric acid and hypochlorous acid

$$Cl_2 + HOH \rightleftharpoons HCl + HOCl \tag{1}$$

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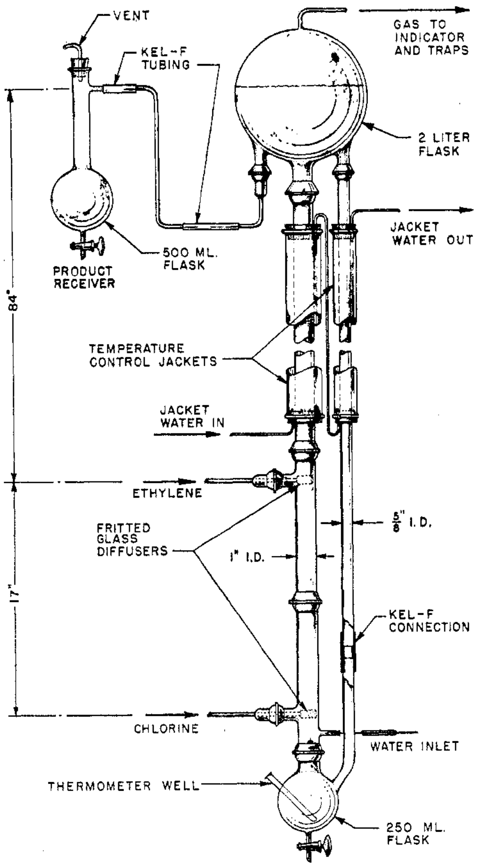


Figure 1. Reactor for Synthesis of Ethylene Chlorohydrin

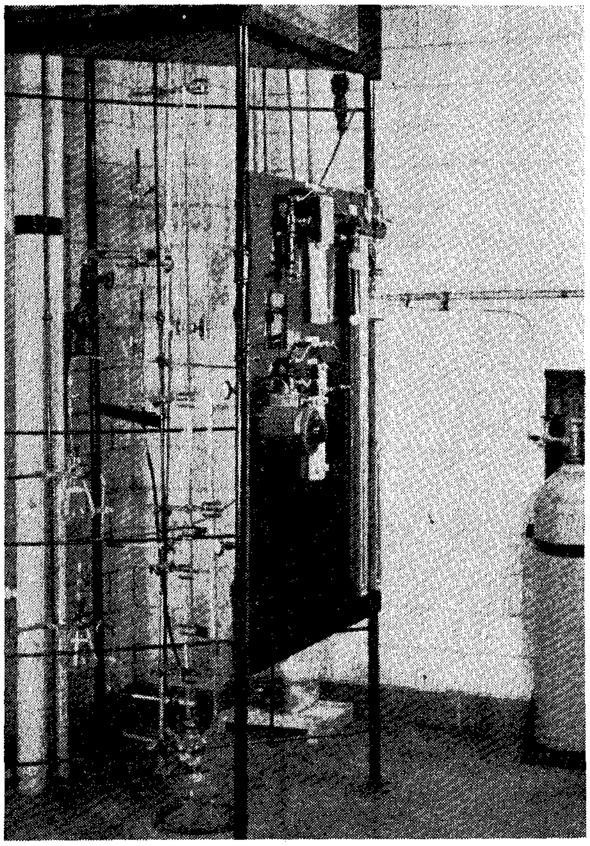


Figure 1A. Reactor for Synthesis of Ethylene Chlorohydrin

Ethylene bubbled into this aqueous solution reacts with the hypochlorous acid to form ethylene chlorohydrin

$$C_2H_4 + HOCl \rightarrow Cl.C_2H_4.OH \qquad (2)$$

The by-product formed in greatest amount is ethylene dichloride, and it may be considered as resulting from the direct addition of chlorine to ethylene

$$C_2H_4 + Cl_2 \rightarrow Cl.C_2H_4.Cl \qquad (3)$$

A second by-product is bis(2-chloroethyl) ether (Chlorex). While there are several postulations as to the mechanism for the ether, it may be represented as being formed at the expense of reactants along with the desired product

$$C_2H_4 + HOCl + Cl.C_2H_4.OH \rightarrow Cl.C_2H_4.O.C_2H_4.Cl + HOH \qquad (4)$$

It was the object of this investigation to study the influence of certain reaction process variables for the synthesis of ethylene chlorohydrin from ethylene, chlorine, and water in a recycle reactor and compare the results from a recycle reactor with those from a single column reactor. Plant (*10*) has recently described a new installation in England that is an industrial application of the recycle principle in ethylene chlorohydrin production.

Experimental

Reactor. The reactor shown in Figure 1 was designed to incorporate some of the features of equipment described by Ferrero and Vandendries (*5*), Britton *et al.* (*1*), and Murray (*8*). It had sufficient flexibility to permit studies of both batch and continuous operations, and it could be used either as a single-column reactor or as a double-column recycle or circulating-type reactor. Because of the highly corrosive nature of the reaction mixture, acidproof materials were used. The body of the reactor was borosilicate glass. The various components were joined together by ground-glass ball-and-socket joints or KEL-F tubing (a polymer of trifluorochloroethylene, a product of M. W. Kellogg Co., Barclay St., N. Y.). A silicone grease was used on the ball-and-socket joints to provide a seal, and the joints were held together tightly by clamps. The main vertical column was of 1-inch internal diameter, and the smaller return column was of $^5/_8$-inch internal diameter.

Operation. Chlorine was introduced into the aqueous reaction liquid near the bottom of the larger column. The chlorine vapor was dispersed as fine bubbles by a fritted glass diffuser and was dissolved rapidly. Ethylene was introduced at a point 17 inches above the chlorine through a similar diffuser, and the ethylene bubbles contacted the aqueous chlorine solution where ethylene and hypochlorous acid reacted to form ethylene chlorohydrin in the aqueous medium. Reaction continued as the bubbles rose through the liquid, and unreacted gases disengaged from the liquid in the overhead flask and passed out the top of the reactor to an indicator solution and to traps.

In continuous operation, water entered the main column at a point just below the chlorine inlet. The water inlet rate determined the rate at which the product was removed from the top of the column through the constant-level arrangement shown in Figure 1. The aqueous chlorohydrin product solution was collected in the product receiver. The normal capacity of the reactor with the recycle arrangement was approximately 3 liters. Heating or cooling liquid was passed through the temperature control jackets that surrounded the upper portions of the two columns. The rapid circulation imparted to the reaction liquid by the gas-lift principle facilitated close temperature control of the reaction liquid within 1° C. of the desired temperature.

For operation of the reactor as a single column, without recycle of the reaction liquid, the bottom flask and the smaller column were removed, and ball-and-socket ground-glass fittings equipped with stopcocks were used to seal the respective unused ball-and-socket joints at the base and top of the column.

A flow diagram of the equipment is shown in Figure 2. The ethylene was 95% pure and was derived from alcohol. Commercial grade chlorine was used from a standard 100-pound

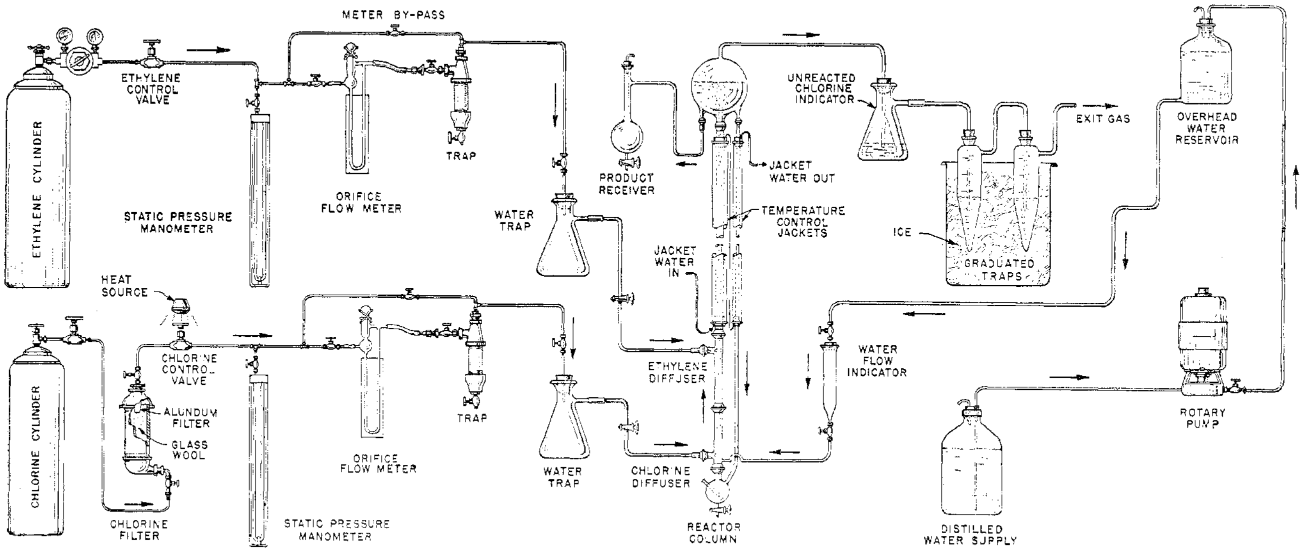


Figure 2. Flow Diagram of Equipment for Synthesis of Ethylene Chlorohydrin

cylinder. The chlorine was passed through a filter that consisted of glass wool and an alundum thimble. The chlorine control valve was heated slightly by an electric light bulb to ensure steady flow of the chlorine. Water traps were provided to prevent the aqueous reaction solution from backing into the rest of the system in the event of a sudden loss of gas pressure.

The reactor was operated with an excess of ethylene. It was desirable that all the chlorine be used before it reached the top of the column so that there would be no possibility of an explosion of unreacted chlorine and ethylene in the disengaging zone above the liquid in the reactor. In order to have a rapid indication of the appearance of chlorine in the unreacted gases, the gases were bubbled through a starch and potassium iodide indicator solution that gave an immediate color change when chlorine was present. Two traps were placed in series in the exit gas line to recover ethylene dichloride stripped from the reaction solution. The traps consisted of graduated vials partly filled with water and immersed in an ice bath. The gases were bubbled through the cold water, which was at a temperature of 2° to 4° C., and ethylene dichloride condensed as an immiscible layer in the bottom of the traps. There was seldom any trace of immiscible dichloride in the second trap.

The procedure used to put the equipment into operation involved first charging the reactor with water and then charging ethylene for about 20 minutes before admitting chlorine. The initial chlorine rates were kept quite low to prevent the appearance of unreacted chlorine in the exit gases. As the concentration of reaction products increased, the gas rates were gradually increased until the desired rates were attained. The appearance of reaction products facilitated the reaction in that gas dispersion in the aqueous medium improved, and gas charge rates could be increased without loss of unreacted chlorine.

Analyses. The analyses included determination of inorganic chlorides (hydrochloric acid), ethylene chlorohydrin, and other organic chlorides. The latter included primarily ethylene dichloride and a small amount of bis(2-chloroethyl) ether and was reported as ethylene dichloride. The hydrochloric acid and ethylene chlorohydrin were determined mercurimetrically (*4*). The hydrochloric acid was determined on one portion of a sample; a second portion was treated with sodium bicarbonate, which selectively hydrolyzed the ethylene chlorohydrin, and the combined chloride determination after hydrolysis permitted the chlorohydrin content to be obtained by difference. During the batch runs, the soluble organic chlorides, other than ethylene chlorohydrin, were obtained by a chloride determination after hydrolysis of a third portion of a sample with sodium hydroxide. The hydrolysis with sodium hydroxide was later found to be unreliable in that it effected only partial hydrolysis of the water-soluble portion of ethylene dichloride. The data with which these determinations are concerned are indicated in the tables to show that the ethylene dichloride values are low. Several other methods were tried for the determination of the water-soluble organic chlorides, and distillation was the procedure finally adopted. Ethylene dichloride forms an azeotrope with water at 72° C., and ethylene chlorohydrin, bis(2-chloroethyl) ether, and water form a ternary azeotrope at 97.3° C. Conveniently, ethylene dichloride and bis(2-chloroethyl) ether are only slightly soluble in water, so it is possible to recover these materials as an immiscible layer by distillation. The distillation column was operated at total reflux, and the immiscible layer was collected in a side arm at the top of the column.

Yields were based on analyzed chlorine. Inasmuch as the dichloride determinations were low for the batch runs, the ethylene chlorohydrin yields are slightly high. However, the data are on a comparable basis, so the qualitative influence of the operating variables remains clearly evident. The yield data for the continuous runs are considered to represent actual conditions.

Discussion of Results

In the synthesis of ethylene chlorohydrin, the amount of by-products present in the reaction medium affects the rate of by-product formation. The amount of by-products present at steady state conditions during continuous operation is greater than when the reaction begins at zero concentration of ethylene chlorohydrin and increases to a given concentration level. Consequently, data from batch operations do not reflect yields at any given concentration; however, batch data do provide information concerning the qualitative influence of certain variables. Accordingly, a number of variables were studied with batch operation of the recycle arrangement, and based on information gained from these runs, conditions were selected for a number of continuous runs with both a single column and the recycle reactor arrangements. The final concentration of the product in the batch runs was generally about 12% ethylene chlorohydrin.

Influence of Reaction Temperature. The influence of the heat of reaction for the formation of ethylene chlorohydrin is limited largely by the fact that only a dilute solution of chlorohydrin is formed. Some indication of the temperature rise in the reaction medium can be obtained from Table I, which shows only a small temperature rise for the particular rates of formation represented by the data.

Table I. Data from Preliminary Batch Run with Recycle

Reactor temperature was not controlled
Room temperature = 26° to 28° C.
Final chlorine rate = 36 grams/hour
Mole ratio, ethylene:chlorine = 1.73

Elapsed Time, Hours	Reactor Temp., ° C.	Products, Wt. %			ClC$_2$H$_4$OH:HCl	
		Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1	28.8	0.83	0.38	...	0.987	2.178
2	30.9	1.82	0.83	0.009	0.990	2.187
3	32.4	2.85	1.31	0.01	0.985	2.174
4	33.8	3.91	1.80	0.01	0.984	2.173
5	34.4	4.89	2.27	0.02	0.979	2.159
6	34.3	5.88	2.72	0.03	0.978	2.159
7	34.3	6.83	3.15	0.03	0.980	2.164
8	34.0	7.71	3.59	0.04	0.972	2.147
9	33.3	8.66	4.00	0.04	0.980	2.163
10	33.1	9.47	4.42	0.05	0.970	2.142
11	32.7	10.31	4.82	0.07	0.969	2.139
12	32.6	11.12	5.22	0.09	0.966	2.132

[a] Values shown are the low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

Table II. Data from Batch Run, with Recycle, at 13° C.

Reactor temperature = 13° ± 1° C.
Final chlorine rate = 36.2 grams/hour
Mole ratio, ethylene:chlorine = 1.73

Elapsed Time, Hours	Products, Wt. %			ClC$_2$H$_4$OH:HCl	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1	0.74	0.34	0.003	0.982	2.168
2	1.28	0.59	0.005	0.985	2.175
3	2.07	0.95	0.007	0.986	2.176
4	2.91	1.33	0.01	0.988	2.182
6	4.57	2.12	0.03	0.977	2.158
7	5.57	2.58	0.03	0.977	2.157
8.5	6.89	3.20	0.06	0.975	2.153
10	8.22	3.83	0.07	0.971	2.144
11	8.99	4.23	0.09	0.964	2.127
12	9.79	4.59	0.09	0.966	2.132
13	10.55	5.00	0.12	0.956	2.110
14	11.39	5.36	0.14	0.962	2.125
Yields for entire run	94.4	98.0	3.8		

[a] No trap was used in gas-outlet line during this run; however, 15 grams of ethylene dichloride was recovered as a separate phase from the reactor. Values shown are the low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

Tables II, III, and IV give the data for three runs over the temperature range 13° to 50° C. In the reaction of ethylene, chlorine, and water to form ethylene chlorohydrin,

$$C_2H_4 + Cl_2 + HOH \rightarrow Cl.C_2H_4.OH + HCl \qquad (5)$$

there should theoretically be 1 mole of ethylene chlorohydrin for each mole of hydrochloric acid formed. However, as the mole ratios indicate, the chlorohydrin is always present in lesser amounts. The theoretical weight ratio is 2.208. In explanation of the variation of the mole ratio from unity, there are the possibilities of decomposition of hypochlorous acid and of its oxidation to chloric acid. There is also the probability of loss of some hypochlorous acid and ethylene chlorohydrin through the formation of bis(2-chloroethyl) ether, as shown by Equation 4. In this connection, the variation of the mole ratio from unity may be used to provide a rough indication of the amount of the ether formed, but because of the influence of other reactions, it would not provide a quantitative measure of the amount of the ether present.

The solubility of ethylene and chlorine in water increases as the temperature decreases; accordingly, it was anticipated that the reactor would operate more smoothly at a low temperature than at some higher temperature. However, the opposite to this was found to be true. At 13° C., the final chlorine rate was limited to about 36 grams per hour instead of the desired 42 grams per hour, because unreacted chlorine appeared in the exit gases whenever attempts were made to increase the chlorine rate.

The data, combined with recorded physical observations, indicate that nothing is to be gained by resorting to low operating temperatures that require refrigeration. A disadvantage of low temperature operation is that ethylene dichloride accumulates in the reaction medium as a separate phase. The presence of the dichloride contributes to the formation of more dichloride, because ethylene and chlorine dissolve in the immiscible phase and react directly.

It is possible that the yield of ethylene chlorohydrin is slightly favored by a reaction temperature approximating 35° C. The results of this work are not conclusive in this respect, but Murray (*8*) also obtained slightly higher yields at about 30° C. than at other temperatures.

In large scale production, the selection of an operating temperature can probably be left to the dictates of convenience. The heat of reaction promotes an increase in temperature, but the final temperature can be controlled to a great extent by the temperature of the feed water. As the temperature of the reaction is raised, increased amounts of ethylene dichloride are stripped from the reaction medium; this facilitates the recovery of the dichloride which can be condensed from the exit gas.

Influence of Mole Ratio of Ethylene to Chlorine. A comparison was made of the influence of mole ratios of ethylene to chlorine of 1.21, 1.48, and 2.85, with other variables held constant. It is readily apparent from the data of Tables III, V, and VI that much more ethylene dichloride is formed at the low ratio than

Table III. Data from Batch Run, with Recycle, at 35° C.

Reactor temperature = 35° ± 1° C.
Final chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 1.48

Elapsed Time, Hours	Products, Wt. %			ClC$_2$H$_4$OH:HCl	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	1.03	0.48	0.007	0.980	2.163
3	2.01	0.92	0.01	0.988	2.181
4	2.92	1.34	0.02	0.985	2.176
5	3.98	1.84	0.02	0.982	2.168
6	5.06	2.35	0.03	0.976	2.155
7	6.16	2.87	0.04	0.973	2.149
8	7.21	3.33	0.04	0.981	2.165
9	8.23	3.82	0.05	0.975	2.152
10	9.13	4.27	0.06	0.968	2.138
11	10.07	4.72	0.06	0.966	2.132
12	10.98	5.16	0.07	0.963	2.127
13	11.83	5.57	0.08	0.961	2.122
Yields for entire run	95.2	98.9	2.9		

[a] Ethylene dichloride recovered = 12.3 grams. Values shown are the low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

Table IV. Data from Batch Run, with Recycle, at 50° C.

Reactor temperature = 50° ± 1° C.
Final chlorine rate = 41 grams/hour
Mole ratio, ethylene:chlorine = 1.47

Elapsed Time, Hours	Products, Wt. %			ClC$_2$H$_4$OH:HCl	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	0.92	0.42	0.006	0.983	2.170
3	2.46	1.16	0.01	0.959	2.117
4	3.64	1.72	0.02	0.958	2.117
5	4.76	2.25	0.03	0.959	2.118
6	5.87	2.77	0.03	0.961	2.122
7	6.89	3.28	0.05	0.953	2.105
8	7.90	3.76	0.06	0.952	2.102
9	8.88	4.24	0.07	0.949	2.095
10	9.85	4.71	0.09	0.948	2.093
11	10.76	5.15	0.10	0.947	2.091
12	11.63	5.58	0.10	0.944	2.085
13	12.50	6.01	0.10	0.942	2.080
Yields for entire run	92.2	97.7	5.1		

[a] Ethylene dichloride recovered = 25.6 grams. Values shown are the low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

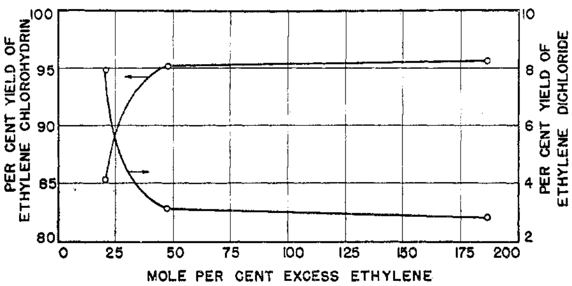


Figure 3. Influence of Excess Ethylene on Yields of Ethylene Chlorohydrin and Ethylene Dichloride

Reactor temperature, 25° C.; final chlorine rate, 42 grams per hour

when ethylene is present in large excess. This is shown graphically in the qualitative curves of Figure 3. Tables V and VI show that at approximately the same final ethylene chlorohydrin concentrations, more than four times as much ethylene dichloride was formed when ethylene was present in 21% excess than when it was present in 185% excess. At the high ethylene excess, most of the dichloride was formed above the 11% chlorohydrin concentration level. A comparison of the data in Tables III and V indicates that approximately three times as much dichloride was formed at the low ratio as was formed with 48% excess ethylene.

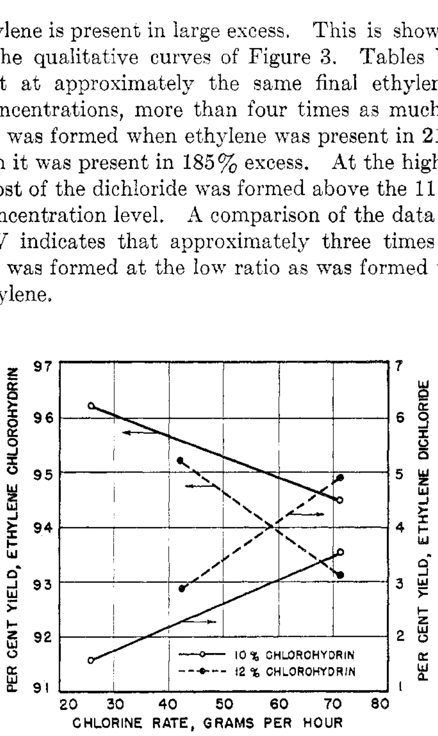


Figure 4. Influence of Gas Flow Rates on Yields of Ethylene Chlorohydrin and Ethylene Dichloride

Reactor temperature, 35° C.; approximately 50% excess ethylene

The ratio of ethylene chlorohydrin to hydrochloric acid decreases relatively rapidly as the chlorohydrin concentration increases at the low ethylene to chlorine ratio. Table V also shows an appreciable amount of ethylene dichloride accumulated in the reactor as an immiscible phase at the low ratio; this condition is unfavorable since it accelerates the formation of the dichloride by-product.

The large amount of ethylene dichloride was probably formed as a result of the retarded reaction of chlorine with water to form hypochlorous acid, as shown by Equation 1. The increase in concentration of hydrochloric acid as the reaction proceeds causes a natural shift to the left in Equation 1. The added effect of the presence of a smaller amount of ethylene to react with hypochlorous acid resulted in more favorable conditions for direct reaction between ethylene and dissolved but unhydrolyzed chlorine to form ethylene dichloride.

With 95% ethylene, there was only a small amount of unreacted and diluent gas at the low ratio. Possibly the presence of a larger amount of inert gas would have reduced somewhat the amount of dichloride formed by stripping it from the reaction mixture. This might have reduced the amount of dichloride sufficiently so that a separate liquid phase would not have formed, for it is in this organic phase that the formation of more dichloride is promoted. For a given mole ratio of ethylene to chlorine there probably is an optimum concentration of inert gases. Although some advantage may be gained by the stripping effect of the exit gases, the decreased partial pressure of ethylene would decrease the rate of its reaction with hypochlorous acid. Excess ethylene itself strips out the dichloride, so that any optimum concentration of inert gases is dependent on such factors as excess ethylene, temperature, and others.

A comparison of the data shows only limited advantage for an increase from 48 to 185% excess ethylene. A very large excess of ethylene would be impractical for large scale production because of the large volume of gas that would have to be recycled. The selection of an optimum ethylene to chlorine ratio must depend upon an ecomomic balance that takes into consideration the purity of the ethylene feed gas.

Influence of Gas Flow Rates. The data of Tables III, VII, and VIII, and the qualitative curves of Figure 4 indicate that low gas rates favor the formation of ethylene chlorohydrin over ethylene dichloride. At a concentration of approximately 10% ethylene chlorohydrin, 4.9 grams of ethylene dichloride was formed at the low gas rates while approximately 14 grams was formed at the high rates. At the 12% chlorohydrin level, 12.3 grams of dichloride was recovered at the intermediate rates while 23 grams was recovered at the high rates. At low gas rates, there are relatively few gas bubbles in any given increment of volume within the reactor; therefore, a given bubble of ethylene has a relatively large volume of solution in which it can dissolve to react with hypochlorous acid in the solution. Also, with a low bubble density, there is relatively low probability that ethylene and chlorine bubbles will come into direct contact and react to form ethylene dichloride. In the range of gas flow rates investigated, after the reactor had attained the desired operating conditions, the chlorine dissolved rapidly and there was no noticeable difference in the rates of solution of chlorine at high and low rates of flow. It would be expected, however, that as gas feed rates increased, consideration would be given to the spacing of chlorine and ethylene injection points to ensure solution of the chlorine.

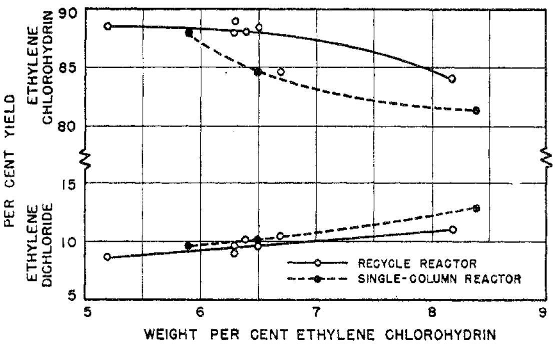


Figure 5. Yields from Continuous Operations of Single-column and Recycle Reactors at Various Concentrations of Ethylene Chlorohydrin

Reactor temperature, 35° C.; approximately 50% excess ethylene

An inherent feature of the reactor used in this work provided for increased circulation rate as gas flow rates increased. Since the height of the reaction zone was fixed, this resulted in a decreased time of contact of ethylene bubbles with the reaction solution.

Table V. Data from Batch Run, with Recycle, and with Low Ethylene to Chlorine Ratio

Reactor temperature = 35° ± 1° C.
Final chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 1.21

Elapsed Time, Hours	Products, Wt. %			$ClC_2H_4OH:HCl$	
	Chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	0.97	0.44	0.004	0.988	2.183
3	2.51	1.20	0.02	0.946	2.089
4	3.68	1.79	0.03	0.932	2.058
5	4.78	2.37	0.04	0.915	2.020
6	5.82	2.94	0.05	0.897	1.980
7	6.79	3.51	0.05	0.975	1.931
8	7.72	4.08	0.06	0.856	1.890
9	8.58	4.63	0.07	0.839	1.852
10	9.59	5.11	0.09	0.849	1.875
11	10.50	5.58	0.10	0.852	1.881
12	11.36	6.02	0.10	0.854	1.886
13	12.29	6.45	0.12	0.863	1.906
Yields for entire run	85.4	98.8	7.9		

[a] Ethylene dichloride recovered = 42.5 grams, including 29 grams withdrawn from the reactor. Values shown are low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

An upper limit of gas rates would exist, beyond which unreacted chlorine would appear in the exit gas stream, but this limit could be extended by a constriction placed in the system to control the rate of circulation.

From an industrial standpoint, extremely low gas rates are impractical since the gas rates directly influence rates of production. An industrial reactor would be operated at as high a rate of production as could be attained without the formation of ethylene dichloride in amounts that would detrimentally affect the economics of the process.

Comparison of Continuous Operation of Single-Column and Recycle Reactors

The reactor, shown in Figure 1, was modified to be operated as a single-column reactor with concurrent flow of the inlet water and feed gases but without recycle of the reaction solution. This represents only one of several possible arrangements for a single-column reactor. Table IX shows the results of the last several hours of three runs at levels of 5.9, 6.5, and 8.4% ethylene chlorohydrin in solution. The data for ethylene dichloride concentrations for all of the continuous runs are considered reliable.

Table IX and Figure 5 show that as the concentration of ethylene chlorohydrin was increased, the yield, based on chlorine, decreased, and the dichloride by-product increased both in concentration and yield. In connection with the physical operation of the single-column reactor, it was observed that the chlorine was well dispersed, but relatively little absorption of chlorine appeared to occur until the bubbles reached the region of ethylene injection. There appeared to be a high probability of direct contact between ethylene and chlorine bubbles.

When chlorine and ethylene were injected into water, the gas bubbles were large initially, and the rate of solution appeared to be slow. As the concentration of products increased, gas dispersion improved, and the rate of solution of the gases appeared to increase. In the continuous operation of a single-column reactor, there is a concentration gradient between the water inlet and the product removal regions, and with an arrangement such as has just been considered, the gases are injected in a region that has a low concentration of reaction products; this would appear to have some disadvantages. In a recycle arrangement, such as shown in Figure 1, the concentration of reaction products is nearly constant at all points in the reactor because of the rapid circulation imparted to the reaction medium. Thus, it appeared that there would be some advantage in the production of ethylene chlorohydrin in a recycle reactor rather than in a single-column reactor of the type considered.

Table X shows data from continuous runs with the recycle arrangement at 5.2, 6.3, 6.7, and 8.2% ethylene chlorohydrin. The yield and ratio data at the 5.9% level in Table IX and at the 6.3% level in Table X are almost identical. A slight advantage is shown by the recycle method in that it was operated at

Table VI. Data from Batch Run, with Recycle, and with High Ethylene to Chlorine Ratio

Reactor temperature = 35° ± 1° C.
Final chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 2.85

Elapsed Time, Hours	Products, Wt. %			$ClC_2H_4OH:HCl$	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	1.04	0.48	0.007	0.989	2.181
3	2.08	0.96	0.02	0.987	2.180
4	2.75	1.27	0.02	0.984	2.172
5	3.86	1.78	0.02	0.981	2.166
6	5.04	2.34	0.02	0.977	2.157
7	6.18	2.87	0.03	0.977	2.157
8	7.30	3.39	0.04	0.976	2.156
9	8.35	3.89	0.04	0.972	2.146
10	9.39	4.42	0.04	0.963	2.127
11	10.39	4.89	0.04	0.963	2.126
12	11.33	5.34	0.05	0.961	2.121
13	12.17	5.75	0.06	0.958	2.116
Yields for entire run	95.6	99.6	2.4		

[a] Ethylene dichloride recovered = 10.0 grams. Values shown are low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

Table VII. Data from Batch Run, with Recycle, and with Low Gas Rates

Reactor temperature = 35° ± 1° C.
Final chlorine rate = 26 grams/hour
Mole ratio, ethylene:chlorine = 1.47

Elapsed Time, Hours	Products, Wt. %			$ClC_2H_4OH:HCl$	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	0.80	0.37	0.005	0.980	2.166
3	1.89	0.88	0.01	0.978	2.160
4.5	3.06	1.42	0.01	0.974	2.152
6	4.05	1.90	0.02	0.964	2.128
7.5	5.12	2.42	0.03	0.960	2.120
9	6.19	2.92	0.03	0.960	2.118
10	6.89	3.24	0.04	0.963	2.127
11	7.57	3.54	0.04	0.968	2.137
12	8.24	3.86	0.04	0.966	2.133
13	8.88	4.18	0.04	0.963	2.127
14	9.52	4.49	0.06	0.960	2.120
15	10.14	4.81	0.06	0.955	2.109
Yields for entire run	96.2	100.6	1.6		

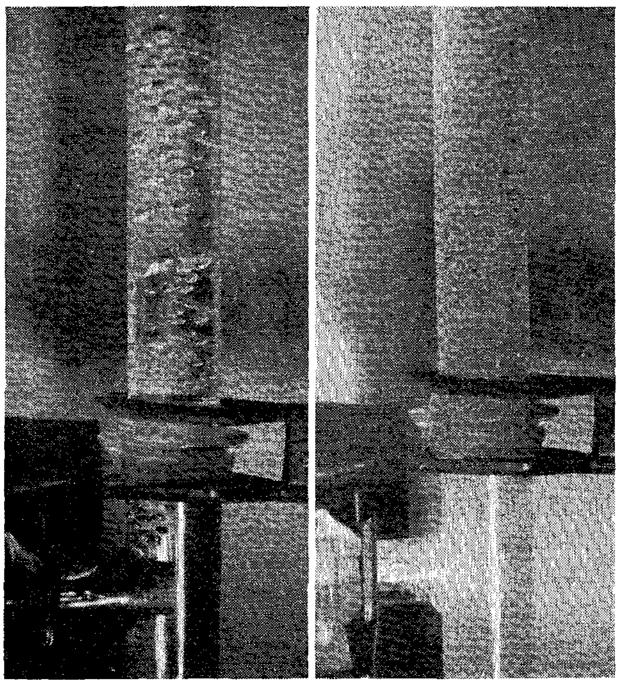
[a] Ethylene dichloride recovered = 4.9 grams. Values shown are low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.

Table VIII. Data from Batch Run, with Recycle, and with High Gas Rates

Reactor temperature = 35° ± 1° C.
Final chlorine rate = 71 grams/hour
Mole ratio, ethylene:chlorine = 1.50

Elapsed Time, Hours	Products, Wt. %			$ClC_2H_4OH:HCl$	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride[a]	Mole ratio	Wt. ratio
1.5	0.94	0.44	0.009	0.978	2.158
3	2.49	1.16	0.01	0.977	2.158
4	4.06	1.89	0.04	0.975	2.153
5	5.95	2.77	0.05	0.974	2.150
6	7.54	3.53	0.06	0.968	2.137
7	9.15	4.30	0.06	0.964	2.128
8	10.63	5.03	0.07	0.958	2.115
9	12.07	5.70	0.11	0.959	2.118
10	13.38	6.37	0.11	0.951	2.110
Yields for 10% chlorohydrin	94.5	98.5	3.6		
Yields for 12% chlorohydrin	93.1	97.1	4.9		
Yields for entire run	91.8	96.4	5.9		

[a] Ethylene dichloride recovered = 32.6 grams; approximately 14 grams recovered at 10% chlorohydrin concentration; approximately 23 grams recovered at 12% chlorohydrin concentration. Values shown are low values of ethylene dichloride determined by hydrolysis with sodium hydroxide.



Initial ethylene dispersion in water with no chlorine injection

Ethylene dispersion during normal operation with simultaneous injection of chlorine; product contains 4% ethylene chlorohydrin

Figure 6. Ethylene Dispersion in Single-Column Reactor

a higher level of concentration. The numerical difference in concentrations is small; however, the recycle reactor was able to operate at approximately a 7% higher chlorohydrin concentration with the same yield. A slight advantage is also shown by the recycle reactor at the other concentration levels.

The batch runs indicated that the ethylene chlorohydrin to hydrochloric acid mole ratio decreased as the product concentration increased. In the results reported for continuous runs, there was in each case a slight increase in mole ratio as the time of reaction at a given concentration level grew longer. The decrease in mole ratio in the batch runs results from an increase in by-product formation as the ethylene chlorohydrin concentration increased. In the continuous runs, a rapid decrease in mole ratio occurred when the water inlet rate was suddenly increased after the reaction medium had reached the desired level of concentration. Then, as this accumulation of by-products was removed by the product stream, the mole ratio slowly increased as the reactor approached steady state conditions.

Tables XI and XII present data from a run at relatively high gas rates and a prolonged continuous run. A comparison of these data indicates that the lower gas rates give more favorable results; this supports the conclusion drawn from batch studies of this variable. The curves of Figure 5 reflect the increased by-product formation and decrease in yield of ethylene chlorohydrin as the concentration level is increased. As with many of the other variables, the selection of a maximum concentration level for industrial production must depend largely upon the maximum yield of by-products that can be tolerated.

Observations of Gas Dispersion

Extensive studies have been reported concerning the formation of gas bubbles in liquids. Much of the work has been concerned with studies of systems where the gases and liquids have been mutually inert. Relatively little appears to have been done with systems that involve extensive mass transfer between the gas and liquid phases, and it is this type of system that is involved in the synthesis of ethylene chlorohydrin.

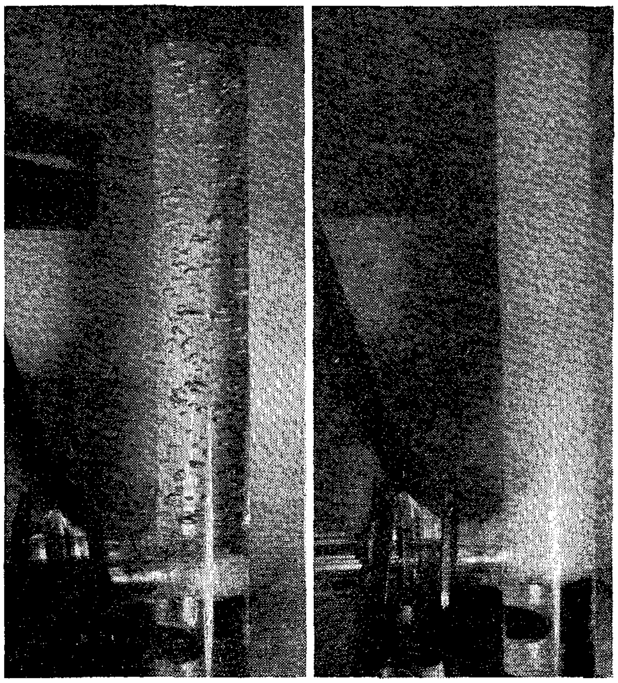
When ethylene and chlorine individually were dispersed into distilled water, the ethylene bubbles initially were in the range of 4 to 8 mm. in diameter, and the chlorine bubbles appeared to be 3 to 6 mm. in diameter. The size of bubbles was somewhat dependent upon gas rates. A slight decrease in bubble size was observed as an individual gas continued to flow into water over a period of time; the magnitude of decrease was greater for chlorine than for ethylene.

Table IX. Results of Continuous Operation without Recycle

Reactor temperature = 35° ± 3° C.
Chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 1.47

Hourly Sample No.	Products, Wt. % Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride	$ClC_2H_4OH:HCl$ Mole ratio	Wt. ratio
	Average Chlorohydrin Concn. = 5.9 ± 0.2%				
1	5.69	2.76	0.87	0.935	2.064
2	6.05	2.90	0.89	0.943	2.083
3	6.12	2.92	0.76	0.948	2.094
4	5.95	2.83	0.74	0.951	2.100
Average yields					
	87.9	92.5	9.7		
	Average Chlorohydrin Concn. = 6.5 ± 0.3%				
1	6.84	3.58	0.97	0.866	1.911
2	6.46	3.36	0.92	0.871	1.923
3	6.32	3.21	1.04	0.891	1.968
4	6.47	3.25	0.97	0.903	1.993
5	6.75	3.34	0.93	0.916	2.022
Average yields					
	84.5	95.4	10.1		
	Average Chlorohydrin Concn. = 8.4 ± 0.6%				
1	7.85	4.11	1.80	0.864	1.908
2	8.17	4.23	1.49	0.874	1.928
3	8.99	4.63	1.64	0.879	1.941
Average yields					
	81.2	92.9	12.9		

When the reactor was put into operation, ethylene was bubbled into the distilled water charge for 20 to 30 minutes before chlorine was introduced. Within a few minutes after chlorine flow had commenced, there was a noticeable decrease in the bubble size



Initial chlorine dispersion in water

Chlorine dispersion during normal operation

Figure 7. Chlorine Dispersion in Single-Column Reactor

Table X. Results of Continuous Operation with Recycle

Reactor temperature = 35° ± 1° C.
Chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 1.47

	Products, Wt. %			$ClC_2H_4OH:HCl$	
Hourly Sample No.	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride	Mole ratio	Wt. ratio
Average Chlorohydrin Concn. = 5.2 ± 0.1%					
1	5.09	2.52	0.55	0.915	2.020
2	5.12	2.53	0.62	0.917	2.025
3	5.21	2.52	0.62	0.936	2.066
4	5.19	2.50	0.68	0.939	2.074
5	5.21	2.50	0.61	0.944	2.086
Average yields	88.2	94.7	8.6		
Average Chlorohydrin Concn. = 6.3 ± 0.1%					
1	6.34	3.06	0.82	0.937	2.069
2	6.28	3.03	0.85	0.941	2.077
3	6.28	3.02	0.84	0.943	2.081
4	6.33	3.02	0.84	0.950	2.097
5	6.35	3.01	0.86	0.956	2.110
Average yields	87.9	93.0	9.5		
Average Chlorohydrin Concn. = 6.7 ± 0.1%					
1	6.66	3.48	0.98	0.867	1.914
2	6.73	3.45	1.00	0.884	1.952
3	6.68	3.40	0.99	0.891	1.967
4	6.77	3.38	1.09	0.907	2.003
5	6.83	3.39	1.03	0.911	2.012
Average yields	84.5	94.7	10.4		
Average Chlorohydrin Concn. = 8.2 ± 0.1%					
1	8.10	4.19	1.16	0.876	1.933
2	8.07	4.14	1.32	0.881	1.946
3	8.15	4.14	1.36	0.892	1.970
4	8.26	4.15	1.34	0.902	1.991
5	8.34	4.15	1.39	0.991	2.011
Average yields	84.0	94.1	11.0		

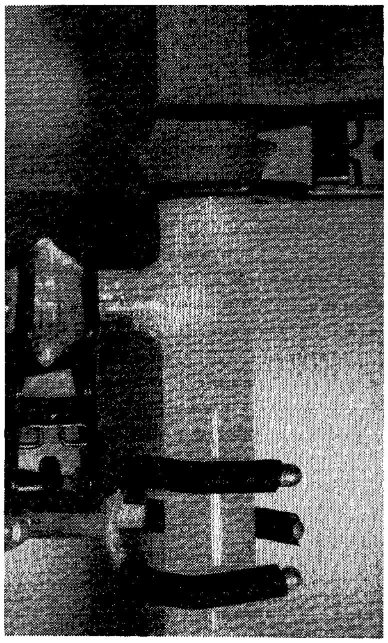
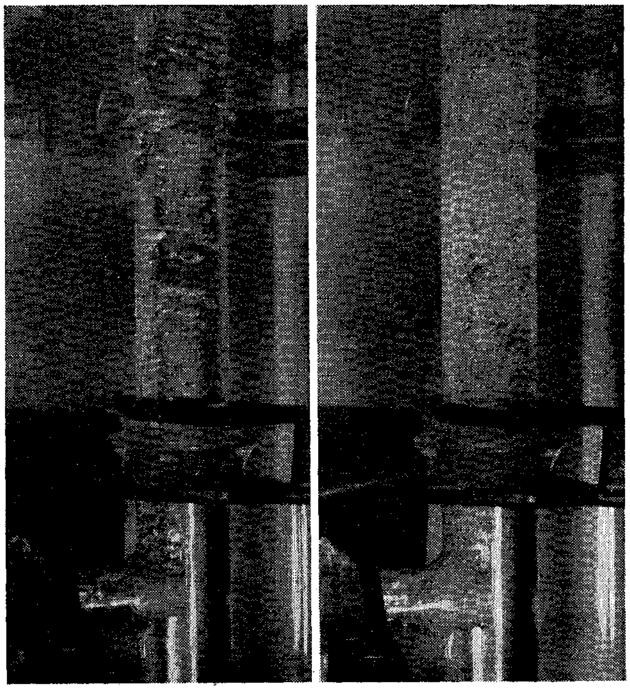


Figure 8. Direct Contact of Chlorine and Ethylene in Single-Column Reactor



Ethylene dispersion in water saturated with ethylene but with no chlorine injection

Ethylene dispersion during normal operation with simultaneous injection of chlorine; solution contains 6% ethylene chlorohydrin

Figure 9. Ethylene Dispersion in Recycle Reactor

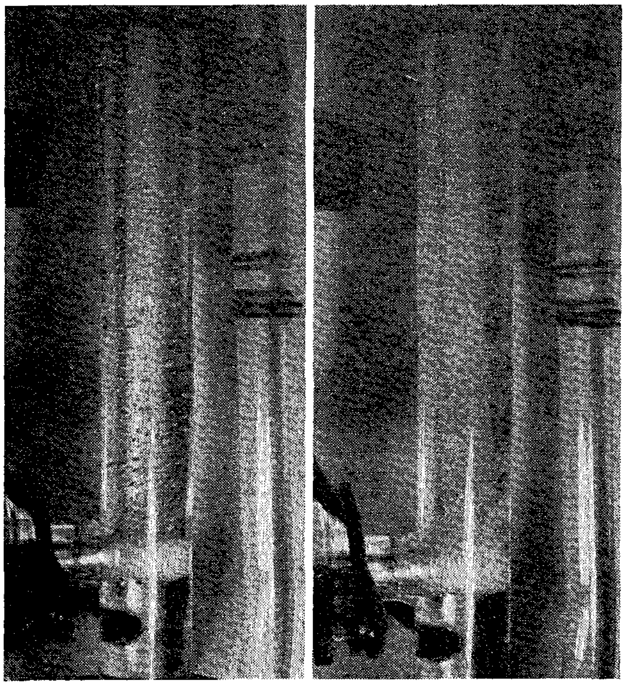
of both gases, and the bubble size continued to diminish as the concentration of products increased. In the recycle arrangement, at an ethylene chlorohydrin concentration of 6%, the ethylene bubbles were approximately 1 to 3 mm. in diameter, and the chlorine bubbles appeared to be from 0.5 to 1 mm. in diameter. These bubble dimensions prevailed within 6 to 8 inches above the points of injection. As a result of mass transfer during reaction, there was a steady decrease in bubble size as the bubbles rose in the column.

Some coalescence of ethylene bubbles was observed when ethylene was bubbled into pure water, but coalescence decreased as the concentration of reaction products increased. This conforms with observations by Pattle (*9*) and Verschoor (*15*), who reported that the presence of organic substances or impurities prevents the coalescence of bubbles through an increase in film resistance. Tests were conducted to determine whether such a film resistance might decrease the solubility of reaction gases at high concentrations of reaction products with a possible contribution to the relatively high yields of by-products. The results indicated that the solubility of ethylene was about the same in distilled water as in a solution that was saturated with ethylene dichloride and contained 6% ethylene chlorohydrin and 3% hydrochloric acid.

Table XI. Results of Continuous Run, with Recycle, at High Rate and at Concentration of 6.4% Chlorohydrin

Av. chlorohydrin concn. = 6.4 ± 0.1%
Reactor temperature = 35° ± 1° C.
Chlorine rate = 71 grams/hour
Mole ratio, ethylene:chlorine = 1.42

	Products, Wt. %			$ClC_2H_4OH:HCl$	
Hourly Sample No.	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride	Mole ratio	Wt. ratio
1	6.27	2.96	0.94	0.958	2.114
2	6.39	3.02	0.90	0.957	2.113
3	6.41	3.03	0.92	0.958	2.116
4	6.42	3.04	0.92	0.956	2.110
5	6.47	3.05	0.86	0.961	2.122
Average yields	88.0	91.8	10.1	...	...
Average ratios	...	...	...	0.958	2.115



Initial chlorine dispersion in water saturated with ethylene

Chlorine dispersion during normal operation; solution contains 6% ethylene chlorohydrin

Figure 10. Chlorine Dispersion in Recycle Reactor

As was indicated by Murray (*8*), there is only a limited change in the surface tension of the liquid as the concentration of reaction products increases. Tests indicate that the changes that do occur can be attributed almost entirely to the influence of ethylene chlorohydrin.

The differences that exist in the dispersion of ethylene and chlorine under different conditions are illustrated in Figures 6 to 11. Figures 6, 7, and 8 show the dispersion in a single-column reactor, and Figures 9, 10, and 11, refer to the recycle reactor. The few exceptionally large bubbles in Figures 6 and 9 resulted from coalescence of bubbles along the top of the side arm—not within the column itself. In the single-column reactor there was noticeable formation of eddy currents near the wall of the column. These currents did not flow downward very far, but they resembled an oscillating motion in relatively localized regions. The formation of swirls and eddies at high gas rates was undoubtedly influenced by the relatively small diameter of the column. The direct contact of rising chlorine bubbles with ethylene in the single-column reactor is clearly evident in Figures 6 and 8. At the 6% ethylene chlorohydrin level in the recycle reactor, 95% of the chlorine was dissolved before chlorine bubbles reached the ethylene injection point. The rapid rate of chlorine solution during normal operation is shown at the right in Figure 10, and the relatively limited opportunity for direct contact of ethylene and chlorine bubbles is shown at the right in Figure 9, where the region below the ethylene inlet is almost entirely free of rising chlorine bubbles.

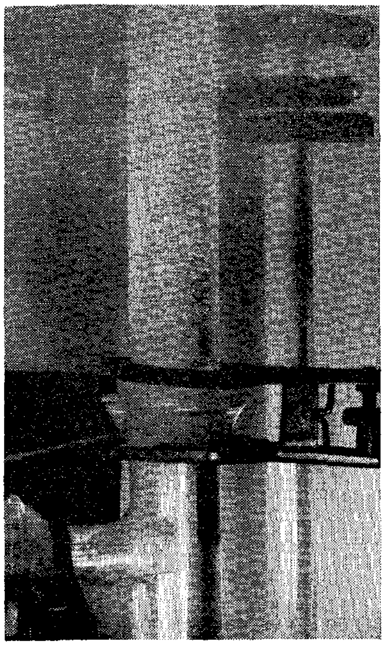


Figure 11. Effect of Chlorine on Ethylene Dispersion after Complete Saturation with Ethylene

Table XII. Results of Prolonged Continuous Run, with Recycle

Av. chlorohydrin concn. = 6.3 ± 0.2%
Reactor temperature = 35° ± 1° C.
Chlorine rate = 42 grams/hour
Mole ratio, ethylene:chlorine = 1.47

Hourly Sample No.	Products, Wt. %			$ClC_2H_4OH:HCl$	
	Ethylene chlorohydrin	Hydrochloric acid	Ethylene dichloride	Mole ratio	Wt. ratio
1	6.11	2.92	0.73	0.949	2.096
2	6.20	2.94	0.82	0.955	2.108
3	6.30	2.98	0.84	0.957	2.112
4	6.41	3.02	0.75	0.960	2.119
5	6.46	3.05	0.82	0.959	2.118
Average yields	88.9	92.9	9.1	...	...
Average ratios	...	...	...	0.956	2.111
Average Chlorohydrin Concn. = 6.5 ± 0.1%					
6	6.44	3.06	0.84	0.953	2.104
7	6.49	3.08	0.90	0.955	2.109
8	6.56	3.11	0.89	0.955	2.109
9	6.65	3.14	0.86	0.960	2.120
Average yields	88.3	92.4	9.6	...	...
Average ratios	...	...	...	0.956	2.111

A high concentration of reaction products is not the only factor that results in excellent dispersion of ethylene. Where the water in the recycle reactor had been saturated with ethylene over a period of 1.5 hours, the injection of only a small amount of chlorine resulted in an ethylene dispersion that was nearly the same as that normally obtained at a concentration of 6% ethylene chlorohydrin. This is illustrated in Figure 11 which shows that, under these conditions, the ethylene dispersion in a solution of 0.1% ethylene chlorohydrin is nearly equivalent to that shown on the right in Figure 9.

Observations of physical operations suggest that the recycle reactor has advantages over the single-column reactor used in this work. The excellent dispersion attained is effectively utilized through rapid dissolution of the reaction gases.

Conclusions

The rate of formation of by-products, including principally ethylene dichloride and bis(2-chloroethyl) ether, increases as the concentration of ethylene chlorohydrin increases.

Temperature studies in the range 13° to 50° C. indicate that a disadvantage of low temperature operation is that by-product ethylene dichloride accumulates in the reaction medium where its presence contributes to the formation of more dichloride. At temperatures of 35° to 50° C., the extent of dichloride accumulation in the reactor is reduced by the stripping action of unreacted gases.

High mole ratios of ethylene to chlorine are favorable to high yields of ethylene chlorohydrin and to the formation of relatively small amounts of by-products. The large quantities of ethylene that must be recycled at high ratios limit practical ratios to about 50% excess ethylene.

With other conditions constant, yields of ethylene chlorohydrin decrease, and by-product yields increase as gas feed rates increase. From an industrial standpoint, the maximum rate of production must be limited by the degree of by-product formation that can be tolerated.

Physical observations and data for continuous operation of a single-column reactor and a recycle-type reactor indicate that the recycle reactor has certain advantages in terms of both yields and smoothness of operation. The rapid circulation imparted to the reaction medium permits the reaction to be conducted at essentially a given concentration of ethylene chlorohydrin rather than with a concentration gradient between the top and bottom of the column.

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Pyrolysis of Oil Shale in Gas Combustion Retort

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Important features of the gas combustion process to recover oil from Green River oil shale are discussed, and data are cited from a pilot plant (6 tons per day) to illustrate certain operational characteristics. Condensation as a stable mist allows the oil to be removed from the shale bed below its dew point. The ratio of gas to solids in the product cooling zone influences strongly the oil-condensation phenomenon, exerting an effect on the extent to which the oil condenses as an aerosol and upon the size and stability of the oil-mist particles. Combustion-zone temperature should be above 1400° F. to ensure a rapid combustion rate but less than 1800° F. to avoid fusing the inorganic constituents in the shale. To recover a high yield of liquid products in a gas circulation process, a low pyrolysis temperature, about 800° to 900° F., is very desirable. Low pyrolysis temperatures are readily attained in the gas combustion process.

PRODUCTION of liquid fuels from oil shale is not a new concept. Shale oil was produced from oil shale long before our modern petroleum industry was established. Before the discovery of petroleum in Pennsylvania in 1859 perhaps as many as 50 oil-shale plants had been erected in the United States for the production of heating and lighting oils. These enterprises were unable to compete with the newly discovered petroleum and soon were forced to close.

In the interim, interest in the production of liquid fuels from oil shale has been closely related to the estimated extent of our petroleum reserves. At times the subject has been merely of academic interest. However, since World War II the consumption rate of liquid fuels has increased to such an extent that the United States is now a net importer of petroleum. This trend has revived interest in the production of fuels from oil shale, so that today we find both Government and industry earnestly working toward the development of processes to produce oil-shale fuels at costs that will make them a feasible petroleum supplement.

Oil shale is a sedimentary rock that contains a solid organic material known as kerogen. When oil shale is heated to a temperature of the order of 800° F., the kerogen is converted by pyrolysis to shale oil, gas, and a carbonaceous residue. The process of heating the oil shale is known as retorting. The crude shale oil can be refined to produce fuels similar to those derived from petroleum. The gases and the carbonaceous residue that remain on the shale are available to supply the energy requirements of the retorting process.

The most promising oil-shale reserves in the United States occur in the Green River formation of Colorado, Utah, and Wyoming. The principal oil-shale measure is about 500 feet thick and has an average assay value of about 15 gallons of oil per ton. The richest part of the 500-foot section is a series of strata commonly referred to as the Mahogany ledge, which