ANOTHER STUDY OF EXOTHERMIC REACTIONS

Try Fluid Bed Reactors for . . . .

Making Chloromethanes

Isothermal character and high heat capacity of beds of inert solids offer an excellent way to control reaction rates and temperatures where large amounts of heat are released

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THE vapor-phase chlorination of methane at 300° to 450° C. involves highly exothermic reactions. If the temperature is not adequately controlled, carbon and undesired high-boiling by-products are formed and actual ignition and explosion may occur. Process control becomes particularly difficult when exhaustive chlorination is desired or hydrogen is present in the methane feed stream.

The isothermal character and high heat capacity of fluidized beds of inert solids appeared to offer the best means for controlling the chlorination. Reaction rate data were obtained and applied to the problem of ignition and pyrolysis, the design of practical reactors, and a method of predicting product composition in relation to feed-stream composition. Fluid-bed reactors were operated and the quality of the products was determined.

Reaction Rates

Experimental Techniques. Rate data for chlorination of methane or chloromethanes were obtained in a simple fluid-bed reactor (Figure 1) consisting of a vertical borosilicate glass tube, 70 mm. in inside diameter and 84 inches long. The tube was filled to a static height of 30 to 48 inches with grade 0000 ground flint (Carborundum Co., Niagara Falls, N. Y.), 90% of which was between 200 and 325 mesh. The reactor was heated with a specially constructed cylindrical heater 2 feet long. The reactor tube was located so that 14 to 18 inches of the reactor extended below the heater. The portion extending above the heater was insulated with 1-inch magnesia. The necessary feed gas supplies were connected to the apparatus through standard metering devices, either rotameters or orifice-type systems. The temperature of the reactor was measured with five thermocouples located within the sand bed. Satisfactory fluidization of the sand was indicated when the thermocouples were within 1° of each other over the total height of the same bed. Superficial gas velocities—i.e., the net rate of flow through the tube—were about 0.1 to 0.75 foot per second.

In studying the rate of chlorination of methylene chloride and chloroform, a liquid stream of the organic feed material was first metered into the top of a falling-film vaporizer. The vapor was then carried into the turbulent bed reactor by a stream of nitrogen fed to the bottom of the vaporizer.

Reaction time was assumed to be the time of contact of the reaction gases with the sand bed. While this is not strictly true, temperature profiles above the sand bed indicated a drop in temperature at the rate of 20° C. per inch after leaving the bed. Six inches from the bed the reaction rate had fallen to about 3% of the reaction rate within the bed; therefore, the error introduced by this assumption is of the order of only a few per cent.

The reaction time, *t*, was calculated from the static height, *h*, of the bed and the superficial gas velocity, *V* by the following equation

$$t = \frac{h(K - d)}{V}$$

where *K* is the ratio of active height to static height and *d* is the ratio of the bulk density of the static bed to the true density of the solid. Values of *K* were shown to be linearly related to *V* for bed heights from 2 to 4 feet. A more complex expression would be required for larger values of *h* to correct for pressure drop through the bed.

In general, the reaction rates were followed by determining the change in chlorine concentration during the reaction time using iodometric techniques. Gas samples were withdrawn from the

Literature Background

Subject	Ref.
Literature review	(*8*)
Reaction kinetics	(*13, 14, 16*)
Reactor design	(*1, 2, 6, 7, 9, 11, 17*)
Prediction of product composition	(*4, 5, 10, 12, 15*)

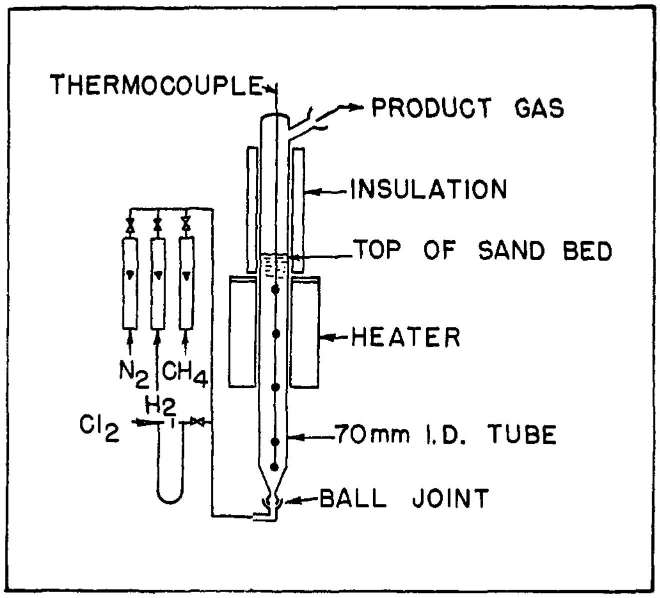


Figure 1. Basic rate data were obtained in this simple fluid-bed reactor

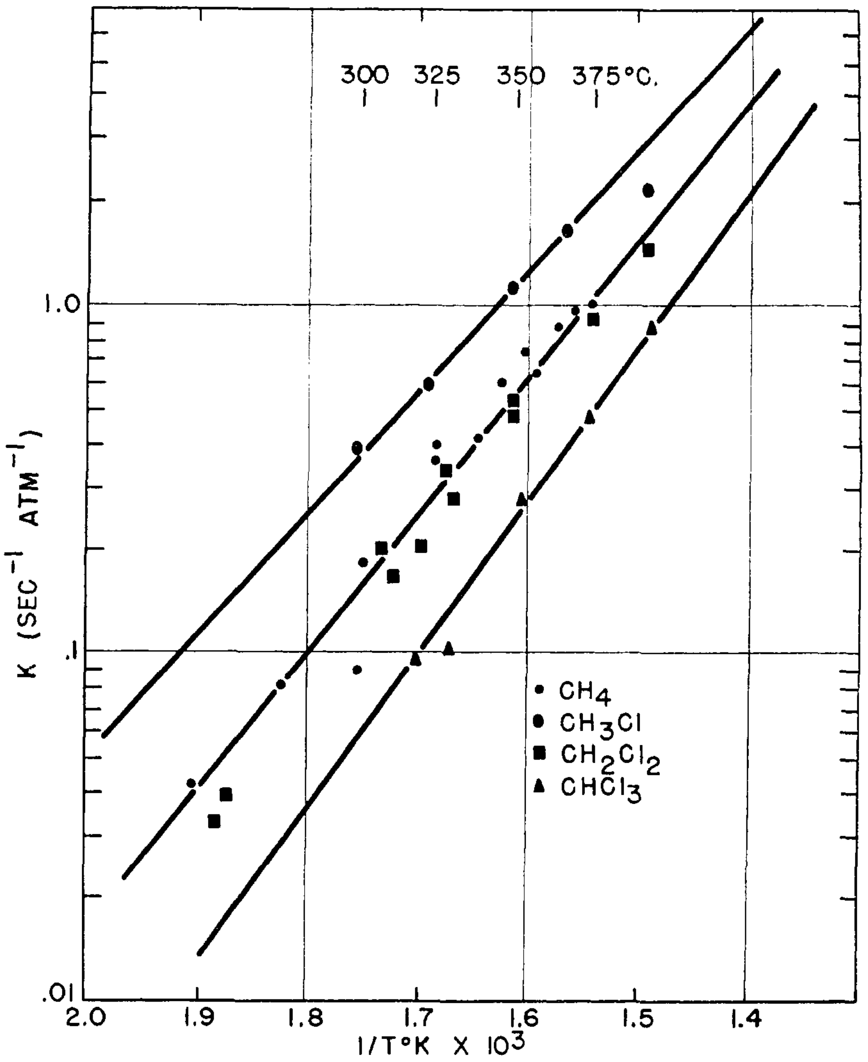


Figure 2. Arrhenius plot of rate data shows equivalent rates for methane and methylene chloride

reaction system into previously calibrated 250-cc. dry, dark, evacuated bulbs. Ten per cent potassium iodide solution was forced into the bulb immediately. After shaking, the solution was transferred quantitatively to a titration flask and titrated with 0.1*N* sodium thiosulfate. When hydrochloric acid determination was desired, sodium iodate was added after the chlorine titration was complete and the iodine liberated was again titrated with thiosulfate to give hydrochloric acid titer. No measurable reaction occurred in the sample bulb.

The rate of reaction of 60% methane–40% hydrogen mixtures with chlorine was also determined in the fluid-bed reactor. Confirmatory information of some interest because of potential catalytic effects was obtained using a sectional nickel tube reactor essentially as described by McBee and Hass (*9*). For rate studies samples were taken through valves located between each of the four sections. Methane or methane-hydrogen was fed to the reactor and chlorine was added and mixed at high velocity at reaction temperature in the first tube. Temperature profile measurements indicated that the reactant gases were at reaction temperature in the first 2 to 4 inches.

Basic Reaction Rate Data

Methane and Chloromethanes. The specific reaction rate constants for the chlorination of methane or chloromethanes were calculated using the first-order equation

$$K = \frac{2.303}{ta} \log \frac{b}{(b - x)} \qquad (1)$$

where *t* is the actual reaction time in seconds, *a* is the initial concentration of methane or chloromethane, *b* is the initial concentration of chlorine, and *x* is the chlorine that has disappeared.

The assumption of a first-order reaction is particularly valid in the case of chloromethanes where the primary reaction is faster than the succeeding reactions. It is less valid in the case of methane but is still permissible if the chlorine-methane ratio is low and a low chlorine conversion is taken.

When the logarithm of the specific reaction rate constant is plotted against the reciprocal of the absolute temperature, the points for methane and methylene chloride are well grouped (Figure 2) and, considering the assumptions involved, a single line can be drawn to represent the most probable rate values for either methane or methylene chloride. The slope of the log *K* *vs.* 1/*T* line for methane or for methylene chloride indicates an activation energy of 18,700 cal.

The rates of chlorination of chloromethanes relative to methane at 400° C., interpolated from Figure 2, are 2.0, 1.0, and 0.5 for methyl chloride, methylene chloride, and chloroform, respectively. The value of 2.0 for methyl chloride is in good agreement with previous work (*14*). These relative values have been used in calculations made to predict the composition of products as a function of reactor feed composition.

Methane-Hydrogen Mixtures. In the studies of the rate of chlorination of methane-hydrogen mixtures a 60% methane–40% hydrogen feed stream was used. Initial studies in the tubular reactor had shown that the methane-hydrogen ratio in the noncondensable gas after chlorination was substantially the same as the feed ratio. Data from the fluid bed reactor, summarized in Table I, confirmed this result over almost the full range of chlorine feed concentrations. This indicated that the rates of chlorination of the two materials were substantially equal at the temperatures being used. The work of Pritchard and others (*16*) is in agreement with this.

Table I. Residual Methane-Hydrogen Ratio as Function of Conversion

Rates of chlorination are substantially equal at temperatures used

(60% CH_4 feed)

Feed Cl_2/ (CH_4 + H_2)	% Conversion	Exit CH_4/H_2 Ratio
0.659	35.0	1.29
1.36	66.4	1.46
2.18	85.2	1.26
2.5	94.4	1.72

Several expressions to define the rate of disappearance of chlorine in this system were used in the calculations. The simple first-order expression (Equation 1, where *a* is now the initial concentration of methane plus hydrogen) is applicable if low conversions are taken. The basic assumption is that the concentration of the chlorine-reactive materials remains constant. This is essentially true if the initial chlorination products are also chlorine-reactive. Attempts to apply this equation to methane-hydrogen mixtures over a broader range of conversion soon lead to difficulty, however, because as hydrogen is consumed the total concentration of chlorine-reactive materials decreases.

A modified rate expression

$$\frac{dx}{dt} = K(a - nx)(b - x) \qquad (2)$$

where a is the initial concentration of chlorine-reactive material, n is the $H_2/(CH_4 + H_2)$ mole ratio, and $b + x$ have previously assigned values, was tested in an attempt to correct for this effect. It gave somewhat better correlation but was still unsatisfactory at high conversions.

Because an expression was desired that would describe the kinetics over the full range of a practical operating process, an empirical approach to correct this equation was taken. The known distribution of products in the chlorination of methane (*9*) was used as a base. The product compositions were recalculated for a feed stream containing 40% hydrogen, assuming equal conversion of methane and hydrogen. From this calculation it was observed that the mole ratio of totally chlorinated material to the chlorine fed—i.e., $(HCl + CCl_4)/Cl_2$—varied between 1.35 and 1.20 while the feed ratio $Cl_2/(CH_4 + H_2)$ increased from 0.3 to the calculated maximum 2.8. The arithmetical average for the first ratio is 1.28. This value was used to express the concentration of completely chlorinated materials as a function of the chlorine consumed. Empirically, then, for the specific feed mixture containing 60% methane the concentration of chlorine-reactive materials at any time can be shown to be equal to the initial concentration less 0.28 times the amount of chlorine consumed. The use of this value in place of n in Equation 2 gives

$$\frac{dx}{dt} = K(a - 0.28x)(b - x) \qquad (3)$$

Values of K calculated from the integrated forms of Equations 1, 2, and 3 (Table II) clearly show the usefulness of Equation 3 at high chlorine to methane-plus-hydrogen feed ratios. This equation was used for all rate constants involving methane-hydrogen mixtures.

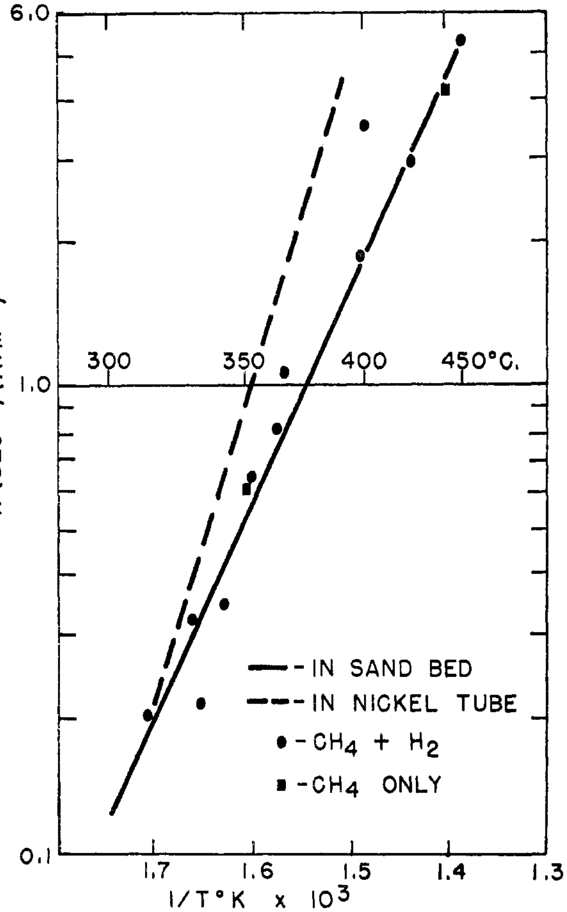


Figure 3. Comparison of data for methane and methane-hydrogen mixtures shows no difference in chlorination rate, but the fluid bed reactor provides a lower activation energy

An Arrhenius plot summation (Figure 3) of over 40 rate determinations covering $Cl_2/(CH_4 + H_2)$ feed ratios from 0.11 to 2.50, temperatures from 290° to 452° C., and pressures from 1.0 to 1.6 atm. demonstrated no practical difference in the rate of chlorination of methane compared with that of methane-hydrogen mixtures. The data from the tubular reactor can be extrapolated to the same specific rate value at 250° C. that is reported by Pease and Walz (*14*), and the slope of the line indicates the 31,000-cal. activation energy obtained by them.

The lower activation energy in the turbulent bed suggests that the 3000-fold greater surface area of the sand bed in comparison to the nickel tube is modifying one of the rate-controlling processes in the chlorination.

Table II. Evaluation of Rate Equations for Methane-Hydrogen

Tubular reactor data show usefulness of Equation 3

Feed Ratio, $Cl_2/(CH_4 + H_2)$	Temp., ° C.	K Sec.$^{-1}$, Atm.$^{-1}$ Eq. 1	Eq. 2	Eq. 3
0.17 to 0.24	350	0.865	0.84	0.875
0.17 to 0.24	400	...	5.68	5.66
0.17 to 0.24	440	...	13.67	12.60
2.0	460	[34.1][a]	1150.0	36.70

[a] Based on incremental portion of total reaction.

Application of Rate Data

Ignition and Pyrolysis Thresholds. In the chlorination reactions involved,

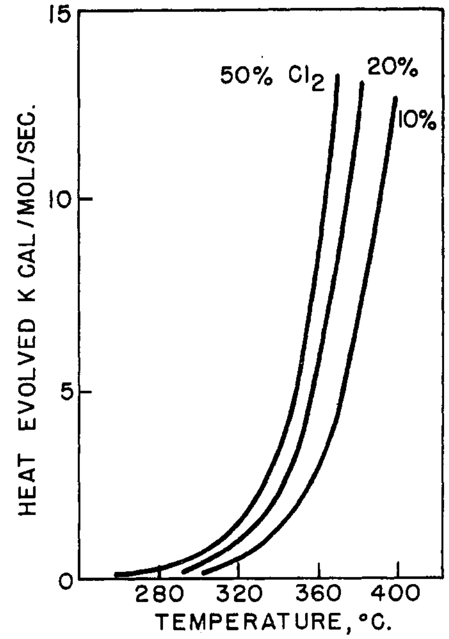


Figure 4. Calculated rates of heat evolution show that chlorine concentration is an important parameter at temperatures above 350° C.

Methane plus hydrogen data

excessive chlorine concentrations may accelerate the reaction beyond the capacity of the equipment to remove the heat of reaction [24,000 and 26,500 cal. per mole of chlorine at 400° C. for methane and 60% methane–40% hydrogen, respectively (*3*)]. Under these conditions, desired reaction products are converted to high-boiling constituents, carbon is deposited, and actual ignition may occur.

The limiting conditions for practical use were approximated by calculating the rate of heat release as a function of chlorine concentration and pressure, using the over-all rate equation for methane-hydrogen chlorination. The reaction time required for the disappearance of 0.01 mole of chlorine at various initial chlorine concentrations, temperature, and pressures is readily calculated. The heat evolved by the reaction of this amount of chlorine (265 cal.) divided by the reaction time gives the rate of heat release. The rate of heat evolution increases logarithmically with temperature. The rate is greatest for 50% chlorine concentration (Figure 4) and only slightly less for 30, 40, and 60% concentrations. Significantly lower heat releases occur as the concentration of chlorine is reduced below 20%. The calculated effect of pressure at 50% initial chlorine concentration (Figure 5) follows a similar trend.

The calculated rates of heat evolution were applied to the problem of ignition and explosion in feed lines to the reactor. Here an adiabatic reaction was assumed to occur and the rates of adiabatic temperature rise were obtained by dividing the rates of heat evolution by the molar heat capacity of the gas stream (9.0 cal. per mole per degree C.). The calculated gas temperatures under adiabatic conditions as a function of time and mixing temperature were then obtained by graphical integration. The resultant calculations (Figure 6) indicate that one volume of methane and hydrogen and one volume of chlorine may be mixed at a temperature of 225° C. with little danger of uncontrollable temperature rise within 5 seconds after mixing. However, at a mixing temperature of 250° C., uncontrolled reactions may occur within 5 seconds.

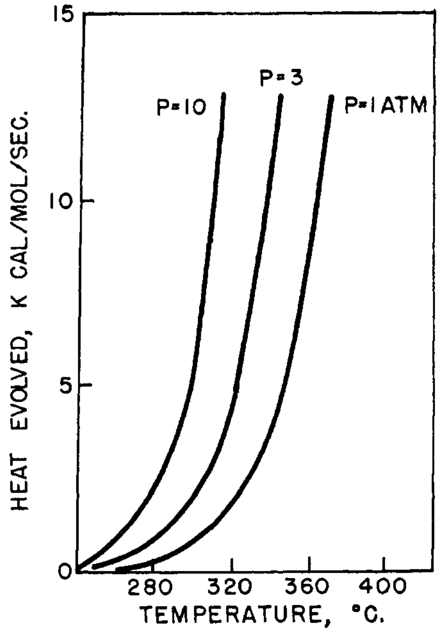


Figure 5. Increased reactor pressures also increase the calculated rate of heat release

Methane plus hydrogen data

Actual thresholds for ignition and pyrolysis in the simple fluid bed reactor were determined experimentally. Chlorine was premixed at various concentrations with the standard ratio of methane and hydrogen. The composition of the gas stream was held constant and the temperature of the bed was allowed to rise slowly. Gas samples were taken at various intervals to determine the hydrogen chloride–chlorine ratios in the product gases. The temperature of the bed was increased to the point where actual flames could be observed within the momentary voids or bubbles within the turbulent sand bed.

The onset of pyrolysis was recognized by observing the temperature at which the concentration of hydrogen chloride in the exit gas increased beyond a calculated level. Theoretically, in the chlorination of methane one mole of hydrogen chloride should be produced for every mole of chlorine reacted. In the chlorination of methane-hydrogen mixtures of the standard concentration it has been calculated, based on stoichiometry and equivalence of reaction rate, that the hydrogen chloride–chlorine ratio should be 1.18. Thus, threshold conditions of ignition and pyrolysis were considered to exist at that point at which this ratio increased above 1.18. Actual firing in the reactor was generally not observed until the hydrogen chloride–chlorine ratio reached about 1.5. The results were plotted (Figure 7) to show the limiting chlorine concentration allowable at various reactor temperatures to avoid extensive pyrolytic reaction when operating with methane-hydrogen mixture. Because the chlorination of methane involves about a 10% lower heat of reaction, somewhat higher concentrations of chlorine could probably be tolerated in this case.

Though flames were sometimes observed in the sand bed when the limiting conditions were exceeded, these flames were rapidly extinguished within the reactor by the motion of the sand. Actually even minor explosions were tolerated. Thus, the use of a fluidized bed of inert solids appears to offer a

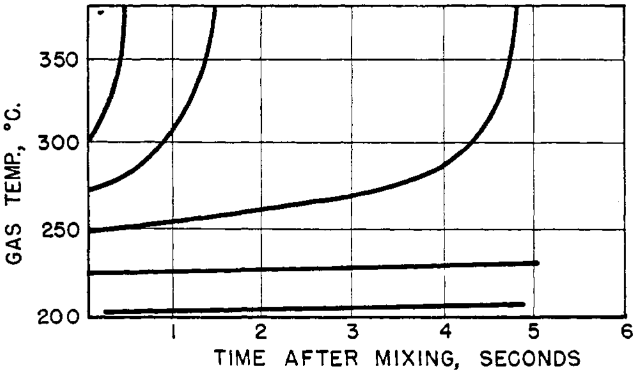
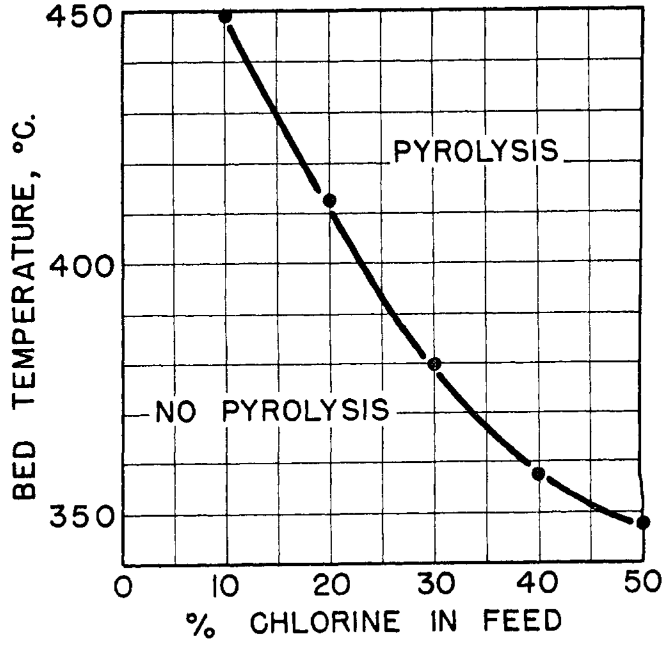


Figure 6. Calculated adiabatic temperatures vs. time show that mixing of reactants in feed lines should be done below 250° C.

Calcd. for 50% Cl_2, 30% CH_4, 20% H_2

Figure 7. Chlorine concentrations and bed temperatures below this curve should be used to avoid excessive hydrogen chloride formation ▶



definite safety advantage in chlorination of gases.

Reactor Design. The reaction rate data, combined with the data on ignition and pyrolysis thresholds, allowed the design of two types of turbulent bed reactors (Figure 8). In the single-stage reactor the methane or methane-hydrogen feed stream enters the bottom of the sand bed, which is maintained at about 410° C. and moves upward at a superficial velocity of about 0.2 foot per second. Chlorine is added to this stream within the sand bed through a central vertical distributor with limiting orifices at various levels such that the maximum chlorine concentration (assuming instantaneous mixing with the entire gas stream at this level) is about 10%. The three-stage turbulent bed reactor is essentially three reactors connected in series and operating at temperatures of 350° to 370° C. In this reactor the chlorine is added to the methane or methane-hydrogen stream in three portions, each portion being mixed with the gas stream before entering the sand bed. The chlorine concentration in the gas stream entering successive stages is below the ignition threshold level. The principles of the three-stage reactor applied to the chlorination of methane-hydrogen mixtures have been presented in some detail (*6*).

Application of rate data to reactor design allowed the successful scale-up of three-stage reactor from the 70-mm. laboratory size up to 6-inch diameter with good reproducibility. The scale-up of the single-stage reactor was not so successful because of the assumptions made in designing the chlorine distributor.

Process Information

Experimental Technique. To obtain yield and quality information, the techniques and reactors described were used with only minor variations and the organic products were condensed, fractionated, and analyzed. In bench scale studies it was inconvenient to provide the bed height necessary to eliminate chlorine completely from the exit gas. This chlorine (about 1%) was troublesome in laboratory distillation of the organic product and a "clean-up" reactor consisting of two 5-foot sections of the nickel tubular reactor, was used to reduce the chlorine to a low level.

The organic products were condensed with the system shown in Figure 9. Carbon-ice condensers were used ahead of the hydrogen chloride scrubbers to guarantee that all high-boiling materials would be collected with the organic product and would not condense in the water scrubber. The water scrubber, used to remove hydrogen chloride from the process stream, was operated at 60° C. to prevent loss of lower chloromethanes in the water. This was followed by a water-ice condenser, a dryer, and a carbon-ice condenser. The noncondensable gases were vented through a gas meter to provide a complete material balance.

The condensed organic products were combined and distilled in a 1-inch by 4-foot helix-packed column equipped with automatic reflux control. Reflux ratios were generally five to one on the flats and ten to one on intermediate cuts. For general product composition purposes, the intermediate cuts were assumed to be binary mixtures of chloromethanes and were analyzed by measuring their refractive index.

When fine detail of product composition became important, samples were fractionated in a Podbielniak Hypercal still. Infrared and mass spectrograph techniques were used where necessary.

Product Distribution. The distribution of products obtained as a function the chlorine-methane feed ratio followed published trends (*9*), but differed in detail, depending on the reactor system used. The product from the single-stage reactor (Figure 10) tends to have more carbon tetrachloride and less intermediate products than that from the tubular reactor, even at the relatively low chlorine-methane feed ratio of about 2.0. This is believed to be the result of poorer mixing of chlorine within the sand bed than in the high gas velocity tubular reactor. This poor mixing causes high local chlorine concentrations which would be expected to lead to increased production of carbon tetrachloride. The product from the three-stage reactor (Figure 11), even at the high chlorine-methane feed ratio of 3.4, produces considerably less carbon tetrachloride than the tubular reactor. This reflects the excellent control of the chlorine concentration obtained by premixing of gases and control of the reaction temperature by the turbulent bed.

By-Product Formation. Yield and product quality are always of extreme importance to a satisfactory manufacturing process. Chlorinated ethylenes and ethanes can be obtained by the pyrolysis of chloromethanes, with elimination of hydrogen chloride. A measure of the extent of formation of these by-products can be obtained by determining the amount of hydrogen chloride produced in relation to the theoretical quantity required by the stoichiometry of the chlorination reaction. A second measure is the quantity of high-boiling material obtained.

In these studies relatively high-purity methane containing about 0.5% of ethane was used. Careful analysis of all the reaction products therefore allowed the determination of an approximate C_2 material balance for several reaction conditions. The extent of by-product formation in the single-stage reactor as measured by these techniques is shown in Table III. At medium-to-high chlorine–feed ratios and reaction temperature of 410° C., 3 to 10% more hydrogen chloride was produced than theoretically required, and high boilers increased from about 2% to 6 to 7% of the organic product. As the chlorine feed ratio increased, the high-boiling products, which consisted of trichloroethylene, perchloroethylene, pentachloroethane, and hexachloroethane, were sixfold more than the amount of ethane fed to the reactor. In the single-stage reactor the ethane fed is converted rapidly to high-boiling materials and condensation or pyrolysis reactions occurs to some extent.

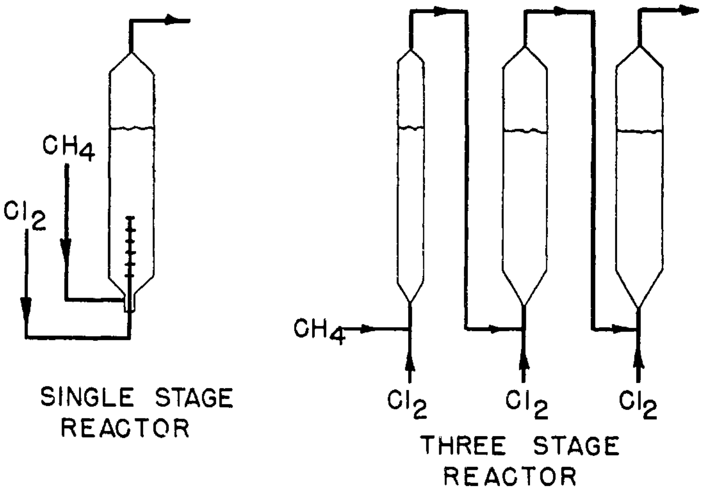


Figure 8. These two types of fluid-bed reactors were evaluated

Similar data for the three-stage reactor are also shown in Table III. In the chlorination of methane at low feed ratios, a small excess of hydrogen chloride but no high boilers were observed. A

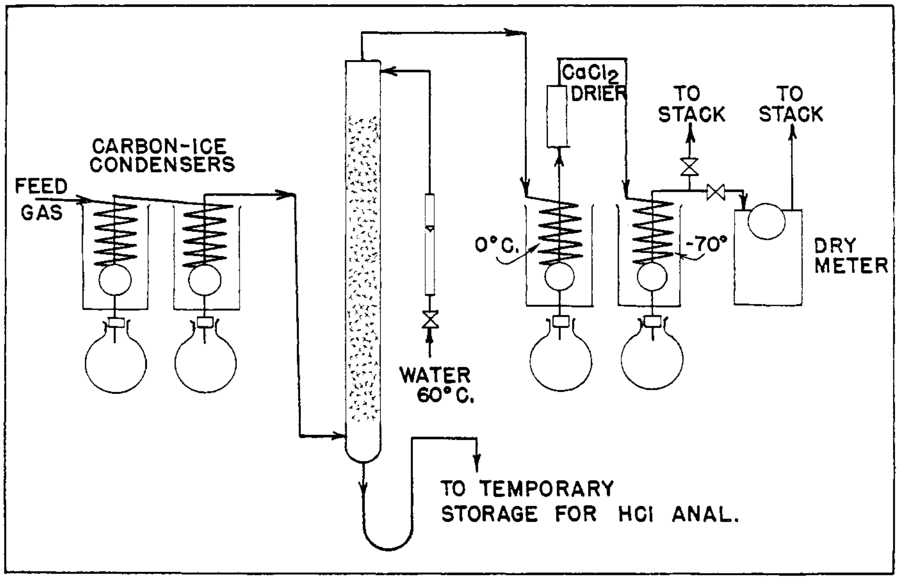


Figure 9. A condenser-scrubber train was used to collect reaction products for subsequent fractionation

careful C_2 balance on this run indicated that no condensation reactions were occurring. At higher chlorine-methane feed ratios, essentially theoretical quantities of hydrogen chloride were produced and high boiler production was at about the 1% level. In the chlorination of methane-hydrogen mixtures, about 2% of high boilers was produced without any excess of hydrogen chloride and these high boilers represented a 100% excess of C_2 in the product over the feed. This again reflects the greater difficulty of controlling the methane-hydrogen chlorination.

It is apparent that if methane is chlorinated to produce large quantities of chloroform and carbon tetrachloride, any C_2's in the feed stream tend to be converted to high-boiling material, particularly if a single-stage reactor with its more rigorous conditions is used. Even natural gas compositions were chlorinated in the single-stage reactor without difficulty or contamination of the chloromethanes, but at the expense of producing appreciably greater quantities of high boilers. Concentrations as high as 15% of ethane or ethylene in the feed stream were used.

Another situation exists, however, when conditions require chlorination at low chlorine feed ratios. In this case all of the possible chlorinated ethanes or ethylenes are observed in the chloromethane boiling range. These components are shown in Table IV for the case where only 0.5% ethane was in the methane feed and the reaction was being carried out at a chlorine-methane feed ratio of about 0.5. Small but recognizable quantities of vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, ethylidene dichloride, methyl chloroform, 1,2-dichloroethane, and trichloroethylene were obtained in the various chloromethane fractions. The separation of these materials to provide high-purity chloromethanes appears to be difficult.

Table III. By-product Formation in Fluid-Bed Reactors

Reactor Type	Feed	Cl_2 Feed Ratio	Reactor Temp., ° C.	% Excess HCl	% High Boilers	Approx. % Excess C_2's
Single stage	CH_4	1.97	410	4	1.8	...
	$CH_4 + H_2$	2.00	410	10	7.0	600
	CH_4	3.45	410	3	5.3	...
Three stages	CH_4	0.52	355	0.7	Nil	Nil
	CH_4	2.28	365	0.0	1.1	...
	$CH_4 + H_2$	2.50	360	0.0	1.8	100
	CH_4	3.41	360	0.0	1.1	...

Table IV. C_2 Components in Products

At low chlorine feed ratio (0.5), all possible chlorinated ethanes or ethylenes are observed in chloromethane boiling range

Main Fraction	Mole %	Impurity	B.P., ° C.	Mole % in Main Fraction
CH_3Cl	49.1	$CH_2{=}CHCl$	−13.9	0.3
CH_2Cl_2	33.1	$CH_2{=}CCl_2$	37	Present
		$CHCl{=}CHCl$	48.4	Present
$CHCl_3$	13.3	CH_3CHCl_2	54.3	0.3
		$CHCl{=}CHCl$	60.3	0.3
CCl_4	4.4	CH_3CCl_3	74.1	0.7
		CH_2ClCH_2Cl	83.7[a]	2.0
		$CHCl{=}CCl_2$	86.9	Present

[a] Forms azeotrope with CCl_4.

Prediction of Product Composition

In manufacturing processes involving the production of a number of products from consecutive reactions, it is highly desirable to be able to predict the ratio of products that will be obtained from a given feed composition, especially where recycle streams of undesired products are necessary to adjust production of individual products to a given market situation. The problem of simple consecutive reactions has been treated for methane chlorination and other reactions (*5*, *10*, *12*, *15*).

The approach in the present case was to use the basic rate data of Figure 2, setting up simultaneous differential equations which express the rate of formation of the various products as functions of their concentration. A specific result can be integrated in terms of one independent variable after setting limits corresponding to any given feed condition.

The derivation of the equations follows the method of Francis and Reid (*4*). The consecutive reactions involved and the designation of their rate constants are:

$$CH_4 + Cl_2 \xrightarrow{K_1} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{K_2} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{K_3} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{K_4} CCl_4 + HCl$$

The stoichiometry indicates that one mole of organic product will be formed for each mole of organic in the feed, and a chlorine balance can be written on this basis:

$$P = W + S + Y + Z \qquad (4)$$

where P is the sum of chlorine molecules and organically bound chlorine atoms at zero time and W, X, Y, and Z are the number of organic molecules containing at least 1, 2, 3, and 4 chlorine atoms, respectively, at time t. By definition then, the concentrations of organic materials present are:

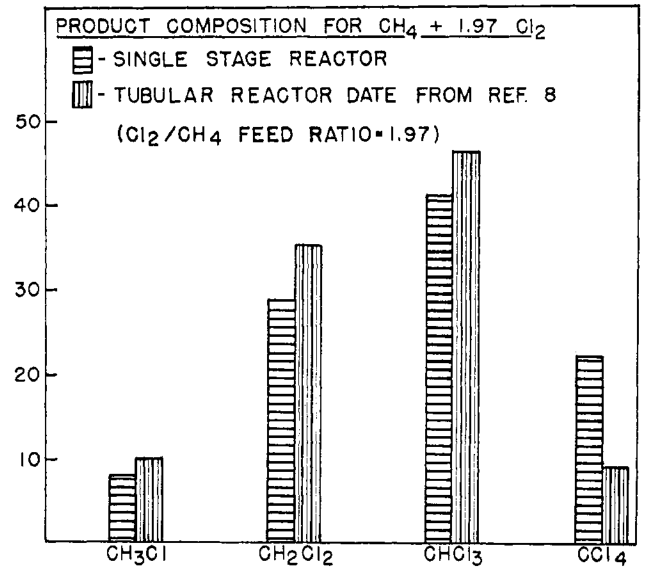


Figure 10. The single-stage reactor produces more carbon tetrachloride than a tubular reactor at the same feed ratio

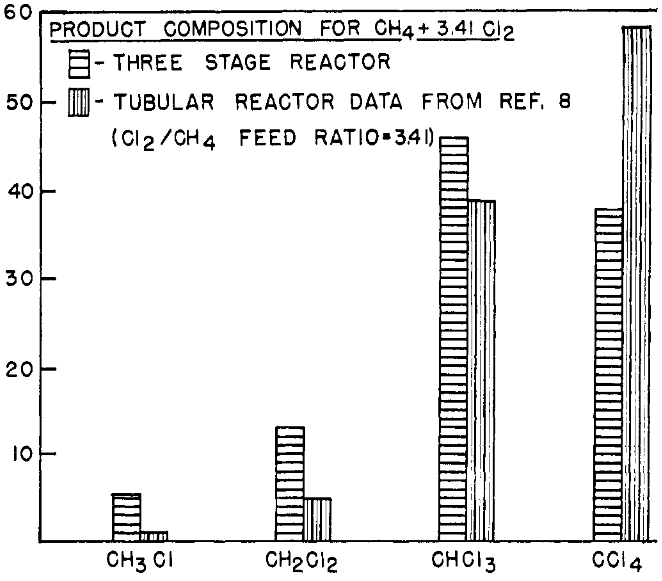


Figure 11. The three-stage reactor favors the production of lower chloromethanes because of premixing of reactants and excellent temperature control

$$CH_4 = 1 - W \quad CH_2Cl_2 = X - Y$$
$$CH_3Cl = W - X \quad CHCl_3 = Y - Z$$
$$CCl_4 = Z$$

The rate of disappearance of methane is then

$$\frac{-d[CH_4]}{dt} = \frac{-d(1 - W)}{dt} = K_1(1 - W)(Cl_2) = \frac{dW}{dt} \qquad (5)$$

Similarly the rate of change of (CH_3Cl) is:

$$\frac{d(W - X)}{dt} = \frac{dW}{dt} - \frac{dX}{dt} = K_1(1 - W)(Cl_2) - K_2(W - X)(Cl_2) \qquad (6)$$

and by substitution

$$\frac{dX}{dt} = K_2(W - X)(Cl_2) \qquad (7)$$

Similarly

$$\frac{dY}{dt} = K_3(X - Y)(Cl_2) \qquad (8)$$

$$\frac{dZ}{dt} = K_4(Y - Z)(Cl_2) \qquad (9)$$

Because at any given time the instantaneous chlorine concentration is the same for all reactions, relative rate expressions can be obtained by dividing Equations 7, 8, and 9 by 5. Thus:

$$\frac{dX}{dW} = \frac{K_2}{K_1}\frac{(W - X)}{(1 - W)} = k\frac{(W - X)}{(1 - W)} \qquad (10)$$

$$\frac{dY}{dW} = \frac{K_3}{K_1}\frac{(X - Y)}{(1 - W)} = m\frac{(X - Y)}{(1 - W)} \qquad (11)$$

$$\frac{dZ}{dW} = \frac{K_4}{K_1}\frac{(Y - Z)}{(1 - W)} = n\frac{(Y - Z)}{(1 - W)} \qquad (12)$$

Equation 10 can be integrated by substitution of variables to give

$$X = \frac{kW - 1}{k - 1} + C(1 - W)^k \qquad (13)$$

After limits have been set for a given feed condition, the value of X can be substituted in Equation 11 and values of Y in terms of W obtained by proper integration. Similar evaluation of Z in terms of W can be made. Assignment of values of W within the limits of the feed condition then allows calculation of X, Y, and Z. The mole fractions of various chlorinated products, by definition of W, X, Y, and Z, are:

$$CH_3Cl = (W - X)/W \quad CHCl_3 = (Y - Z)/W$$
$$CH_2Cl_2 = (X - Y)/W \quad CCl_4 = Z/W$$

Values of W, X, Y, and Z can be correlated with P by Equation 4 to define the necessary chlorine feed.

The validity of this method of approach is best demonstrated by applying the equations to the case where only methane and chlorine are being fed to the reactor. Calculated values of X, Y, Z, and P for various values of W are shown in Table V. The corresponding mole fractions of products as a function of P are presented graphically in Figure 12. Direct comparison of these curves with experimental results is shown in Figure 13, where both the data of McBee and Hass (*9*) and the present data have been tabulated. There is excellent agreement of data from both sources with the calculated curve for methyl chloride and satisfactory agreement with the curve for methylene chloride. Experimental values for chloroform concentration are definitely

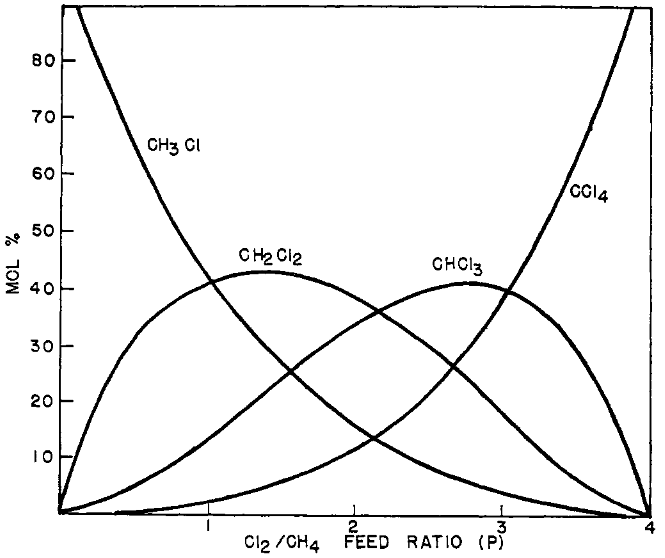


Figure 12. The general equations for predicting product composition from relative rate data gave these curves for the direct chlorination of methane

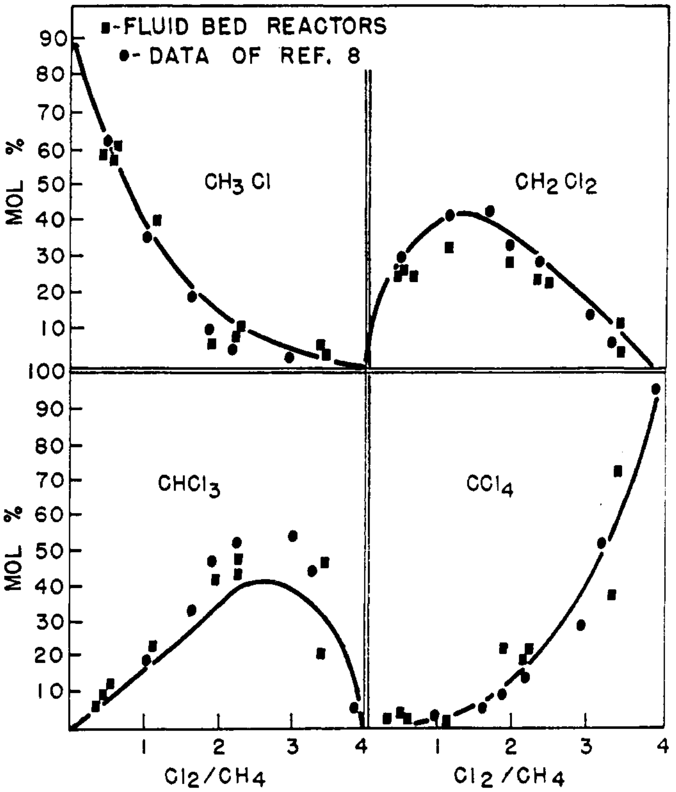


Figure 13. The calculated product compositions compare favorably with experimental results and previously reported data for all products except chloroform

higher than indicated by the calculated curve. The McBee data taken from a tubular reactor are higher than the fluid bed data recorded by the authors. The carbon tetrachloride curve follows the data of McBee rather closely, but for products obtained in the fluid-bed reactor there appear to be discrepancies, depending on the type of reactor used. The generally good agreement of the calculated curves with experimental results substantiates the accuracy of the relative rate data that were obtained and the validity of the equations developed.

The relative rate expressions developed for predicting product compositions are also applicable where recycle streams of undesired chloromethanes are involved. Thus, where abnormal proportions of chloromethanes are desired in the manufacturing process, this calculation can be used to define the feed and recycle compositions necessary to produce the desired end ratio of products. Thus, for example, a mixture of methane and methyl chloride can be chlorinated to produce an increased quantity of methylene chloride (*11*). By appropriate adjustment of feed conditions and definition of limits it is possible to apply the relative rate equations to even more complex situations. For example, this type of calculation has been made for feed streams of methane, methylene chloride, and chloroform to produce an end product containing abnormal proportions of methyl chloride and carbon tetrachloride. Satisfactory agreement between calculated and experimental results was obtained (Table VI).

Table V. Values of *W, X, Y, Z,* and *P* from Integration of Equations 10, 11, and 12 for $CH_4 + Cl_2$ Feed

W	*X*	*Y*	*Z*	*P*
0.1	0.01	0.0031	0.00002	0.11032
0.2	0.04	0.00290	0.00008	0.24298
0.3	0.09	0.01057	0.00057	0.40104
0.4	0.16	0.02690	0.00191	0.58881
0.5	0.25	0.05673	0.00540	0.81213
0.6	0.36	0.10683	0.02036	1.08719
0.7	0.49	0.18749	0.03145	1.04893
0.8	0.64	0.31611	0.07375	1.82986
0.9	0.81	0.52940	0.17753	2.41693
0.95	0.9025	0.69787	0.30793	2.85830
0.97	0.9409	0.78867	0.40700	3.10657
0.99	0.9801	0.90778	0.59882	3.47670
0.999	0.9980	0.98618	0.84915	3.83233

Table VI. Satisfactory Agreement Found in Prediction of Product Composition in Chlorination

Organic Feed, Mole %			Cl_2 Feed, Mole/Mole Org.		Product Composition, Mole %			
CH_4	CH_2Cl_2	$CHCl_3$			CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
0.904	0.906	0	0.545	Obsd.	45.7	32.5	18.1	3.7
				Calcd.	50.8	38.0	10.3	0.9
0.823	0.177	0	0.514	Obsd.	35.2	38.0	23.3	3.3
				Calcd.	40.5	43.7	14.3	1.5
0.71	0.10	0.19	0.493	Obsd.	24.1	23.4	42.8	9.6
				Calcd.	28.8	25.2	39.9	6.1
0.632	0.156	0.212	0.541	Obsd.	21.2	28.0	43.1	7.5
				Calcd.	24.0	28.5	40.0	7.5

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