METHYL CHLORIDE FROM METHANOL AND HYDROCHLORIC ACID - A PETROCHEMICAL REACTOR DESIGN STUDY

by

P.N. Bruce

INTRODUCTION

Methyl Chloride continues to maintain an important role as a petrochemical intermediate in a variety of synthesis processes. Originally used principally as an anaesthetic, refrigerant and in the synthesis of dyes, it has now entered such fields as fire extinguishers and the production of methyl siloxanes and quaternary compounds. The principal route to methyl chloride production is the hydrochlorination of methanol. The chlorination of methane or methane rich gases is also used where market considerations justify the separation of chloroform, methylene chloride and carbon tetrachloride which are also formed by this process route. In the methanol- based process(1), 35% aqueous hydrochloric acid is contacted with methanol by bubbling both vapours through an aqueous solution of zinc chloride catalyst at 140 - 160° C. Water formed during the reaction has a dilution effect on the acid, part of which is recycled to the reactor, thus leaving large volumes of dilute acid for disposal. The disposal of this acid has been a problem until recent times when development in the chlorine cycle facilitated uses in (i) pickling of steel and (ii) oxidation to chlorine by the Deacon process.

To date there has been little data published on the kinetics of the methanol-HCl reaction to facilitate the systematic design of reactor for this process. The reaction involves the simultaneous rate processes of interphase mass transfer and chemical reaction and hence the efficient dispersion of the reactant vapours is essential. The present study was undertaken to explore the kinetics of the above vapour-liquid reaction system and develop a rational approach to the design of an industrial scale reactor.

THEORY OF REACTION MECHANISM

The uncatalysed reaction of methanol and hydrochloric acid can be represented by the following mechanism.

(1) $CH_3OH + HCl \rightleftarrows CH_3O^+H_2 + Cl^-$

(2) $CH_3O^+H_2 + Cl^- \rightleftarrows CH_3Cl + H_2O$

These are the usual steps in nucleophilic substitution reactions initiated by proton transfer(2).

In the presence of aqueous zinc chloride, the reaction is likely to proceed by the following steps:

(3) $ZnCl_2 \rightleftarrows Zn^{++} + 2Cl^-$

(4) $CH_3OH + Zn^{++} \rightleftarrows CH_3O^+HZn^+$

(5) $CH_3O^+H\,Zn^+ + Cl \rightleftarrows CH_3Cl + Zn^+OH$

(6) $Zn^+OH + H^+ \rightleftarrows Zn^{++} + H_2$

In view of the higher charge on the Zn^{++} ions, steps (4) and (5) will proceed at a faster rate than steps (1) and (2). The reaction rate will also increase with zinc chloride concentration since step (3) is instantaneous. The low solubility of methyl chloride in the reaction mixture and the removal of Zn^+OH ions by step (6) would reduce the concentration of these components, thus making the rate of the reverse reaction quite low.

The overall reaction, as illustrated in steps (1) to (6), can be simplified into two parallel reactions, both contributing to the conversion of methanol at different rates. These reactions may be summed up as:

$$\overset{k_7}{\rightleftarrows}$$

(7) $ZnCl_2 + CH_3OH + HCl \rightleftarrows CH_3OH + H_2O + ZnCl_2$

$$\overset{k_8}{\rightleftarrows}$$

(8) $CH_3OH + HCl \rightleftarrows CH_3Cl + H_2O$

where $k_7 \gg k_8$

EXPERIMENTAL

A schematic layout of the apparatus used for this study is shown in fig. 1. The reactor was specially designed for the

exacting corrosive environment and is shown in detail in fig. 2. The experimental procedure consisted of heating the metered methanol and hydrochloric acid streams and feeding the mixture of these hot vapours into hot aqueous zinc chloride solution in the well-agitated reactor vessel. Constant liquid volume was maintained for each run by withdrawal, where necessary, of reactor liquid. Product vapours were continuously withdrawn to maintain a constant reactor pressure close to atmospheric. These vapors were water-cooled to remove water and HCl, ice cooled to remove methanol, and the dry methyl chloride was metered with a dry gas meter. All condensed liquid was recovered for mass balance checks and the methyl chloride was sampled for infra-red analysis using a Perkin Elmer 257 Spectrophotometer. Reactor liquid samples were also withdrawn in 10 ml. aliquots and quickly frozen prior to analysis. HCl and $ZnCl_2$ were determined by potentiometric titration against 0.1N sodium hydroxide and methanol by the colorimetric method based on the formation of an orange-red complex with ceric ammonium nitrate[3] . Samples from the condensers and traps were similarly analysed for HCl, methanol and water.

RESULTS AND DISCUSSION

The results of the main series of experiments are shown in Table 1. The tabulated concentrations of methanol, hydrogen chloride and zinc chloride are mean values over the test period. The volume recorded as the 'volume of the reactor contents' is the volume measured whilst the vapour was bubbling through, and this includes the gas present in the dispersion.

1) Effect of Reactant Holding Time on Conversion

In some of the runs shown in Table 1, the volume of the reactor contents has been set at different values with a constant feed rate to show the effect of reactant 'holding time' on conversion. The general effect is illustrated in Fig. 3. The 'holding time' of the limiting reactant, i.e. methanol, is here expressed as (volume of reactor contents)/(molar feed rate of methanol). As is expected, the conversion increases with increased holding time of methanol.

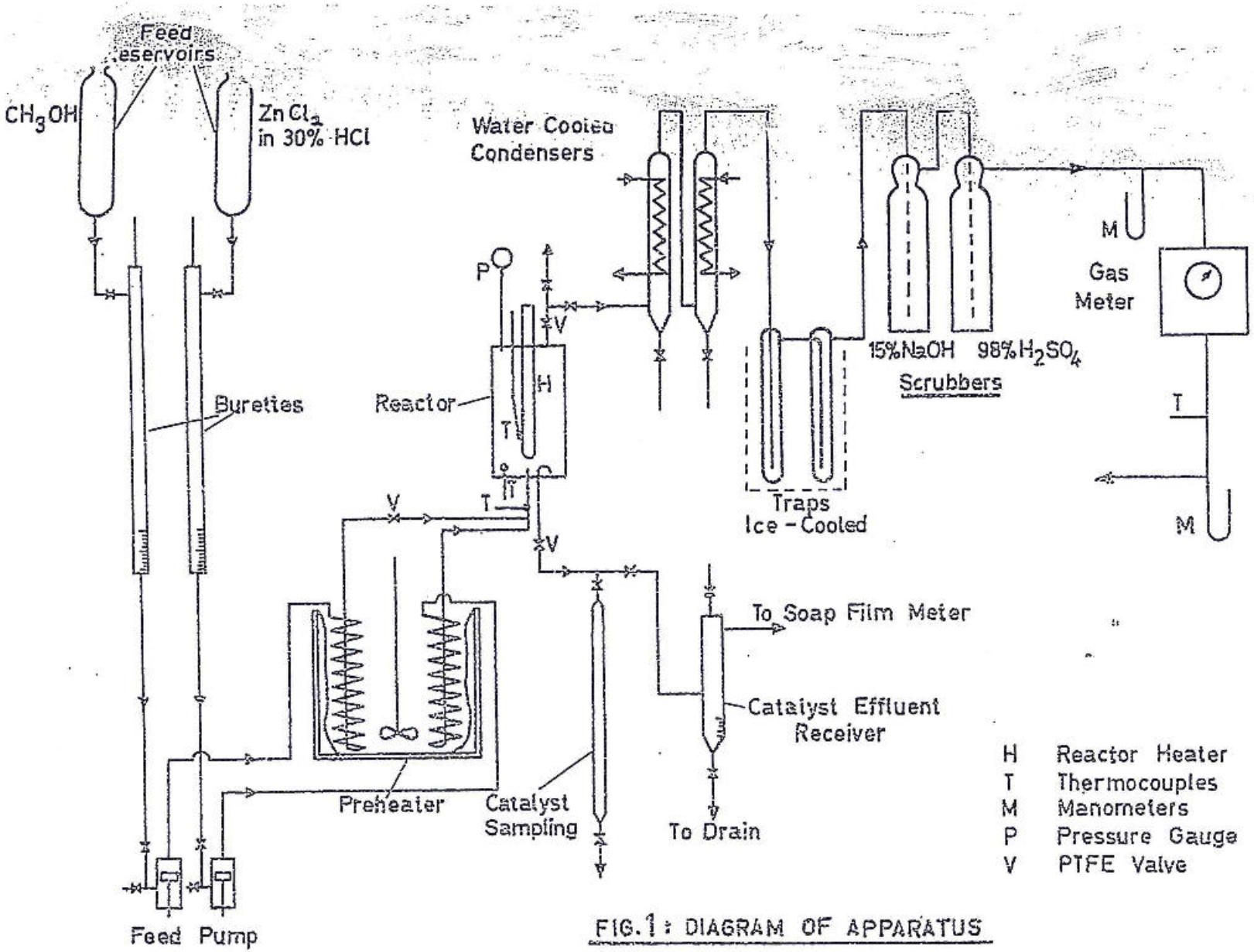


FIG. 1 : DIAGRAM OF APPARATUS

(ii) Effect of Stirrer Speed

If the stirrer were completely effective in eliminating mass transfer resistance, variation in the speed of the stirrer should have no effect on the conversion. The results shown in fig. 4, though limited due to the stirrer mechanism, suggest that this is so. The absence of any significant mass transfer resistance was confirmed by an order of magnitude calculation based on the correlation for mass transfer coefficients from bubbles presented by Calderbank and Moo-Young (4). Photographs of the dispersion showed that the size of bubbles present was about 1.0mm. diameter. Assuming a gas hold up of 10%, it was calculated that the driving force required for mass transfer was sufficiently small even at the highest rates of reaction at 160°C for the variation in methanol concentration between the interface of the bubbles and bulk of the liquid to be less than 3%.

(iii) The Rate Equation

In order to correlate data on the rate of the reaction, a rate equation of the form,

$$r = k C_a^{\alpha} C_h^{\beta} C_z^{\lambda} \quad \ldots\ldots\ldots\ldots (2)$$

was assumed where:

$k = A \exp(-E/RT)$, and C_a, C_h and C_z are the concentrations of methanol, hydrogen chloride and zinc chloride respectively in the liquid phase. This equation was expressed in logarithmic form and a multiple linear regression carried out on the data in Table 1 to find the best values of the coefficients. This resulted in the following rate equation:

$$r = 10.35 \exp(-4172/T) C_a^{0.34} C_h^{-0.10} C_z^{0.37} \quad \ldots (3)$$

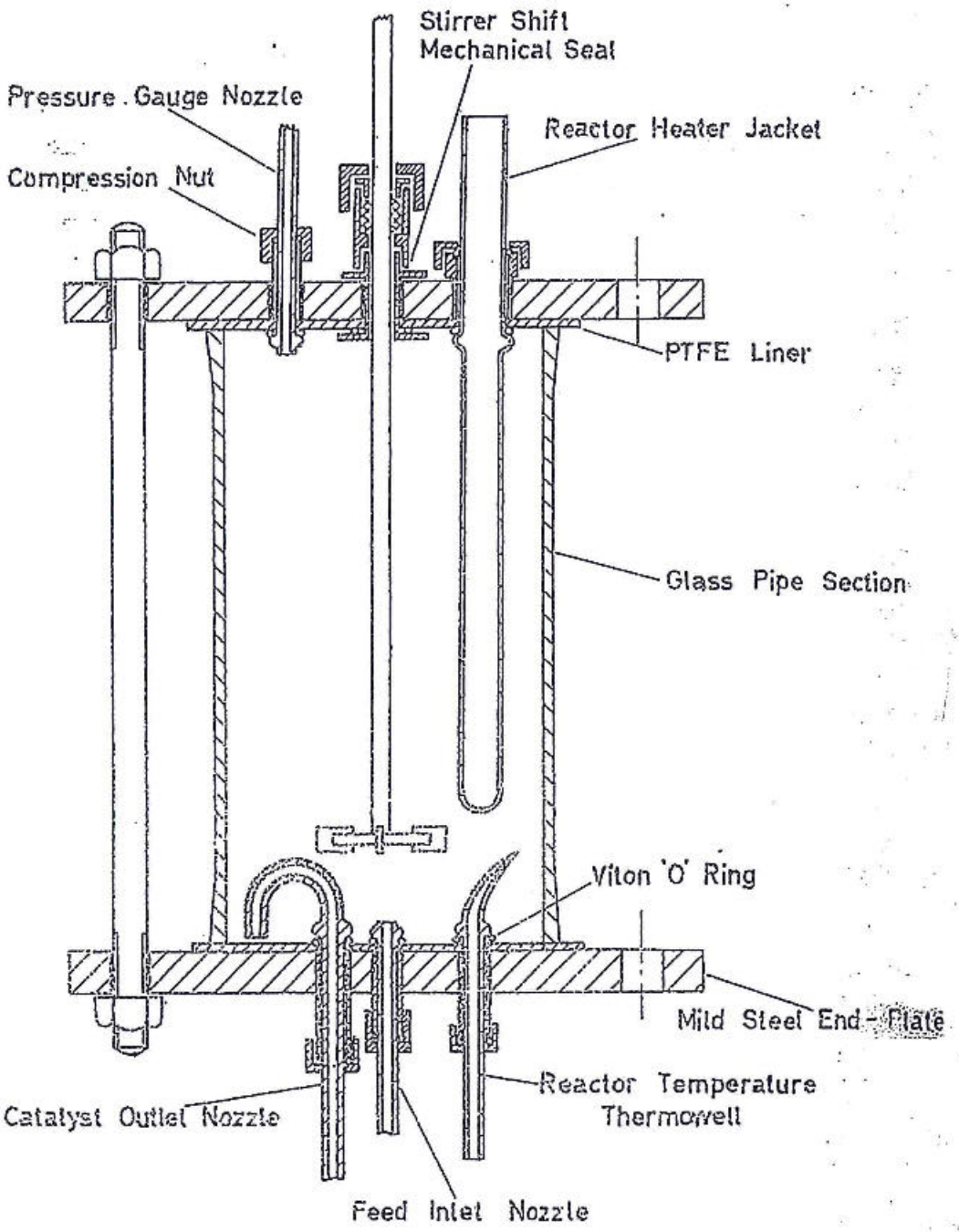


FIG.2: DETAILS OF REACTOR

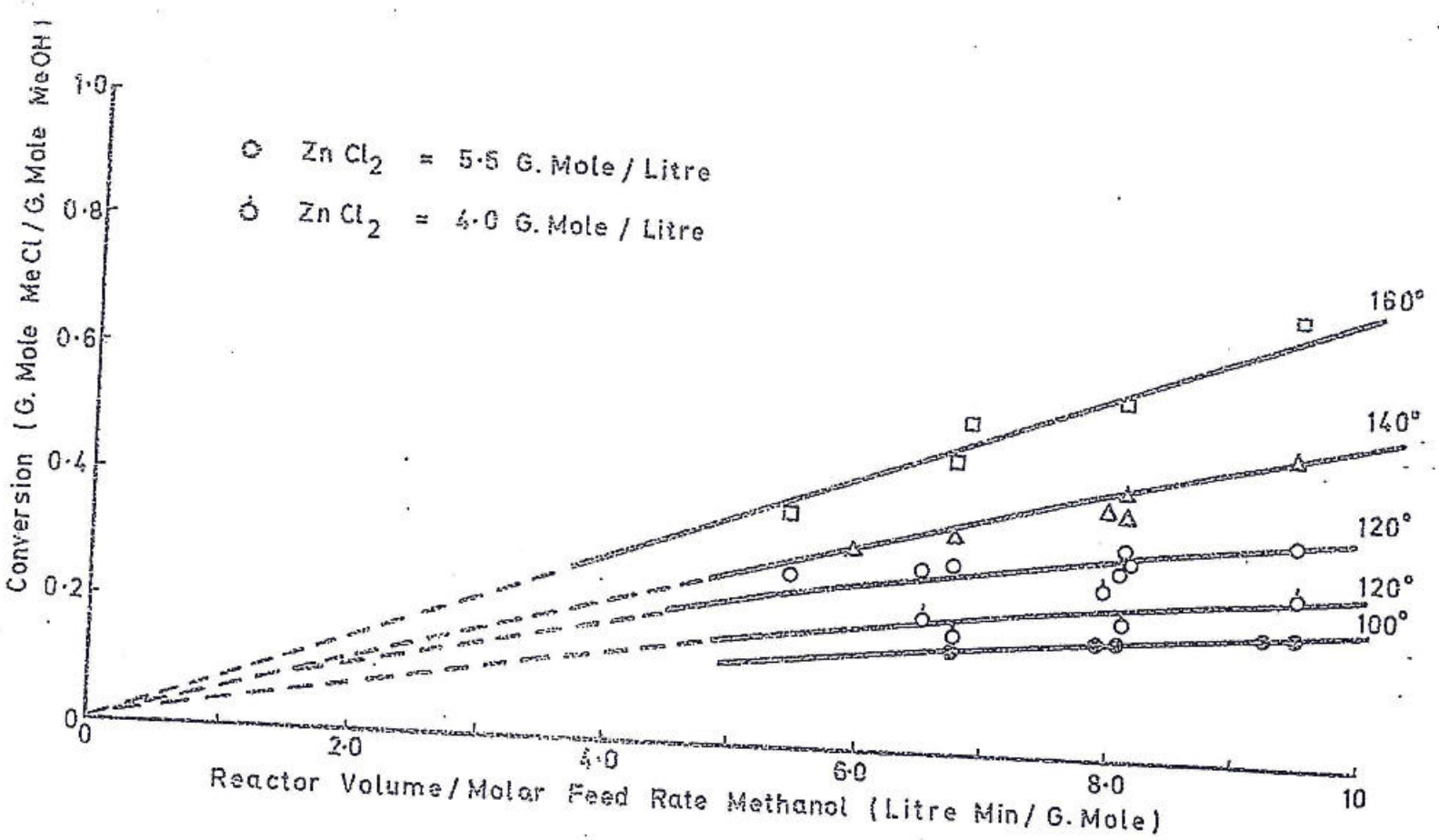


FIG. 3 GAS-LIQUID REACTION

EFFECT OF RATIO (REACTOR VOLUME : METHANOL FEED RATE) ON CONVERSION

where the rate of reaction r has units of g. mole methyl chloride produced per min., per litre of dispersion. The ranges of variables covered by this correlation are:

T :- 373 - 433°K

C_a :- 0.33 - 3.65 g. mole/litre

C_h :- 0.56 - 5.93 "

C_z :- 2.00 - 9.50 "

The regression with the above values of the coefficients fitted the data of Table 1 with a residual error of 14% in the reaction rate.

(iv) Phase Equilibrium

If the stirrer is effective in eliminating mass transfer resistance and maintaining uniform concentrations in the reactor liquid, it might be expected that a steady state would be set up, in which phase equilibrium would exist between the liquid phase containing dissolved reactants and the outgoing vapour. Analysis of the contents of the condensers and scrubbers for methanol and hydrogen chloride enabled partial pressures of these constituents P_a and P_h respectively in the outgoing vapour to be determined. Knowing the concentration in the liquid phase, equilibrium constants $H_a = P_a/C_a$ and $H_h = P_h/C_h$ were calculated. Table 2 shows average values of these results for zinc chloride concentrations at each temperature. At the extremes of the zinc chloride concentrations the equilibrium constants are estimated to be in error by not more than 30%. Under the conditions of operation an ideal vapour-liquid stage was obviously not fully approached in the reactor, however the results give a quantitative representation for this type of flow system.

APPLICATION TO REACTOR DESIGN

Basic Relationships

From the data presented above, it is possible to design a bubble-contact methyl chloride reactor on a rational basis. Consider the single stage reactor shown in Fig. 5 operating in a steady state.

Let: Y_{ao}, Y_{ho} and Y_{wo} be the mole fractions of methanol, hydrogen chloride and water respectively in the feed.

Y_{al}, Y_{hl}, Y_{wl} and Y_{gl} be the mole fractions of methanol, hydrogen chloride, water and methyl chloride respectively in the outlet.

C_{al}, C_{hl} and C_{zl} be the concentrations (g. mole/litre) of methanol, hydrogen chloride and zinc chloride respectively in the reactor liquid.

m = flow rate of methanol (g. moles/min)

X_l = fraction of methanol converted to methyl chloride at the outlet

X_o = fractional conversion at the inlet (normally zero for the first stage)

In the steady state, the rate of mass transfer to the liquid is qual to the rate of chemical reaction in the liquid, that is for ethanol,

$$60\, k_{LA}{}^{a}\, V_l (C^*_{al} - C_{al}) = r_l V_l \quad .. \quad .. \quad .. \quad (4)$$

ere C^*_a = the concentration at the interface

k_{LA} = liquid phase mass transfer coefficient (cm/sec), the vapour phase resistance being assumed negligible.

V_l = reactor volume.

The least favourable case for mass transfer occurs when the incoming vapour is well mixed with the vapour already in the reactor. Then:

$$C_{al} = \frac{y_{al} P_1}{H_a} \quad .. \quad .. \quad .. \quad .. \quad (5)$$

A material balance over the reactor is given by:

$$m(X_1 - X_o) = r_1 V_1 \quad .. \quad .. \quad .. \quad .. \quad (6)$$

Combining equations (4), (5) and (6) these results for methanol,

$$C_{al} = \frac{Y_{al} P_1}{H_a} - \frac{m(X_1 - X_o)}{60 V_1 k_{LA} a} \quad .. \quad .. \quad .. \quad (7)$$

and similarly for hydrogen chloride,

$$C_{hl} = \frac{Y_{hl} P_1}{H_h} - \frac{m(X_1 - X_o)}{60 V_1 k_{Lh} a} \quad .. \quad .. \quad (8)$$

The rate equation (3) is the further relation required in the calculation. However, at high conversions allowance needs to be made for the fact that the reaction does not go to completion. There is insufficient information to characterize completely the reverse reaction. As an approximation however, if phase equilibrium is assumed between the outgoing vapour and the liquid, the concentration of methanol in the liquid which would be in chemical equilibrium is given by,

$$C_{ae} = \frac{1}{K H_a} \frac{Y_{gl} Y_{wl}}{Y_{Hl}} P_1 \quad .. \quad .. \quad (9)$$

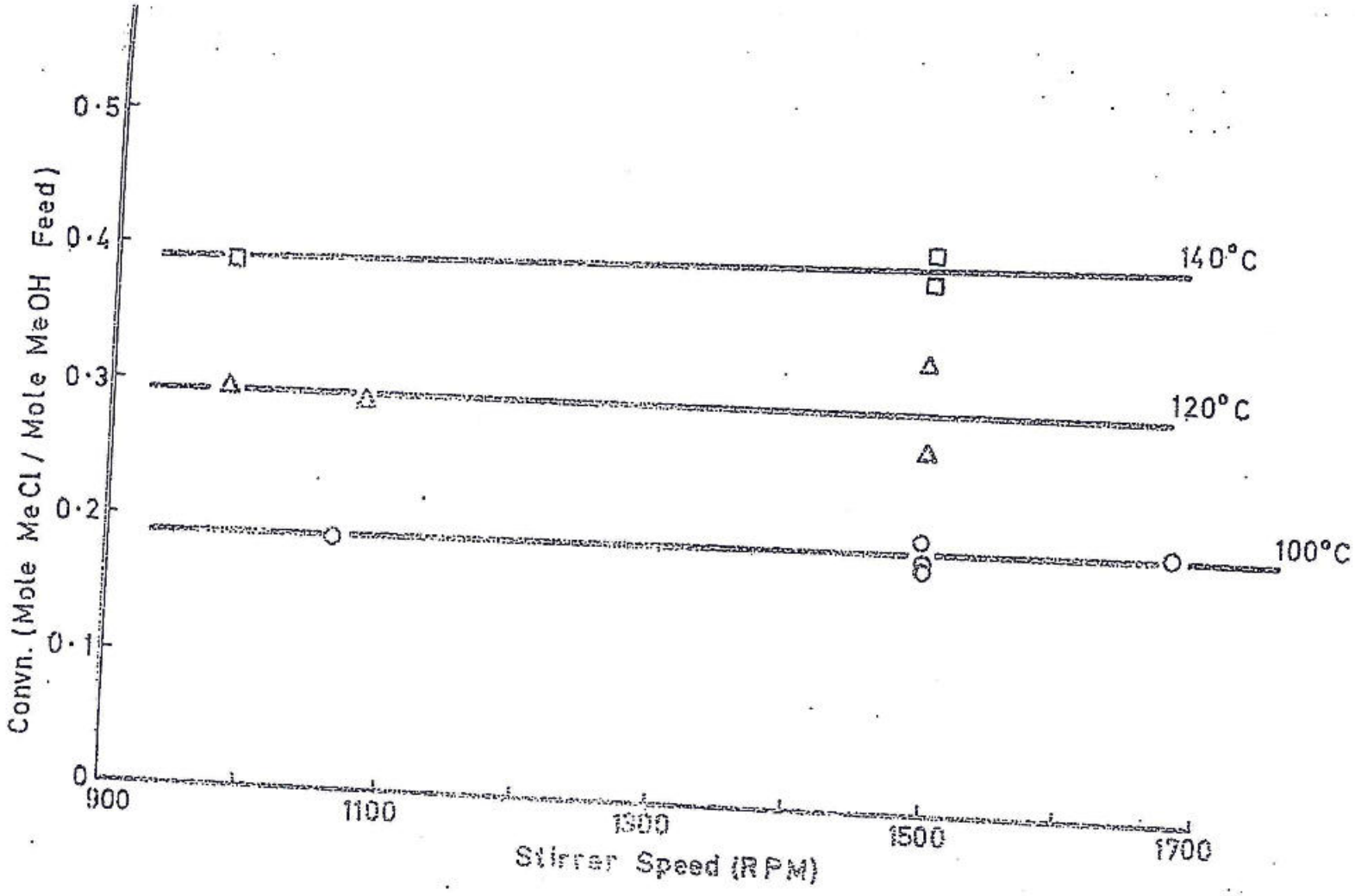


FIG. 4 EFFECT OF STIRRER SPEED ON CONVERSION AT CONSTANT REACTOR VOLUME : METHANOL FEED RATE RATIO

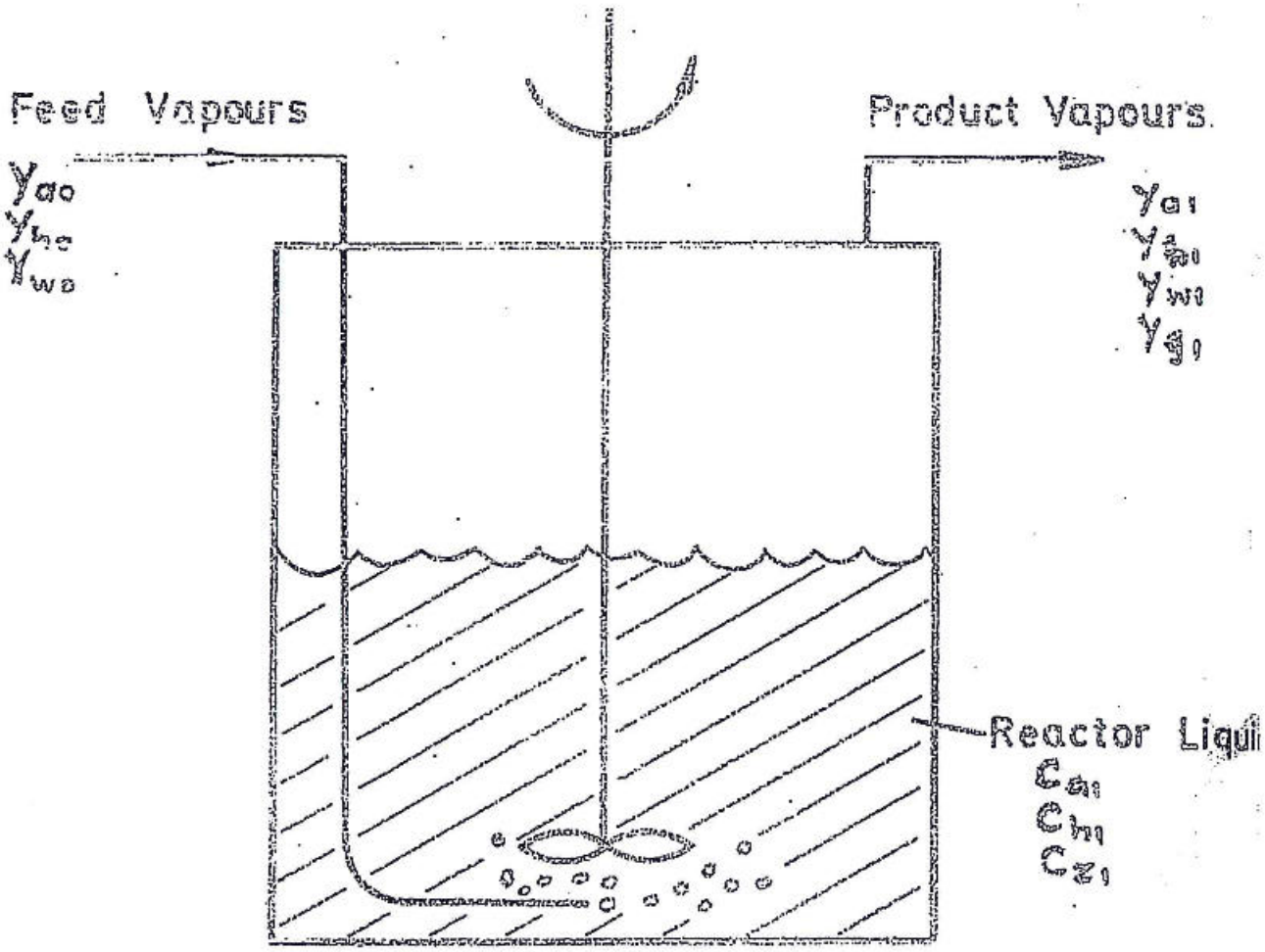
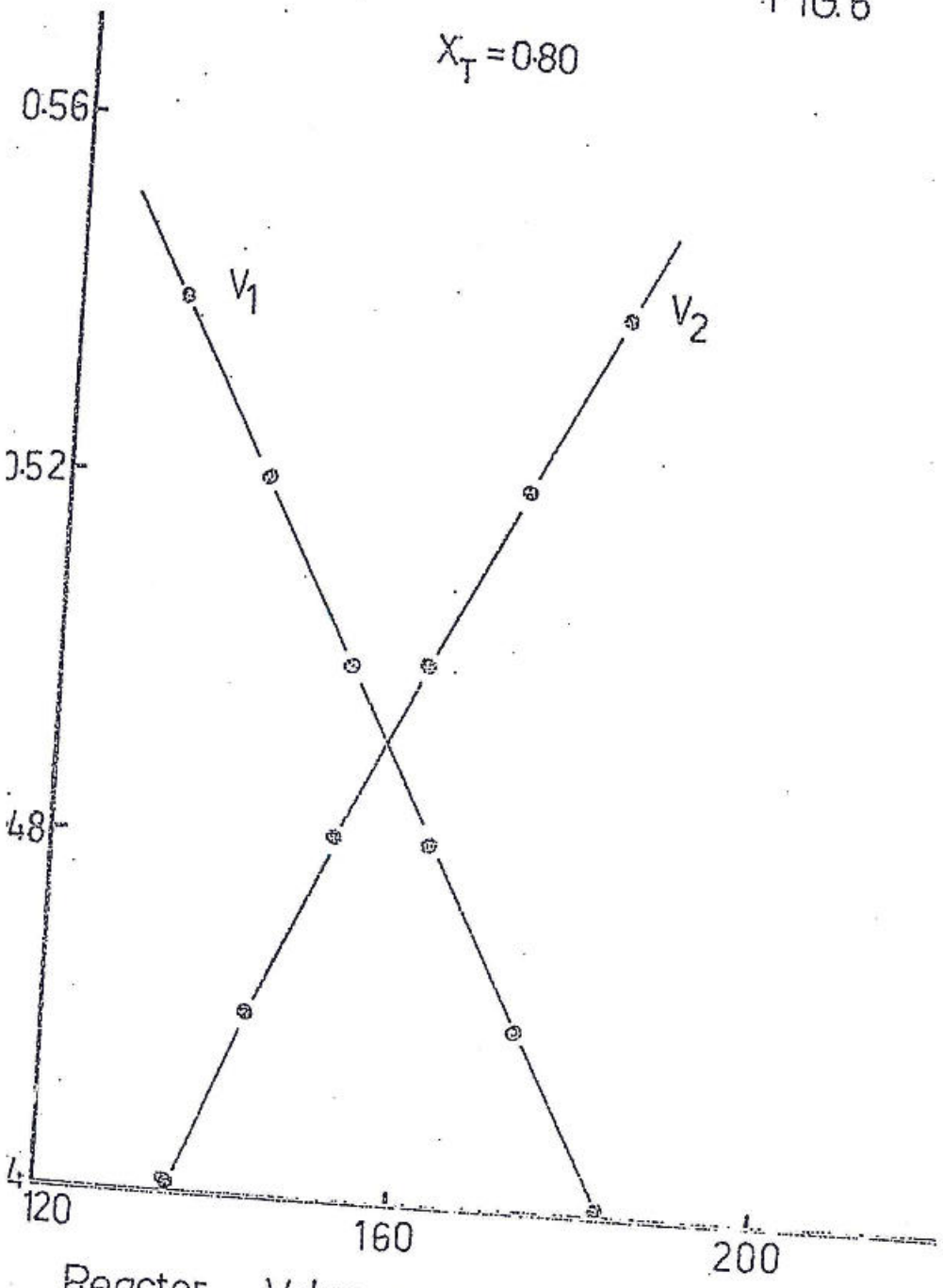


FIG. 5 TYPICAL GAS LIQUID REACTOR

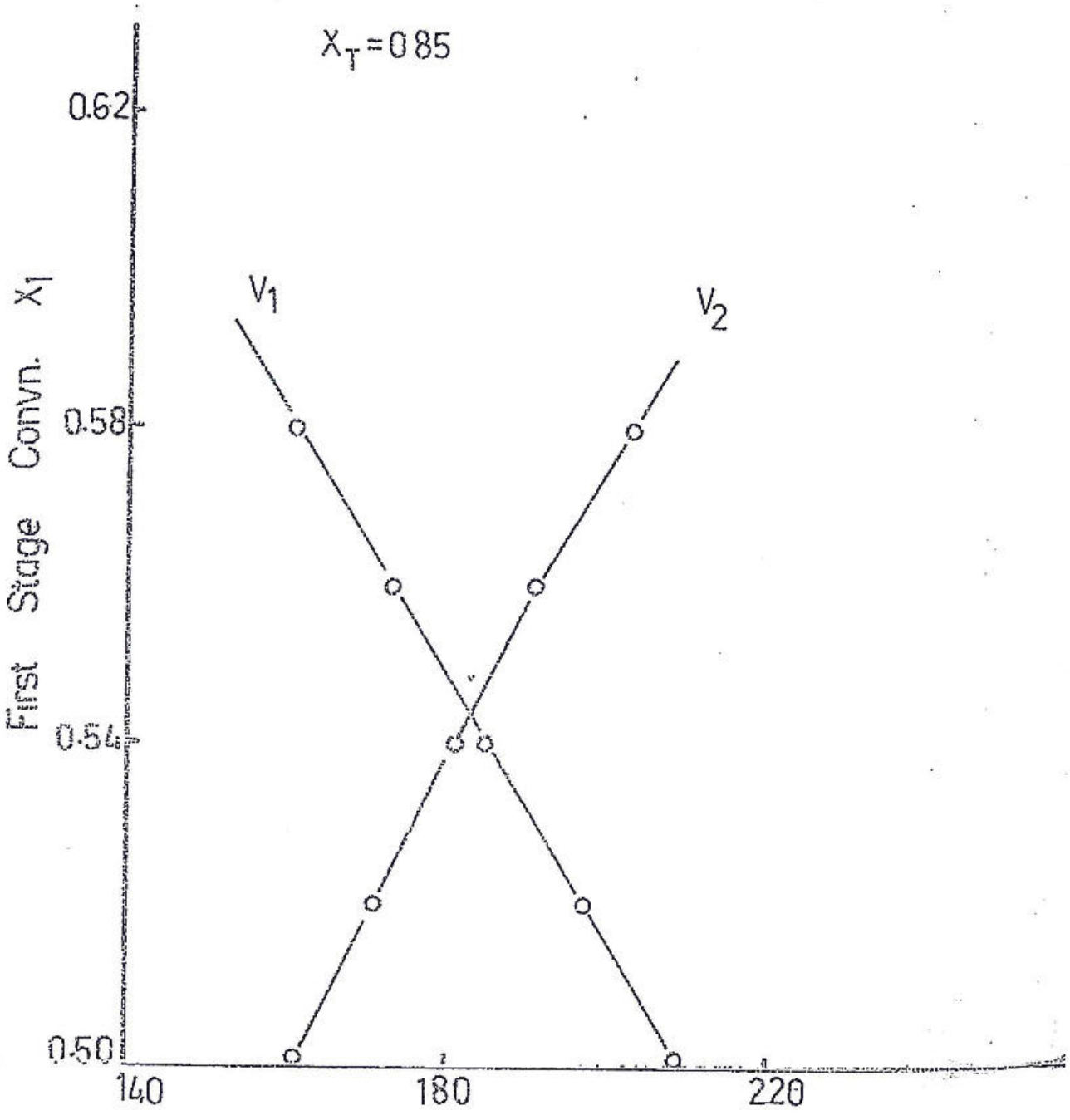
FIG. 6



Reactor Volumes V_1 or V_2 (Litres)

t of First Stage Convn. on Reactor Volumes

FIG. 7



Effect of First Stage Convn. on Reactor Volun

At chemical equilibrium the rate of the reverse reaction is equal to the rate of the forward reaction, which, assuming equation (2) holds, is $k\, C_{ae}^{\alpha}\, C_{hl}^{\beta}\, C_{l}^{\lambda}$. This is therefore the rate of the reverse reaction in the reactor and must be subtracted from the forward rate to obtain the net rate r_l:

$$r_l = k(C_{al}^{\alpha} - C_{ae}^{\alpha})\, C_{hl}^{\beta}\, C_{zl}^{\lambda}$$

which in terms of the rate constants of equation (3) becomes:

$$r_l = 10{:}35 \exp(-4172/T)\,(C_a^{0.34} - C_{ae}^{0.34})\,C_h^{-0.10} C_2^{0.37} \quad ..(10)$$

Calculation Procedure

The procedure for calculating the volume of reactor required for a given conversion X_l at a particular temperature $t^{o}C$ and reactor pressure P_l is as follows:

(i) Take the value X_l and calculate Y_{al}, Y_{hl} and Y_{wl}, hence $P_s = P_l\, Y_{wl}$

(ii) Use P_s to determine C_{zl} from the following empirical relationship based on published data[5] for vapour pressures of aqueous zinc chloride solutions,

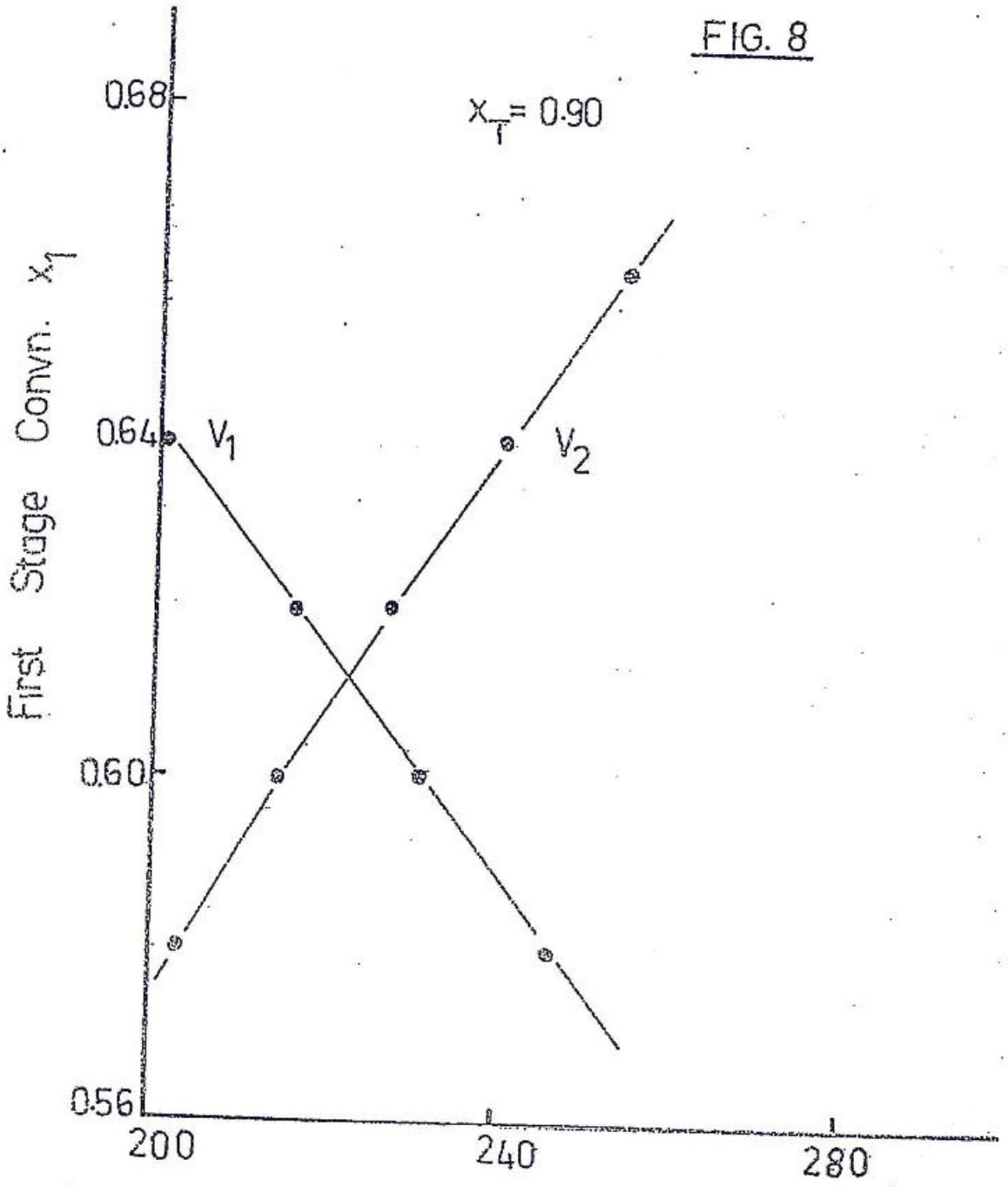
$$C_z = 22.28 + 0.141(t - 77 \log_{10} P_s).$$

This neglects the effect of dissolved methanol and hydrogen chloride on the vapour pressure of water vapour.

(iii) Assume a reactor volume V_l

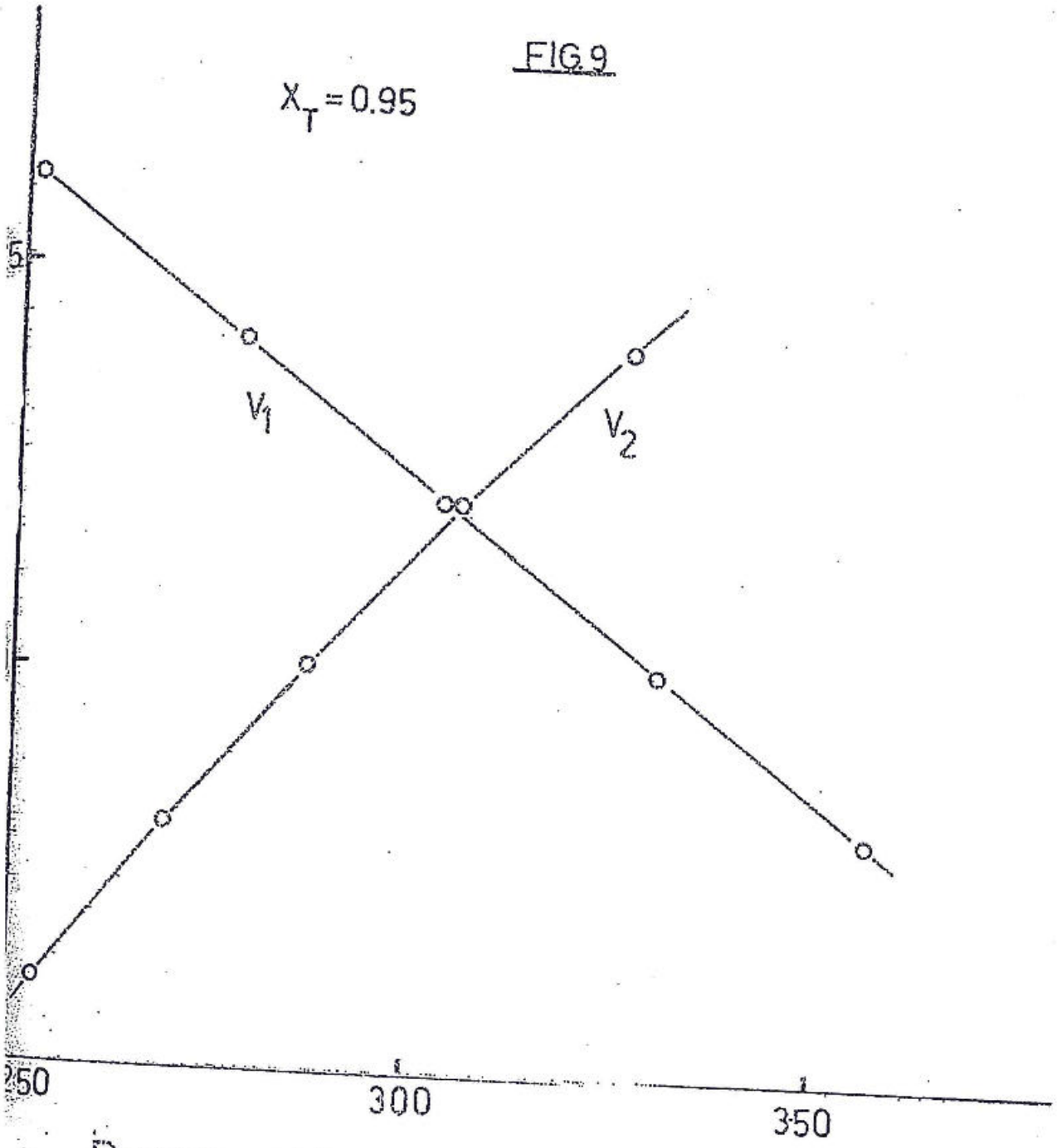
(iv) Calculate C_{al} from equation (7) using the assumed V_l and values of Ha from Table 2.

FIG. 8



Effect of First Stage Convn. on Reactor Volume

FIG.9



ct of First Stage Convn. on Reactor Volumes

(v) Calculate C_{hl} similarly from equation (8)

(vi) Determine C_{ae} from equation (9) and calculate r_1 from equation (10)

(vii) Calculate V_1 from equation (6) and repeat steps (iii) to (vii) until V_1 calculated = V_1 assumed.

Commercial reactors of this type operate with two reactors in series to effect an economic overall level of conversion in excess of 85%. For all practical purposes two reactors of equal size are used hence the design procedure was extended to meet this requirement.

(viii) Allow a pressure drop for reactor 2 to assume a value P_2.

(ix) The second stage conversion is taken as, $X_2 = X_{overall} - X_1$.

(x) Carry out the same procedure as steps (1) to (vii).

(xi) Repeat calculations for stages (1) and (2) for the same overall conversion but at different values of X_1.

Repeat (x) for the desired levels of overall conversion.

The above calculations were carried out on an IBM 1620 computer with the following data inputs:

Reactor Temperature, ^oC	= 140
Feed rate, g. mole methanol/min	= 75
Mole HCl/mole methanol	= 1.2

Mole H_2O/mole methanol	=	5.7
P_1, mm Hg	=	1100
P_2, mm Hg	=	1000
$k_{La}a$, sec^{-1}	=	0.48
$k_{Lh}a$, sec^{-1}	=	0.88

Figs. 6 - 9 show the results expressed as first stage conversion X_1 vs. reactor volumes V_1 and V_2 at overall conversion levels X_T of 0.80, 0.85, 0.90 and 0.95 respectively. The intersection of the V_1 and V_2 plots represent the point where $V_1 - V_2$ and thus the conversion X_1 can be read off directly.

Comparison of Model with Commercial Reactor Performance

One of the objectives of this study was to provide a model which represents an existing commercial reactor system with a view to the redesign of the system for achieving higher conversions. Fig. 10 shows the reactor system in question which operated with reactor volumes of 1020 litres each(6). Analyses were made of the reaction mixture with variables such as methanol 'holding time,' temperature and pressure closely approximating those of the reactor used in this study. A comparison of the plant reactor and the model based on the present design calculations follows:

	Conversions %			
	Reactor 1	Reactor 2	Total	V_R(litres)
Model	62	28	90	222
Plant	58	20	78	1020

The above figures reflect the limiting effect of diffusional resistance in the plant reactor and it was suspected that dispersion was indeed poor. This was substantiated by plant tests of the dispersion nozzle in use which showed that slightly less than $0.25V_R$ was effective in the reactor.

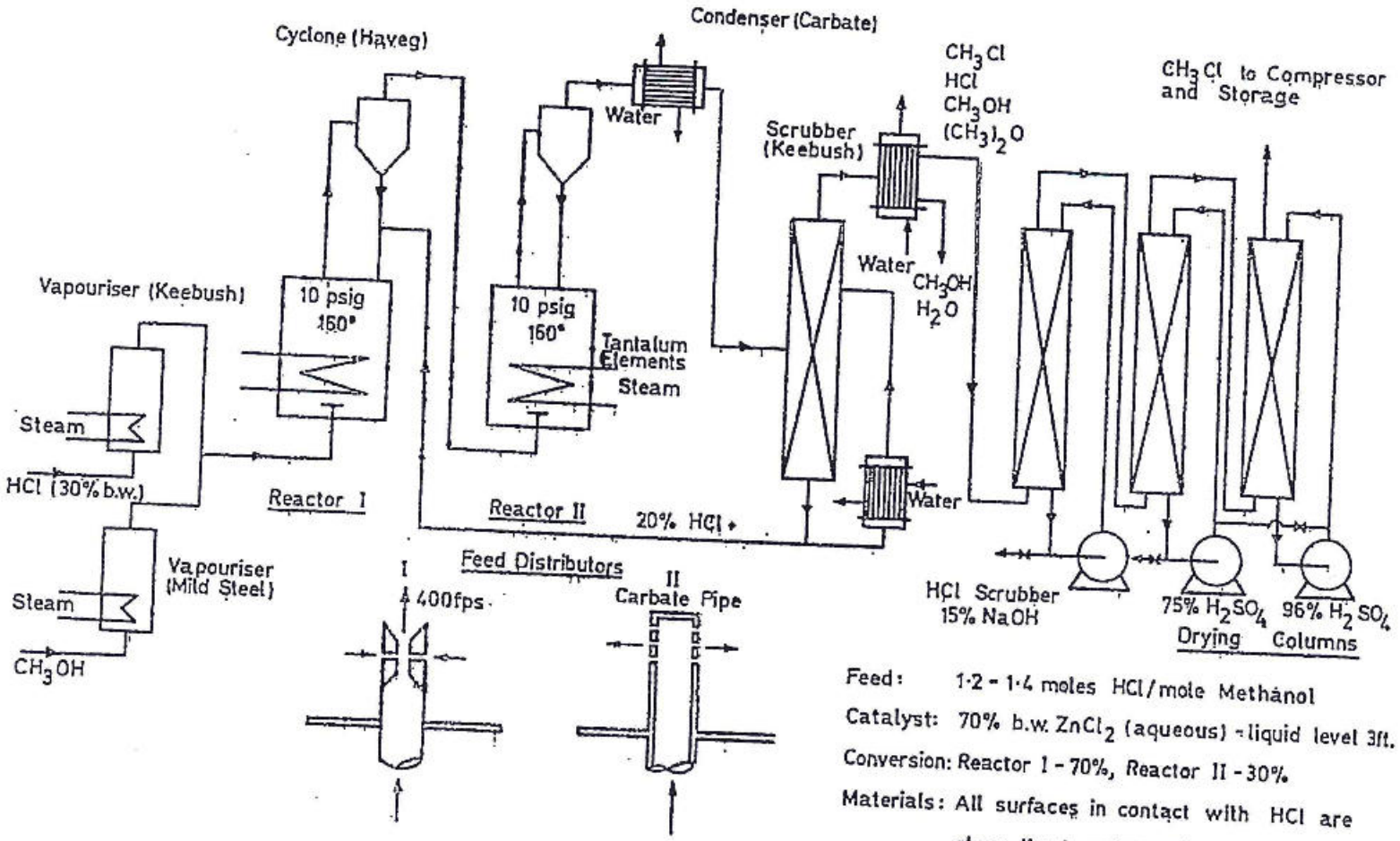
CONCLUSIONS

The results of the foregoing study points to the following conclusions:

(1) The gas-liquid reaction of methanol and hydrogen chloride is diffusion controlled as thus requires a high level of dispersion of HCl, comparable with that obtained with the turbine stirrer used in the experiments.

(2) Although the reactor did not appear to represent an ideal physical equilibrium stage, steady state operation ensures predictable reaction rates.

(3) The model developed from this study forms the basis for the rational design of gas-liquid reactors for the hydrochlorination of methanol to methyl chloride on a commercial scale.



Feed: 1·2 - 1·4 moles HCl/mole Methanol

Catalyst: 70% b.w. $ZnCl_2$ (aqueous) - liquid level 3ft.

Conversion: Reactor I - 70%, Reactor II - 30%

Materials: All surfaces in contact with HCl are glass-lined except when shown otherwise.

FIG.10: FLOW DIAGRAM OF 500 lb/hr METHYL CHLORIDE PLANT

NOTATION

a	-	Interfacial area of contact per unit volume of dispersion (cm^{-1})
C	-	Concentration in the liquid phase (g. mole/litre)
H	-	Phase equilibrium Coefficient, H = P/C, mm. Hg. litre g. $mole^{-1}$
K	-	Thermodynamic Equilibrium Constant
k_L	-	Liquid phase mass transfer coefficient (cm/sec)
ml	-	Methanol feed rate (g. mole/min)
P_l	-	Reactor Pressure (mm.Hg)
P_a, P_h	-	Partial Pressure (mm.Hg)
P_s	-	Vapour pressure of water over zinc chloride solution (mm.Hg)
r	-	Rate of methyl chloride formation (g. mole/litre. min)
T	-	Temperature, ^oK
V	-	Volume of dispersion in reactor (litres)
X_o, X_i, X_T	-	Fractional conversion of methanol
Y		Vapour phase mole fractions

SUBSCRIPTS

a	–	Methanol
g	–	Methyl Chloride
h	–	Hydrogen Chloride
w	–	Water
O	–	Inlet to first reactor
1	–	Outlet from first reactor
2	–	Outlet from second reactor

REFERENCES

1. B.I.O.S. Report No. 1662, 'Methyl Chloride Production at I.G. Farben. Hoechst,'1947 London. H.M. Stationery Office.

2. Noller, C. R., 'Chemistry of Organic Compounds,' W.B. Saunders (1965).

3. Duke, F.R., Ind. Eng. Chem. Anal, Ed. 17. 572, (1945).

4. Calderbank, P.H. & Moo-Young M.B., Chem. Eng. Sci., 16,1, 40 (1961).

5. Timmermans, J., 'Physico-chemical Constants of Binary Systems,' V ol. 3, 1960, Interscience, New York.

6. Kolker, L.A., U.S. Patent 2; 847; 484; 1958.

NOTES TO CONTRIBUTORS

ALEJANDRO BRAVO CHARCAP, M.Sc. (UWI) is an Assistant Professor of Chemical Engineering at the National University of Peru.

P.N. BRUCE is a Senior Lecturer in Physical Chemistry and in Petroleum Refinery Engineering in the Department of Chemical Engineering.

R.A. DENNIS is a lecturer in Engineering Design and Strength of Materials in the Department of Mechanical Engineering.

Z.M. KONASIEWICZ is a lecturer in Science of Materials and Chemical Process Industries in the Department of Chemical Engineering.

D.R. Mc GAW is a lecturer in Transport Phenomena in the Department of Chemical Engineering.

C.V. NARAYAN is a lecturer in Graphics and Strength of Materials in the Department of Mechanical Engineering.