# Kinetics of palladium catalysed partial oxidation of methane

M A Lourdu Antony Raj[a]*, G M Madhu[a]& Y Jagannadha Rao[b]

[a]Department of Chemical Engineering, R.V. College of Engineering, Bangalore 560 059, India

[b]Department of Chemical Engineering, M.V.J. College of Engineering, Bangalore 560 064, India

Email: antony_mal@yahoo.com

Catalytic partial oxidation of methane to methanol has been investigated in a pressures range of 5-15 kg/cm² and at different temperatures (573-763 K) in quartz-lined reactor using asbestos supported palladium catalyst. The effect of process variables namely, reaction temperature, ratio of the weight of the catalyst to molar flow rate of methane ($W/F_{A0}$), pressure on conversion of methane and selectivity to reaction products like methanol, carbon dioxide, carbon monoxide were investigated. The kinetic study carried out indicated first order rate for the main reactions. From the effect of temperature on rate constant, activation energy and frequency factors were evaluated. The rate constants are found to be 2.53 and 1.84, activation energies are found to be 186948.60 and 162231.08 for the two main reactions.

**Keywords**: Partial oxidation, Catalytic oxidation, Methane, Methanol, Palladium
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Methanol is manufactured on a large scale since it forms one of the important petrochemical commodities produced in the world. There is a widespread use of methanol in the manufacture of variety of chemicals and is also an alternate fuel which is in increased demands. Methanol can be produced from natural gas, coal, biomass and petroleum. Conversion of natural gas to methanol appears to be one of the most promising alternatives in utilizing abundantly available natural gas[1]. Methanol is obtained from natural gas via syngas or by direct partial oxidation. Production of methanol by partial oxidation does not need much energy. Hence, in the present study an attempt has been made to produce methanol and to study its kinetics of formation by a single step catalytic partial oxidation of methane in presence of 5% palladium catalyst supported on asbestos. Homogeneous and heterogeneous methods of producing methanol from partial oxidation of methane have been investigated by several authors[2-23]. One of the most significant strategies in commercial production of methanol has been in the use of natural gas as the feed stock. There are a number of factors that contribute to the use of natural gas[24]. The present study mainly deals with production of methanol from the partial oxidation of methane catalysed by palladium. Catalytic partial oxidation of methane to methanol has been investigated in a pressure range of 5-15 kg/cm² and at different temperatures (573-763 K) in quartz-lined reactor using asbestos supported palladium catalyst.

## Experimental Procedure

### Materials

Palladium catalyst supported on asbestos was procured from S.D. fine chemicals Ltd., Mumbai. The surface area of the catalyst was determined by a multipoint BET method using nitrogen adsorption. The surface area of catalyst was found to be 74.8 m²/g. The particle size used was 40 microns. The catalyst was activated prior to use. Methane (99.9% pure) and air (zero grade) were obtained from Bhoruka gases, Bangalore. Purity of the gases was checked using Nucon gas chromatograph.

### Experimental set-up and procedure

The experimental set-up used in the present investigation was designed and fabricated similar to the one used by Chellappa and Viswanath[20]. The set-up consists of flow metering units, pre-heaters for air and methane, a quartz-lined reactor, product collection and sampling units as shown in Fig. 1. The flow meters employed in this study were orifice meters made from mild steel to withstand high pressure. One of them was used for measuring the flow rate of air and the other for measuring the flow
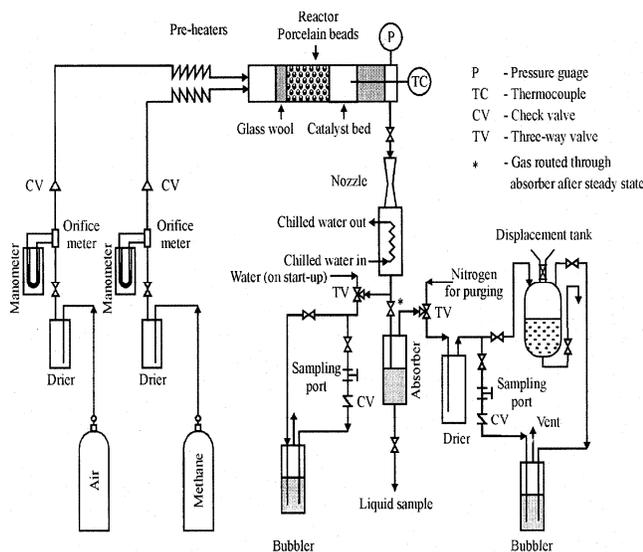
Fig. 1—Schematic diagram of the experimental set-up

rate of methane. The gases were dried by passing through silica gel placed in mild steel container before metering. Preheaters for air and methane were of 10 mm (outer diameter) ×3 m mild steel coiled tubes packed with 3 mm stainless steel balls to provide sufficient area for heat transfer. Heating was done to a maximum of 500 K, achieved using a series of heavy-duty insulated heating tapes of 2 kW each. To prevent heat loss to the surroundings, glass wool insulation was made and claded with aluminum sheet. The reactor charged with the catalyst, was made of a 25 mm inner diameter (ID) ×32 mm outer diameter (OD) and 500 mm long stainless steel tube fitted with a 20 mm (ID)×25 mm (OD) and 400 mm quartz tube to have a close fit. The quartz tube was positioned with end nuts on both sides. About 15 cm of the quartz tube was packed with glass wool to confirm adequate mixing and heating of the gases before they reach catalyst bed. After the bed, quartz tube was packed with glass wool for about 3 cm to hold the catalyst-supported palladium in place. The reactor was heated with a heavy-duty heating coil of 2 kW and the temperature of the heating coil was regulated by varying the voltage with the help of a dimmerstat. The whole systems were made leak proof. By closing the inlets to orifice meters of air and methane, the valves of the respective cylinders were opened and maintained at a desired pressure by opening the valves. Chilled water was circulated through the cooling coil with the help of a fractional HP magnetic impeller pump and the absorber by-pass was lined up. Methane was fed into the reactor first to provide an

atmosphere rich in methane so that at any given time the methane air mixture was well above the upper explosive limits. After an interval of few minutes air was introduced into the reactor and pressure was gradually raised to a desired value. The pressure of the reactor was controlled with the help of a heavy-duty needle valve fixed at the exit of the reactor and reactor pressure was measured with the help of Bourdon type pressure gauge installed just before the valve. The temperature of the bed was measured using a K-type thermocouple, capable of measuring temperature from 0 to 1000°C. Care was taken to ensure rapid removal of products to prevent the formation of formaldehyde and other byproducts. For the rapid removal of products from the reaction zone a nozzle type assembly was used as an outlet. The nozzle was made of SS316 stainless steel having a throat diameter of 2 mm. After steady state was attained, the product gases were passed through water to absorb any condensable material and uncondensable gases were dried, metered and analyzed. A liquid sample from the absorber was analyzed for methanol and formaldehyde. Nucon gas chromatograph was used to analyze gas samples using thermal conductivity detector (TCD). Liquid samples were analyzed by chemical method and also in gas chromatograph using flame ionized detector (FID).

## Results and Discussion

The experiments were conducted in order to study the effect of process parameters such as pressure and the temperature of the reaction, and $W/F_{A0}$ (ratio of weight of catalyst to methanol flow rate) on reaction rate. Further, their effect on the conversion and the selectivities to form various products were analyzed.

The conversion is calculated as

$$\% \text{ Conversion} = \frac{\text{Moles of methane converted}}{\text{Moles of methane fed}} \times 100$$

The selectivity is calculated as

$$\% \text{ Selectivity} = \frac{\text{Carbon present in desired product}}{\text{Carbon present in all products}} \times 100$$

**Effect of temperature on conversion and selectivity**

The experiments were conducted at different temperatures (573-763 K) maintaining the $W/F_{A0}$, and pressure constant. The results of these experiments are shown in Figs 2-5. It is observed that the
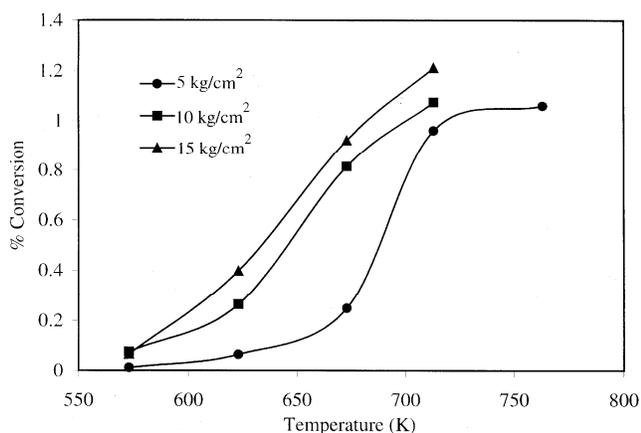
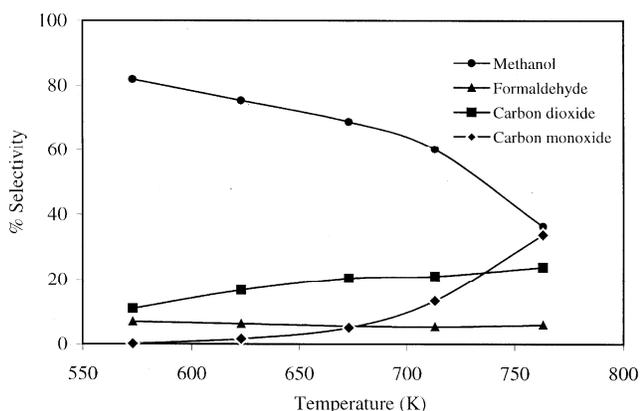Fig. 2—Effect of temperature on methane conversion at 5, 10 & 15 kg/cm$^2$



Fig .4—Effect of temperature on product selectivity at 10 kg/cm$^2$



Fig. 3—Effect of temperature on product selectivity at 5 kg/cm$^2$



Fig. 5—Effect of temperature on product selectivity at 15 kg/cm$^2$

conversion of methane increases with increase in temperature at all the pressures in the range of temperature studied. In respect of selectivity, the carbon dioxide was found to be present at low pressure (5 kg/cm$^2$). The selectivity of carbon monoxide increased marginally with increase in temperature at high pressures, whereas at low pressures and at high temperatures the increase in selectivity of carbon monoxide was predominant. This may be due to the decomposition of methanol. The selectivity of methanol decreased with increase in temperature at all pressures studied. The selectivity to formaldehyde increased with rise in temperature at all pressures. These results were found to be in agreement with the observations made by earlier investigators[18,20]. In the present case also the conversion level increased with increase in temperature. But, increase in conversion was not so significant in the temperature range of 713-763 K. Hence, all further experiments were conducted at 713 K only, where the product formed was in measurable quantities.
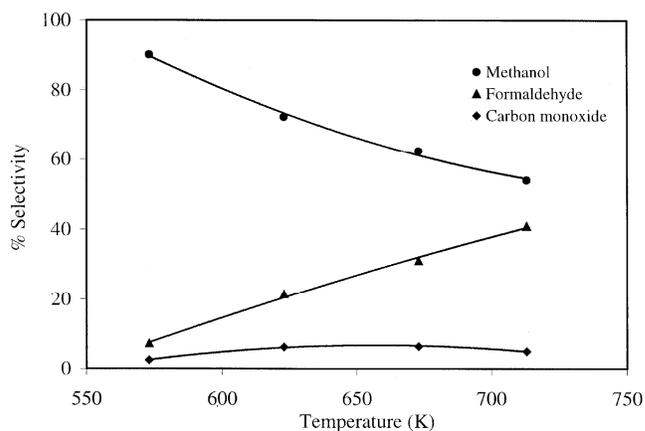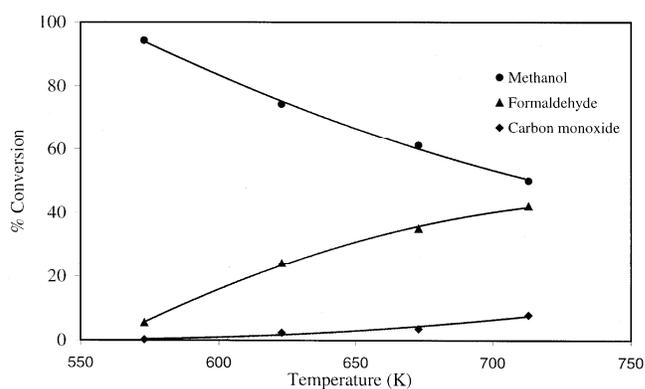
### Effect of $W/F_{A0}$ on conversion and selectivities

The experiments were conducted at various $W/F_{A0}$ values varying from 0.293 to 0.773 kg.cat.h/ kg mole methane at 713 K. The flow rates of methane and air were also kept constant. The experiments were conducted at different pressures (5, 10, 15 kg/cm²) and $W/F_{A0}$ .The results are represented in Figs 6-9. It is seen from the figures that the conversion of methane increased with increase in $W/F_{A0}$, this is due to more of catalyst and oxygen due to less conversion. Selectivity of methanol was found to increase considerably with increase in $W/F_{A0}$ at all pressures, whereas the selectivity to formaldehyde increased marginally with increase in $W/F_{A0}$. The selectivity to carbon dioxide decreased with increase in $W/F_{A0}$ at all pressures studied. Traces of carbon monoxide were found in all the experiments studied and its selectivity was maximum only 2.5% at 5 kg/cm². The influence of $W/F_{A0}$ values on selectivity should not be viewed
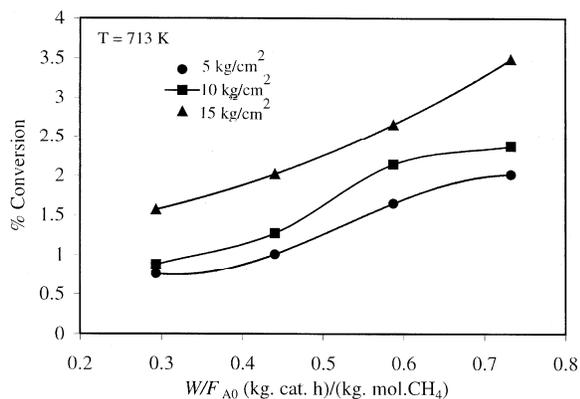
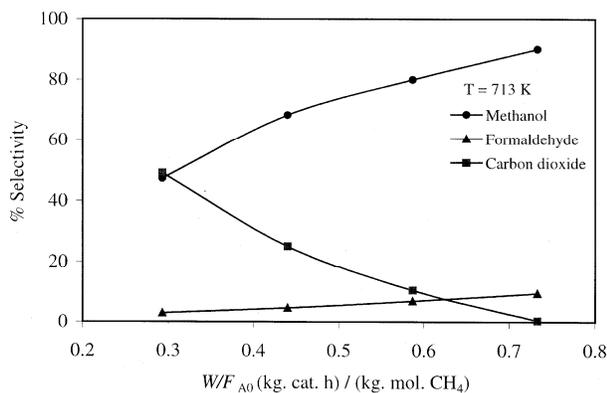Fig. 6—Effect of $W/F_{A0}$ on methane conversion at 5, 10 & 15 kg/cm$^2$



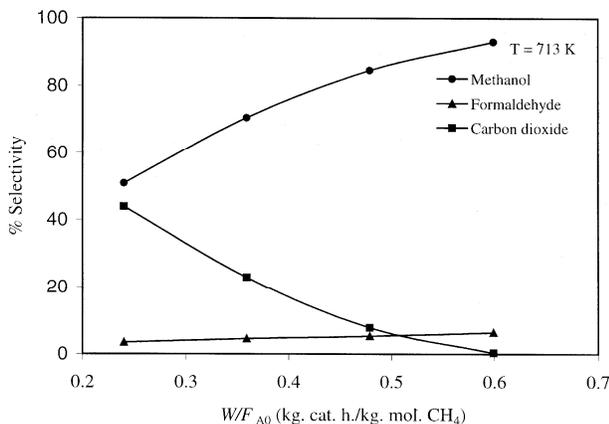Fig. 7—Effect of $W/F_{A0}$ on product selectivity at 5 kg/cm$^2$



Fig. 8—Effect of $W/F_{A0}$ on product selectivity at 10 kg/cm$^2$



Fig. 9—Effect of $W/F_{A0}$ on product selectivity at 15 kg/cm$^2$



Fig. 10—Effect of pressure on methane conversion
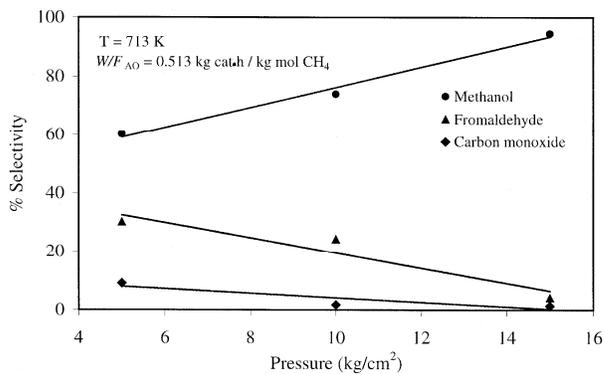


Fig. 11—Effect of pressure on product selectivities

separately without taking into consideration the effect of the same on conversion. Therefore, optimum value of $W/F_{A0}$ was not being fixed.

**Effect of pressure on conversion and selectivities**

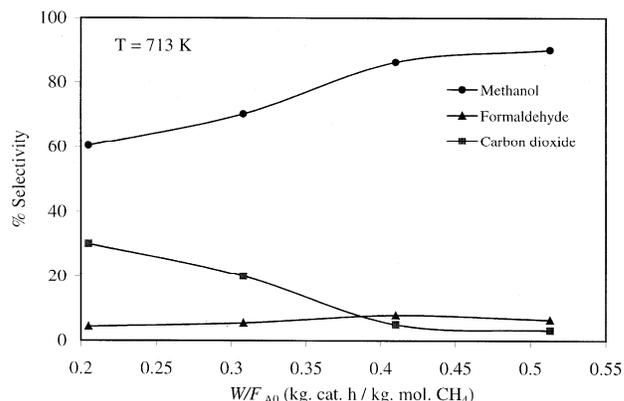The effects of pressure on the conversion of methane and selectivity to methanol, formaldehyde, carbon monoxide, and carbon dioxide have been studied. The experiments were conducted at varying pressures from 5 to 15 kg/cm², keeping temperature constant at 713 K and $W/F_{A0}$ at 0.513 kg.cat.h/kg mole of CH$_4$. At this value of $W/F_{A0}$ the highest pressure (15 kg/cm²) was achieved that could be operated and maintained easily under laboratory condition. Also the utilization of catalyst would be more, for higher $W/F_{A0}$ values. The results of these experiments are shown in Figs 10 and 11. It can be seen from the

figures that the conversion increased with increase in pressure. Difficulty of maintaining the high pressure and also to use methane economically, experiments were not carried out beyond 15 kg/cm². The selectivity of methanol increased with increase in pressure whereas for both formaldehyde and carbon monoxide the selectivity decreased with increase in pressure.

**Kinetics of oxidation of methane to methanol**

Integral method of analysis was adopted to determine the order and rate constant of the processes. Oxidation of methane to methanol involves the following five consecutive reactions:

$$CH_4 + 1/2\ O_2 \rightarrow CH_3OH \qquad \qquad \dots(a)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \qquad \dots(b)$$

$$CH_4 + O_2 \rightarrow HCHO + H_2O \qquad \qquad \dots(c)$$

$$CH_3OH \rightarrow HCHO + H_2 \qquad \qquad \dots(d)$$

$$CH_3OH \rightarrow CO + 2H_2 \qquad \qquad \dots(e)$$

The products formed during the reaction indicate the occurrence of the reactions as per Eq. (a) and Eq. (c). Hence, these steps were considered for studying the reaction kinetics. Earlier investigators[20] have reported that the reaction rate is only a function of methane concentration (A). Assuming first order, the rate expressions for these individual reactions may be written as

$$-r_1 = k_1\ C_A \qquad \qquad \dots(1)$$

$$-r_2 = k_2\ C_A \qquad \qquad \dots(2)$$

The net rate of reaction is written as

$$-r_A = (-r_1) + (-r_2) = (k_1 + k_2)\ C_A = k\ C_A \qquad \qquad \dots(3)$$

For catalytic reactions the rate of reaction is given by

$$\frac{W}{F} = \int_0^x \frac{dX}{-r} \qquad \qquad \dots(4)$$

For the component A (methane) and for first order gas phase reaction, the performance equation is

$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{kC_A} = \frac{1}{kC_{A0}} \int_0^{X_A} \frac{1 + \varepsilon_A X_A}{1 - X_A} dX_A \qquad \dots(5)$$

Integration of Eq. (5) results in

$$kC_{A0} \left( \frac{W}{F_{A0}} \right) = (1 + \varepsilon_A) \ln \left( \frac{1}{1 - X_A} \right) - \varepsilon_A X_A \qquad \dots(6)$$

for small values of $\varepsilon$, Eq. (6) reduces to

$$\ln \left( \frac{1}{1 - X_A} \right) = kC_{A0} \frac{W}{F_{A0}} \qquad \qquad \dots(7)$$

The Eq. (7) shows that a plot of $\ln \left( \dfrac{1}{1 - X_A} \right)$ versus $\dfrac{W}{F_{A0}}$ is linear, having a slope equal to $kC_{A0}$.

The rate equation in terms of the products methanol (C) and formaldehyde (D) for first order reactions may be written as

$$\frac{dC_C}{dt} = k_1 C_A \qquad \qquad \dots(8)$$

$$\frac{dC_D}{dt} = k_2 C_A \qquad \qquad \dots(9)$$

Dividing Eq.(8) by Eq.(9) and then integrating one gets

$$\frac{C_C - C_{C0}}{C_D - C_{D0}} = \frac{k_1}{k_2} \qquad \qquad \dots(10)$$

$$C_C = \frac{k_1}{k_2} C_D \qquad \qquad \dots(11)$$

A plot of $C_C$ versus $C_D$ is linear having a slope of $k_1/k_2$. The rate constants vary with temperature and the dependency of rate constant with temperatures follows Arrhenius equation, $k = k_0 e^{-E/RT}$. The rate constants and order of the two reactions "a" and "c" were found by the integral method as explained earlier, for all the pressures studied at 713 K. Plotting the graphs of $\ln \left( \dfrac{1}{1 - X_A} \right)$ versus $\dfrac{W}{F_{A0}}$ fits the data reasonably well (Fig. 12). The results were found to follow the first order rate law. From the slopes of these plots the values of $k$ ($k = k_1 + k_2$) are calculated and listed in Table 1.
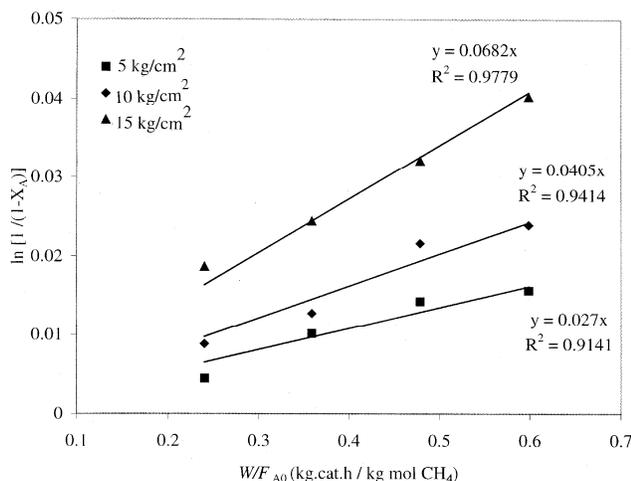
Fig. 12—Plot of ln $[1/(1-X_A)]$ versus $W/F_{AO}$ at 5, 10 and 15 kg/cm$^2$ and 713 K

Table 1—Values of rate constants at different pressures and 713 K

| Sl No. | Pressure kg/cm$^2$ | $k_1+k_2$ L/kg cat h | $k_1/k_2$ L/kg cat h | $k_1$ L/kg cat h | $k_2$ L/kg cat h |
|---|---|---|---|---|---|
| 1 | 5 | 0.2059 | 10.924 | 0.1886 | 0.0173 |
| 2 | 10 | 0.3089 | 14.947 | 0.2895 | 0.0194 |
| 3 | 15 | 0.5202 | 12.702 | 0.4822 | 0.0380 |

**Effect of temperature on rate constant**

Experiments were performed at 673 K, 713 K, and 733 K at 5 kg/cm$^2$ pressure due to ease of operation and low consumption rate of methane. Further, the effect of pressure on $k$ is not very significant. Fig. 13 shows the Arrhenius plot. The data fits reasonably well and the values of frequency factor and activation energy for the two reactions considered were evaluated and reported. The values are in good agreement with the earlier reported values[18,20]. The complete rate equations taking temperature effect into consideration are given as

$$r_1 = 2.5304e^{-186948.6/RT}C_A$$

$$r_2 = 1.8433e^{-162231.08/RT}C_A$$

Plot of methanol versus formaldehyde at 5, 10, and 15 kg/cm$^2$ at 713K following Eq. (11) were made and were found to vary linearly. The slopes of the lines give $k_1/k_2$ (Fig. 14). The values of $k_1$ and $k_2$ are presented in Table 1.
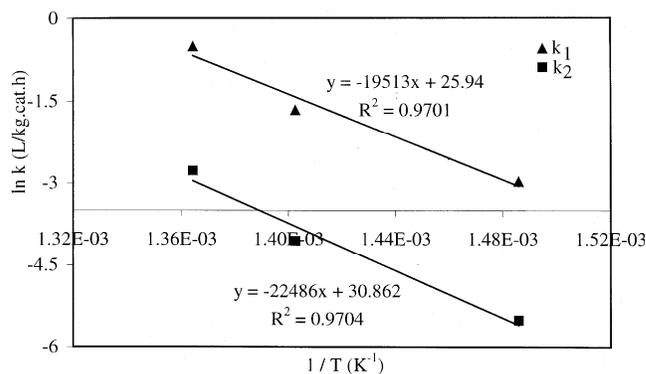


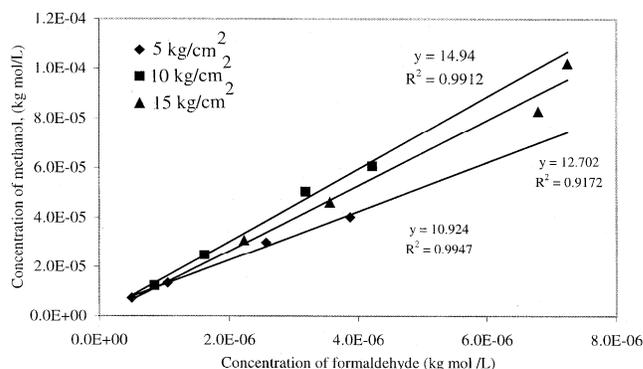Fig. 13—Arrhenius plot for reaction represented by equation "a"



Fig. 14—Plot of concentration of methanol versus concentration of formaldehyde at 5, 10 and 15 kg/cm$^2$ and 713 K

**Conclusion**

In the present investigation, an attempt has been made for the kinetic study of the partial oxidation of methane to methanol using asbestos supported palladium catalyst employing tubular fixed bed reactor. The effect of temperature, $W/F_{A0}$ and pressure on conversion of methane and selectivities to various compounds have been studied and reported. The kinetics of the reaction was found to follow first order law with respect to methane for methanol formation reaction and first order with respect to methane for the formaldehyde reaction. Both reactions obeyed Arrhenius equation. The conversion obtained was very low and could be improved by carrying out experiments at higher pressure or with different combinations and concentrations of catalyst. The present study clearly indicates the production of methanol by partial oxidation of methane.

**Nomenclature**

$C$  = concentration, kg mole m$^{-3}$
$F$  = flow rate of reactant, kg mole.h$^{-1}$
$k$  = reaction rate constant, mole m s$^{-1}$

$X$ = conversion
$W$ = weight of catalyst, kg
$\varepsilon_A$ = volume expansion factor

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