THE DIRECT CONVERSION OF METHANE TO METHANOL BY A HIGH PRESSURE PARTIAL OXIDATION REACTION

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INTRODUCTION

The conversion of methane to a liquid storageable fuel is a desirable alternative to compressed natural gas. The simplest liquid is methanol presently formed by the steam reforming of methane to synthesis gas followed by the high pressure catalytic conversion of the synthesis gas to methanol. The process is most economic for large (2000 tonne/day) plants and must be located near large reserves of natural gas or near an appropriate pipeline. The simpler partial oxidation route offers the advantage of directly converting methane to methanol in a single step reaction. The potential for the partial oxidation route together with an economic evaluation has been reported by Edwards and Foster (1) who showed that, provided the selectivity for methanol formation is about 77%, the partial oxidation route has an economic advantage over the conventional synthesis route with no penalty for conversions as low as 4%.

Much has been published on the combustion of methane to CO_2 and H_2O but very little has been concerned with the intermediate formation of methanol. Gesser et al. (2) recently reviewed the controlled oxidation of CH_4 to CH_3OH emphasizing the free radical mechanistic aspects. The heterogeneous catalytic studies was reviewed by Foster (3) and Pitchai and Kleir (4). Although the literature indicated some potential catalysts (5) no commercial viable reaction system has been developed. Before embarking on a study of the catalytic conversion of CH_4 to CH_3OH we attempted to establish a base-line study by examining the homogeneous reaction (6,7,8,9) and here report a summary of the results with methane.

EXPERIMENTAL

The experiments were performed in a glass lined tubular reactor (0.36 cm ID, 3.3 mL heated volume). Reaction temperature was indicated by a steel sheathed thermocouple probe in the reaction zone.

Gases (2% N_2 in CH_4 and pure O_2) from the respective cylinders were thoroughly pre-mixed before entering into the reactor by passing them through a mixing cross filled with Teflon turnings. Nitrogen was deliberately introduced into the feed gas so as to act as an internal reference. The pressures at various points were monitored by calibrated pressure transducers. The reaction products were analyzed by gas chromatography with a thermal conductivity detector using an 8-port sampling valve and two columns -- 5A molecular sieve and a Porapak S column.

Using N_2 as an internal reference it was possible to measure the changes in the ratio $(CH_4/N_2)_{in}$ to $(CH_4/N_2)_{out}$ and so determine the conversion and material balances. Selectivity was calculated in terms of total carbon products. The water yield was invariably greater than that of the methanol. Formaldehyde was found in trace quantities and was determined colorimetrically (10).

Experiments were conducted by first adjusting the gas flows and, when stable, the temperature of the reactor was raised to the desired value. The on-line analysis was then performed over a period of several hours.

The residence time was usually about 2 minutes but varied from 0.2 to about 5 min with no obvious effects on the products.

RESULTS

The effect of temperature on CH_3OH conversion at different temperatures and pressures is shown in Figure 1. At higher O_2 concentrations the increase in temperature significantly increases the conversion. The possible CH_4 conversion is a maximum of twice, and a minimum of half, the O_2 consumed. Calculated conversion of greater than twice the O_2 consumed were due to errors in the CH_4/N_2 ratios

measured and the accompanying errors in the differences of two large numbers. Material balances were usually good (within 100 ±10%) for carbon but poor for oxygen.

The results in Figure 2 show the effect of temperature on the methanol selectivity at various O_2 concentrations. As the temperature is increased the selectivity passes through a maximum which is at lower temperatures for lower O_2 concentrations.

The methanol selectivity decreases as the O_2 concentration increases as shown in Figure 3.

The effect of pressure on the methanol selectivity was determined in another reactor (0.4 cm ID, 5.7 mL reactor volume). The results are given in Table 1 and clearly show that for a given oxygen concentration in the feed gas and, given reaction temperature, pressure had a positive influence on methanol selectivity; especially at above 50 atm. Thus, at an oxygen concentration of 5 to 6% in the feed gas and a reaction temperature of about 453°C, the methanol selectivity increased from 65% at 35 atm to 76% at 50 atm and at 65 atm it was 83%. A similar trend was observed at the other oxygen concentrations used in this study.

DISCUSSION

Much of the earlier work on partial oxidation of methane has been conducted in static reactors (11,12). Limited studies have been performed employing flow reactors at high pressures (13,14,15). Boomer et al. (16) showed that at a pressure of 180 atm, temperature of 475°C and 3.2% oxygen concentration in the feed gas, a maximum methanol selectivity of 74% could be obtained. The methane conversion at the above conditions was only 1.9%. Similar results were reported by Pichler and Reder (14), and Wiezevich and Frolich (15). Brockhaus and Franke (17) from their studies on the partial oxidation of methane under cool flame conditions were able to obtain a combined selectivity of methanol and formaldehyde of up to 91%. However, the conversion per pass was of the order of 2%. In comparison to all of the studies reported to this date on homogeneous gas phase oxidation of methane, our results seem to be the most promising in that a methanol selectivity of 83% at a conversion level of 8% per pass could be obtained.

The high methanol selectivities observed in our experiments can be explained by the type of the reactor used and the reaction conditions employed in the study. Several workers (18,19) have identified surface reactions such as oxidation, decomposition of oxygenated products and coke formation to be responsible for the decrease in methanol selectivity. Surface reactions were found to be important in metal reactors, packed reactors and also at low reaction pressures (20). In our study, probably the surface reactions were of less importance due to the use of a glass lined and/or high pressure where diffusion to reactor wall would not be significant.

The proposed mechanism for the partial oxidation of methane at high pressure (12) suggests that the reaction between the peroxide radical CH_3O_2 and methane resulting in the formation of methylhydroperoxide and methyl radicals may compete strongly with the decomposition of the peroxide radical. The methylhydroperoxide radical then decomposes into methoxy and hydroxy radicals and methanol is formed by a reaction between the methoxy radical and methane. Hence, higher pressures favour the methanol selectivity and our results as shown in Table 1 support this view. Although in the present work the maximum reaction pressure employed was 65 atm, earlier experiments (6,21) showed that an increase in pressure to 125 atm had lower methanol selectivity. Thus at an oxygen concentration of 5% in the feed gas the methanol selectivity was found to decrease from 81% at 50 atm to 25% at 125 atm. The maximum methanol selectivity may occur between 65 and 125 atm and this has yet to be established.

CONCLUSIONS

In this study we showed that methanol selectivities of 75 to over 80% at 8 to 10% conversion levels per pass could be obtained during the partial oxidation of methane in the tubular reactor operated at about 65 atm, 450°C and a residence time of about 4 min. The methanol selectivity was observed to depend significantly on

the oxygen concentration in the feed gas and reaction pressure. Oxygen concentrations less than 5% and reaction pressure higher than 50 atm were found to be conducive for higher methanol selectivity.

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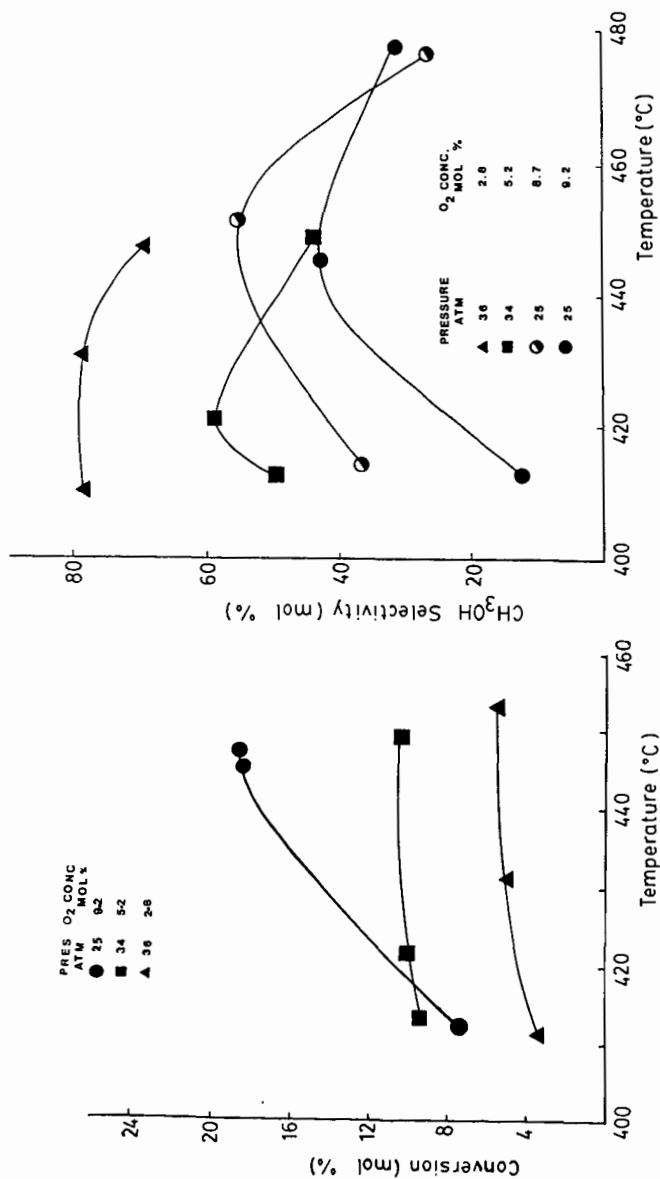
Figure 1. Effect of reaction temperature on conversion at different combinations of reaction pressure and oxygen concentrations in the feed gas.

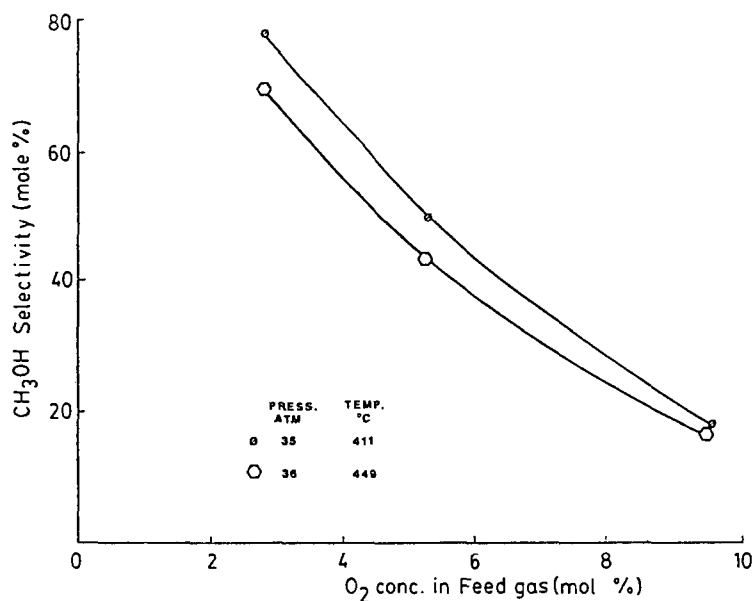Figure 2. Variation in methanol selectivity with reaction temperature.

Figure 3. Effect of oxygen concentration in the feed gas on methanol selectivity.

Table I. The effect of varying reaction pressure on methanol selectivity at different oxygen concentrations in the feed gas.

Run #	Reaction Conditions			Residence Time min	Conversion mol%	Selectivity, mol%*			CH_3OH Yield mol%
	Temperature °C	Pressure atm	O_2 Conc. mol%			CH_3OH	CO	CO_2	
29	455	34.0	10.3	2.5	7.5	59.8	25.1	15.1	4.5
28	453	34.7	6.0	3.5	8.1	64.9	20.7	14.7	5.3
27	450	34.4	2.1	3.2	3.9	77.0	10.7	12.3	3.1
26	453	50.0	8.0	2.8	7.5	56.5	23.9	19.3	4.3
24	451	50.0	6.7	3.7	9.5	76.0	12.6	11.4	7.2
25	451	50.0	3.5	4.6	5.9	76.7	12.6	10.7	4.5
32	456	65.4	7.4	4.5	11.0	66.5	22.6	10.9	7.3
31+	456	65.3	5.1	4.1	8.0	83.0	10.7	6.4	6.6
33	468	65.6	2.6	3.7	5.3	81.5	9.6	8.9	4.3

*Average of at least 4 on-line analysis.
+Reducing the heated zone from 45 cm to 35 cm increased the CH_3OH selectivity to 84.5%.