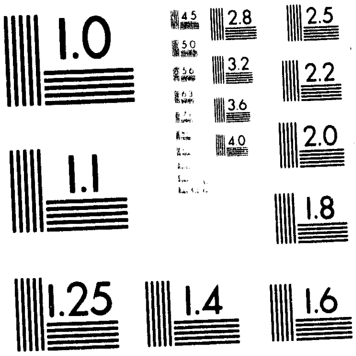
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Direct Conversion of Methane to Methanol in a Non-Isothermal Catalytic Membrane Reactor

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DIRECT CONVERSION OF METHANE TO METHANOL IN A NON-ISOTHERMAL CATALYTIC MEMBRANE REACTOR

CONTRACT INFORMATION

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METC Project Manager	Venkat K. Venkataraman
Period of Performance	July 19, 1990 to October 1, 1993

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J
Modify the reactor system.	—	—	—								
Verify the roles of the catalyst and the membrane.				—	—						
Optimize CH_3OH yield.						—	—	—	—		
Annual Report.										—	—

Abstract

The direct partial oxidation of CH_4 to CH_3OH has been studied in a non-permselective, non-isothermal catalytic membrane reactor system. A cooling tube introduced coaxially inside a tubular membrane reactor quenches the product stream rapidly so that further oxidation of CH_3OH is inhibited. Selectivity for CH_3OH formation is significantly higher with quenching than in the experiments without quenching. For CH_4 conversion of 4% to 7%, CH_3OH selectivity is 40% to 50% with quenching and 25% to 35% without quenching.

OBJECTIVES

The abundance of natural gas and the steadily growing world consumption of CH_3OH have increased the need for better ways to convert CH_4 to CH_3OH. Currently, the commercial process for CH_3OH production from CH_4 involves the high-temperature, highly-endothermic steam reforming of CH_4, followed by low temperature CH_3OH synthesis. The direct partial oxidation of CH_4, unlike steam reforming, is highly exothermic, and does not require energy input. A one-step conversion would simplify the utilization of the vast natural gas reserves, many of which are located in remote areas.

The objectives of this study are to demonstrate the effectiveness of a membrane reactor for the partial oxidation of CH_4 and to better understand the mechanisms inside the membrane reactor. The specific goals are to demonstrate that we can improve CH_3OH yield and to determine the optimal conditions for reactor operation.

BACKGROUND INFORMATION

Thermodynamically, the partial oxidation reaction of CH_4

$$CH_4 + 1/2\ O_2 \rightarrow CH_3OH \qquad \Delta G_{700\ K} = -22\ \text{kcal/mol}$$

is feasible, but the reactions

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2\ H_2O \qquad \Delta G_{700\ K} = -136\ \text{kcal/mol}$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \qquad \Delta G_{700\ K} = -189\ \text{kcal/mol}$$

are more favored (1). This means that CH_3OH, an intermediate product, would not be present if the process went to completion. Thus, most published studies of partial oxidation of CH_4 by O_2 report significant selectivity for CH_3OH only at very low CH_4 conversions.

Both homogeneous and heterogeneous oxidation processes have been studied. Helton (2) found that with 6.5% O_2 in the feed gas, selectivities to CH_3OH were 30% to 35% with 99% O_2 consumption at 5 MPa and 675 K. Foulds et al. (3, 4) and Foral (5) reported that, for an O_2 concentration of 8%, the selectivities to CH_3OH were 30% and lower. Recently, Chun and Anthony (6, 7) reported CH_3OH selectivities between 30% to 40% at an O_2 concentration of 4.35%. All of these studies reported that CH_3OH selectivities decreased with increased temperature and O_2 concentration. For example, when the O_2 concentration in the feed gas increased to 9.5%, Helton (2) observed that selectivities to CH_3OH decreased to 25% or 30%. Foulds et al. (4) observed the selectivity to CH_3OH decreased from 38% at an O_2 concentration of 5% to 28% at an O_2 concentration of 7.5%.

Hunter et al. (8), and Yarlagadda et al. (9), using pressures from 2 to 12.5 MPa and temperatures from 625 to 755 K, observed CH_3OH selectivities over 80% at CH_4 conversion levels up to 10%. Hunter et al. (8) also observed that the addition of sensitizers (e. g., higher hydrocarbons) to the system reduced the reaction temperature and increased the selectivity to CH_3OH. This indicated that natural gas was a better feed than pure methane. However, their results have been difficult to reproduce in other laboratories (10, 11).

PROJECT DESCRIPTION

Selective and continuous removal of CH_3OH from the reaction zone will increase CH_3OH selectivity, but no process has been successfully demonstrated. Another way to increase CH_3OH selectivity is to inhibit further oxidation of CH_3OH. A modified membrane reactor design was used in an attempt to remove CH_3OH from the reaction region before further oxidation. A cooling tube was inserted inside the membrane reactor so that the system operated non-isothermally. A low temperature region was created within the reactor by the cooling tube, and the product stream reaching this region was quenched. Further oxidation of CH_3OH was effectively inhibited and the selectivity to CH_3OH was increased.

High Pressure System

A high pressure membrane reactor system (designed for a pressure of 10 MPa) was built for this study (Figure 1). Brooks mass flow controllers were used to meter the reactant gases into the system. A 1-m long, 6.35-mm OD stainless steel tube was used to mix CH_4 and O_2 before they enter the reactor. A stainless steel reactor was designed to allow leak-free connection of the ceramic and metallic parts. A quartz tube was inserted into the reactor to isolate the hot stainless steel surface from the reactant mixture. The reactor was externally heated by a Mellen cylindrical furnace. The pressure

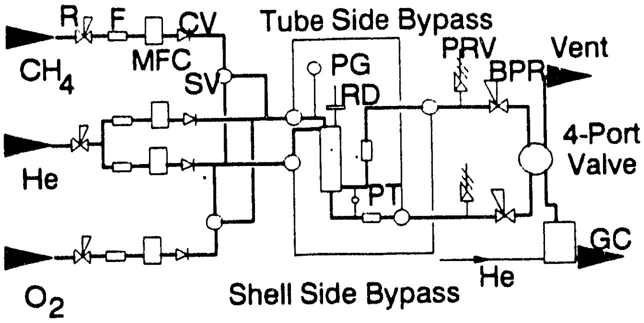

Figure 1. System Diagram

of the system was controlled by TESCOM back-pressure regulators installed downstream of the reactor. On-line analysis was done by an HP 5890 gas chromatograph equipped with a thermal conductivity detector.

Catalyst

A 6.35 mm OD stainless steel tube was used as a model plug flow reactor to carry out catalysts studies. A CuO/SiO_2 catalyst, T - 1506, from United Catalysts Inc. formed only a trace amount of CH_3OH. Several molybdena based catalysts prepared in this laboratory were used and the best was 1.5% MoO_3/SiO_2, which yielded 25% selectivity to CH_3OH in the model reactor. A V_2O_5/SiO_2 catalyst was a good catalyst for CH_2O formation. Neither $FeO_3/MoO_3/SiO_2$ nor MoO_3/Al_2O_3 catalysts produced CH_3OH under our experimental conditions. Thus, MoO_3/SiO_2 was used in the membrane reactor.

Quenching Method

A tube with cooling water inside was inserted into the center of the membrane tube (Figure 2) to create a low temperature zone in the reactor. The product stream was collected from the tube side of the membrane. The flow of the gas stream through the membrane was perpendicular to the cold front, and when the gas reached the cool region, its temperature decreased rapidly. Experiments run without quenching indicated that quenching inhibited further gas phase reactions. Without quenching, the temperature of the region inside the reactor was more uniform, but it was probably not isothermal.

Experimental Operation

Ceramic membranes with an average pore diameter of 5 nm and an outer diameter of 10 mm were used. The 15 cm-long membrane tube was glued to two supporting, nonporous α-alumina tubes. The catalyst layer (average thickness was approximately 1 mm) was wrapped on the outside of the membrane by an aluminium foil with small holes. With quenching, the temperatures of outer wall of the reactor were 770 to 830 K. Lower temperatures were used (690 to 710 K) in the absence of quenching because of the smaller radial temperature gradient inside the reactor. Chromel-alumel thermocouples with 304 stainless steel sheaths were inserted to measure the temperatures of the catalyst bed and the exit cooling water. A reactant mixture (8% O_2 in CH_4) was fed into the shell side of the membrane reactor with a flow rate of 0.2 to 0.5 L/min. The residence time in the shell side was about 10 to 20 s, including the time for preheating. The stream permeated radially through the catalyst layer and the membrane and was then quenched. This low temperature stream then left the reactor for GC analysis.

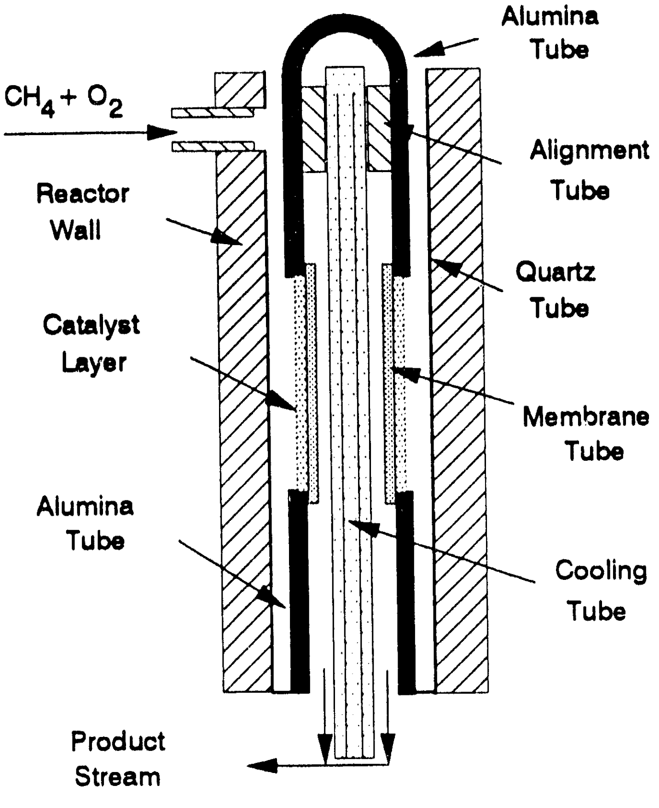

Figure 2. Reactor Diagram

RESULTS AND DISCUSSION

The selectivity to CH_3OH was 40 to 50% with the quenching at a CH_4 conversion level of 4 to 7%.

Without quenching, this selectivity decreased to 25 to 35% at similar CH_4 conversion levels. Methanol selectivity is plotted in Figure 3 as a function of CH_4 conversion at a constant flow rate of 0.5 L/min and a constant pressure of 3.5 MPa. The CH_3OH selectivities decreased with increased CH_4 conversion. With quenching, CH_3OH selectivity was about 50% at 4% CH_4 conversion and about 40% at 7% CH_4 conversion. Without quenching, CH_3OH selectivity varied from 35% at 3% CH_4 conversion to 25% at 7% CH_4 conversion. Quenching significantly improved CH_3OH selectivity in this process.

Although the cooling tube improved CH_3OH selectivity, it also caused the membrane to break, due to the large radial thermal gradient and the different axial thermal expansion between the hot stainless steel reactor wall and the cooler ceramic tubes. To solve this problem, a porous metal tube with 0.5 μm pore size was used instead of ceramic membrane. Results from both ceramic membranes and porous metal tubes are included in Figure 4. Although CH_3OH selectivities were almost the same for both ceramic membranes and porous metal tubes, the methane conversions were slightly higher when ceramic membranes were used.

Figure 5 shows that the combined selectivities of CH_3OH and CO were almost constant at 85 to 90%, with the rest being CO_2, both with and without quenching. Helton (2) made the same observation. Carbon dioxide was detected at low CH_4 conversions in this study, but CO was detected only when CH_3OH or CH_2O were detected. These results indicated that CO_2 was formed from direct oxidation of CH_4, but CO may have formed from oxidation of CH_3OH and CH_2O. This is in agreement with the observations by Spencer et al. (12, 13). Thus, when quenching was used, the CO selectivity decreased as CH_3OH selectivity increased.

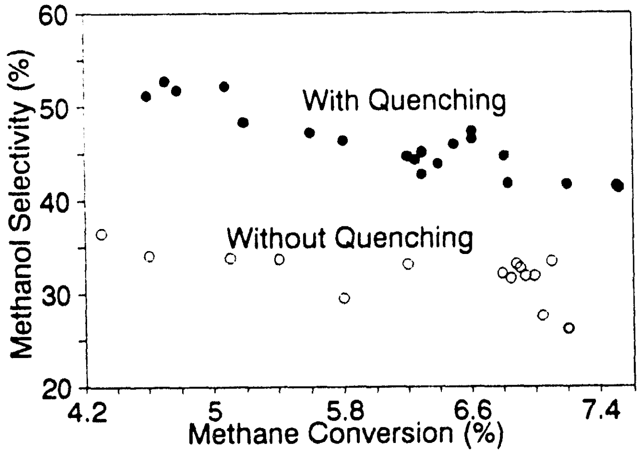

Figure 3. CH_3OH Selectivity vs CH_4 Conversion

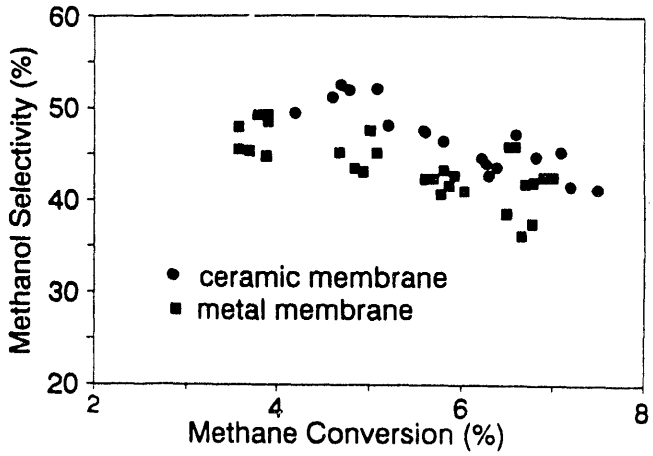

Figure 4. CH_3OH Selectivity vs CH_4 Conversion

Our selectivities to CH_3OH without quenching were almost the same as those recently published (Table 1). With quenching, CH_3OH selectivities were higher, even though we used pure CH_4. Higher selectivities to CH_3OH might be expected for natural gas. Formaldehyde selectivities were 1 to 3% at low CH_4 conversion (about 4%), and it was detected only in trace amounts at higher CH_4 conversion. Carbon, hydrogen and oxygen mass balances were all in the range of 100±5%.

Other quenching methods have been reported (2, 15, 16). Dowden and Walker (15) injected liquid water directly into their product stream, and this cooled the stream below 473 K within 30 ms. No comparison data were presented without quenching. Wilms (16) also described a rapid quenching method. At pressures of 4 to 6 MPa and temperatures

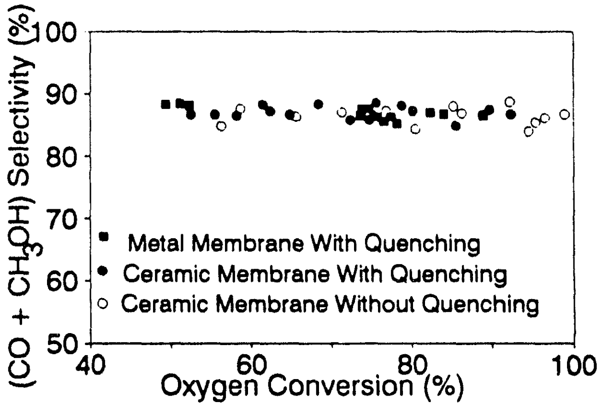

Figure 5.
Combined Selectivity vs O_2 Conversion

Table 1. Recently Studies on CH_4 to CH_3OH

T (K)	P (MPa)	Feed	Catalyst	CH_3OH Selectivity (mol%)	CH_4 Conversion (mol%)	Reference
660-730	5.0	Nat. Gas 5 - 6% O_2	MoO_3/SiO_2	25-35	5-7	2
723	5.0	Nat. Gas 5% O_2	Quartz	20-30	2-6	19
650 - 730	3 - 5	CH_4 4-8% O_2	No	30-35	4 - 4.5	3, 4
[illegible]	10	Nat. Gas 5% O_2	No	30-35	3 - 5	5
738	6.2	CH_4 3.8% O_2	Sand	34.9	2.9	20
738	6.2	CH_4 7% O_2	Sand	13.2	5.2	20
705 - 770	5.0	CH_4 4.35% O_2	Pyrex	35 - 40	2 - 4	6, 7
770 - 779	5.0	CH_4 4.35% O_2	FeMo, CuMo/Ti, V/Si, Sn/Ti	25 - 30	2 - 4	6, 7

between 743 and 793 K, CH_4 and air were mixed in a small stainless steel reactor. After a residence time of 0.3 to 1.2 min. the mixture was quenched by expansion through a Delaval nozzle. A maximum CH_3OH selectivity of 85% was reached, but the CH_4 conversion was low, only 0.01 to 0.1%. Although these studies concluded quenching was useful, a comparison study by Helton (2) found that quenching had no influence on product selectivities. He cooled the product stream below 535 K at the exit of the reaction zone by cryogenic quench. Selectivities for products were the same as those without quenching.

The quenching method we used has several advantages over previous approaches (2, 15, 16). No extra water is added into the product stream and thus the downstream separation is simplified. The small gas-stream pressure drop makes recycling of unconverted CH_4 easy. A significant difference from previous approaches is that this method quenches the product stream within the reactor instead of after the reactor exit. Quenching improved the process by inhibiting further reactions of CH_3OH. The cooling tube also removed the reaction heat and thus the reaction temperature could be better controlled. In other reactor configurations, reaction heat can raise the reaction temperature, which can accelerate CH_3OH oxidation.

Large discrepancies in CH_3OH selectivities and CH_4 conversions have been reported, with CH_3OH selectivities ranging from less than 10% (17) to over 80% (8, 9, 14). Brown and Parkyns (18), and Burch et al. (11) suggested that CH_3OH selectivity is sensitive to temperature distribution, flow configuration, and detailed reactor design.

FUTURE WORK

The temperature measured for the catalyst layer is about 470 K when the temperature of exiting water from the cooling tube was about 300 K. This temperature is not high enough to catalyze the reaction. The catalyst layer may act as a high surface area material to inhibit free-radical, gas-phase reactions. The membranes, both ceramic and metal membranes, do not effect any separations. Thus the roles of catalyst and membrane in this process will be investigated. Systematic experiments will be performed to better understand the mechanisms inside the reactor, and suitable conditions will be determined to obtain optimal CH_3OH yield.

Low oxygen concentration have been used to stay below the explosion limit. This means the yield of methanol is small. One possibility to increase CH_4 conversion is to use air-like mixture instead of pure O_2. A reactant mixture above the upper explosion limit of methane may be used. Under our experimental conditions, this limit is about 25%. methane in air.

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