

## PARTIAL OXIDATION OF METHANE TO SYNGAS USING FAST FLOW MEMBRANE REACTORS

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Previous studies have shown that high methane conversions and selectivities to syngas can be achieved while operating at very high space velocities and relatively low methane/oxygen feed ratios. This has been accomplished at relatively high temperatures (~1000°C) in a monolith reactor. (1, 2) The monolith reactor is characterized by an open pore structure which permits very fast gas flows and results not only in high syngas yields, but autothermal operation as well.

Achieving autothermal behavior is significant because a reactor which operates autothermally requires heat only during ignition. In the case of Schmidt and coworkers (1, 2), ignition occurs by passing an ammonia/air mixture over the monolith at around 300°C. Once ignited, the temperature increases rapidly to the steady state temperature, and the ammonia/air mixture is replaced by the methane/oxygen mixture. If industrial scale reactors could be operated autothermally, a significant amount of capital can be saved due to the fact that the reactor must be heated only during startup.

Although these results are very promising, this reactor configuration presents several problems. It requires operating at relatively high temperatures and the use of a different gas mixture during startup. In addition, at these high temperatures and low methane/oxygen feed ratios the potential for an explosion exists due to the possibility of flame flashback. As a result, this reactor configuration could never be implemented industrially due to safety concerns.

Therefore, we attempted to achieve high syngas yields and autothermal behavior while operating in a safer, industrially favorable environment. The intention was to operate at high space velocities, but at significantly lower temperatures. This was accomplished with the use of a highly active 3% Rh supported on TiO<sub>2</sub> catalyst. This catalyst was used in previous studies on the methane partial oxidation reaction in which the reactor was operated at lower space velocities and diluted gas feeds. (3)

In this case, a small amount of the 3% Rh catalyst (only 30 mg) was used in a fixed bed reactor which was operated at millisecond residence times and a methane/oxygen feed ratio of 2/1. The results are shown in Table 1. Despite the fact that the total feed rate was varied between 235 and 1500 cc/min there was very little change in conversion and selectivity. Methane conversion remained between 55 and 70% and CO selectivity remained around 90%. In addition, oxygen conversion was 100% in all cases.

However, under these conditions, relatively high conversions and selectivities were achieved at steady state temperatures in the range of 500-600°C. Although the yields are lower than Schmidt and coworkers, the reaction temperatures were significantly lower. In addition, the system was ignited under methane/oxygen mixtures at 320°C which is several hundred degrees lower than the ignition temperatures using the monolith, thus eliminating the need for the ammonia/air mixture. Another benefit of the Rh catalyst was that it was stable and did not deactivate for several days.

Despite the fact that the use of the 3% Rh catalyst in the fixed bed reactor allowed for safer operation than the monolith reactor, a difficulty still exists. Although the temperatures with the fixed bed were drastically lower than with the monolith and the possibility of explosion has been lowered, the potential for an explosive mixture still exists. An oxygen rich mixture still contacts a high temperature surface, and if the high flow reactor system is to be implemented in industry, the potential for explosion must be eliminated.

Therefore, a reactor scheme was conceived which would allow for high space velocities and overall low methane/oxygen feed ratios while separating the gas reactants until reaching the catalyst surface. The idea of using a separate oxygen feed for methane oxidation was based on previous work in our group on the distribution of oxygen during the methane oxidative coupling reaction. (4) The implementation of the new reactor scheme opens up the possibility of practical applications for the partial oxidation of methane to syngas and also the oxidative dehydrogenation of alkanes.

The membrane reactor consists of a highly porous membrane tube, with one end sealed, which is placed concentrically inside a quartz tube. The upper portion of the membrane tube is made impermeable using a ceramic glaze, leaving only a small length at the lower portion of the tube permeable. The catalyst is placed around the permeable portion of the membrane tube forming a ring in between the membrane tube and the outer quartz wall. Oxygen is fed to the membrane tube and flows exclusively inside the membrane tube until reaching the permeable portion at the bottom of the tube where it permeates to the shell side and immediately contacts the catalyst surface. Methane is fed to the shell side and flows in the annular space between the membrane wall and the quartz wall. In this scheme, the reactants mix only in the region where the catalyst is located, and because 100% oxygen conversion was achieved in every previous experiment, the possibility of oxygen rich mixtures developing is negligible. The membrane wall itself is highly permeable allowing for the use of fast flowrates in the range of millisecond residence times. Thus, the overall methane/oxygen feed ratio can remain low while operating at high space velocities in a reactor configuration which is both safe and economical.

The membrane reactor successfully achieved its goal of obtaining high conversions and selectivities while providing a safe operating environment. Table 2 shows the effect of feed rate on conversion and selectivity using 60 mg of catalyst and a methane/oxygen feed ratio of 2/1. The minimal amount of catalyst that can be used is 60 mg as this is the amount required to completely surround the permeable portion of the membrane tube.

The results are similar to those in the case of the fixed bed reactor in that for a significant change in feed rate (300 cc/min to 1080 cc/min) there is only a slight change in conversion and selectivity. Methane conversion remained primarily between 65 and 75%, CO selectivity remained around 90% and hydrogen selectivity remained primarily around 70%. Once again oxygen conversion was 100% in all cases.

Although methane conversion is slightly lower in the membrane reactor than in the fixed bed reactor, the membrane reactor is the preferred reactor due to the safety factor. Complete oxygen conversion is achieved indicating that the possibility of oxygen rich mixtures, and therefore the possibility of explosion, is negligible. Most industrial reactors are operated well below optimal yields for safety reasons, and a 5% drop in conversion is acceptable if a safe operating environment is assured.

Further experiments were conducted in the membrane reactor in an attempt to increase methane conversion. As soon as a safe reactor configuration had been developed, it was desired to determine if the yields could be improved within this system. The operational variable on which syngas production was most dependent was the methane/oxygen feed ratio. Because the methane and oxygen feeds are kept separate until contacting the catalyst, the partial oxidation reaction could be studied at lower methane/oxygen feed ratios. Table 3 shows the effect of the methane/oxygen feed ratio in the membrane reactor using 60 mg of catalyst.

Methane conversion varies from as high as 64% at the lower ratios to as low as 44% at the higher ratios. Hydrogen and CO selectivities vary from 22 and 67% at low ratios to 82 and 90% respectively at high ratios. However, even at low methane/oxygen ratios, oxygen conversion remains at 100%.

The important result obtained is that both CO and hydrogen selectivities were lower at the lower feed ratios, particularly when the ratio is less than 2/1. The hydrogen selectivity falls below 25%, and the CO selectivity falls below 70%. This is an indication that the partial oxidation reaction is no longer dominant, and the complete combustion reaction begins to occur. This effect can be explained by the fact that at the lower feed ratios, more oxygen is available to form carbon dioxide and water. At higher feed ratios, the concentration of oxygen is low and hence methane reacts to form CO instead of CO<sub>2</sub>.

The decreasing of temperature would seem to justify the above conclusion. At lower feed ratios, the temperature is significantly greater than at the higher ratios. At feed ratios less than 2/1, the steady state temperature rises above 700°C, but at ratios greater than or equal to 2/1 the temperature is in the 500°C range. The higher temperature can be accounted for by the reaction of hydrogen and oxygen to form water and the occurrence of complete combustion which has a higher heat of reaction than partial oxidation. In addition, as methane conversion decreases the heat generated decreases and the temperature decreases.

The effect feed ratio has on methane conversion is interesting. Although 100% conversion of oxygen is achieved at low feed ratios, methane conversion levels off at 64%. This is not expected because as the concentration of oxygen increases higher methane conversions would be expected due to the fact that oxygen was the limiting reagent in all experiments. Additional oxygen should result in higher conversions, but instead results in more of the reacted methane being converted to CO<sub>2</sub> and water. At higher feed ratios, the reactor operates as expected as the methane conversion begins to decrease.

After it had been determined that the conversion could not be significantly increased by varying the operational parameters of the membrane reactor, an attempt was made to increase conversion by allowing the unreacted methane to participate in another reaction. For this purpose a new, double bed reactor was designed to allow for a second catalyst bed and a third reactant feed downstream from the first catalyst bed.

The double bed reactor is identical to the membrane reactor in the upper portion allowing for autothermal behavior of the partial oxidation reaction. The difference is that an additional quartz tube is placed concentrically inside the quartz reactor shell downstream from the first catalyst bed. At the top of the additional tube is a quartz cross which serves the purpose of supporting a second catalyst bed. The quartz tube is open at both ends allowing for an additional reactant to be fed over the second catalyst bed and downstream from the first catalyst bed.

The reaction chosen for the second bed was the dry reforming reaction. The hypothesis was that the unreacted methane from the partial oxidation reaction would react with carbon dioxide which would be added downstream and over the second catalyst bed. The dry reforming reaction is very endothermic, but an enormous amount of heat is evolved from the reaction in the first bed and the original hypothesis was that the heat from the first bed reaction could be used to drive the reaction in the second bed.

Initial results indicated that feeding carbon dioxide downstream would increase methane conversion, but only slightly. The reason was that the first catalyst bed did not provide enough heat to sustain the very endothermic dry reforming reaction over the second catalyst bed. It was observed that the temperature of the second catalyst bed decreased upon introduction of carbon dioxide to the reactor. This indicates that the dry reforming reaction does occur, but there is not enough heat available to sustain the reaction.

It was then decided to continue to feed carbon dioxide downstream from the first bed, but to increase the temperature of the second bed to provide enough heat for the dry reforming reaction. In this experiment, 60 mg of the Rh catalyst were used in both beds and the methane, oxygen and carbon dioxide feed rates were maintained at 500, 250 and 60 cc/min respectively as the second bed temperature was increased. Table 4 shows the effect of the second bed temperature on conversion and selectivity.

The results indicate that high methane conversions can be achieved while maintaining high CO and hydrogen selectivities. At a second bed temperature of 700°C, methane conversion reached 83% with CO and hydrogen selectivities of 85 and 64% respectively. These high syngas yields have been obtained in a reaction environment which is safe and could be modified for industrial use.

In addition, further studies with the double bed reactor indicate that both catalyst beds can be operated autothermally if oxygen is used as the downstream feed instead of carbon dioxide. In this case, the second bed temperature rapidly increases upon introduction of the downstream oxygen feed. This indicates that a second ignition occurs in the reactor and that both beds operate autothermally.

The double bed reactor served the purpose of increasing conversion, but there was still no explanation for the fact the operational parameters had little effect on conversion and selectivity in the fixed bed and membrane reactors. It was not until theoretical reactor simulations were conducted that the reason became clear.

The theoretical model is similar to the elementary step model proposed by Hickman and Schmidt (5), and is used to evaluate results from the fixed bed reactor. The mechanism consists of twenty-one elementary steps which are combined with the reactor mass balances. All of the kinetic parameters used in the model are taken from previous studies. The only modification is that the activation energy for CO desorption was lowered due to the fact that the CO surface concentration was significantly higher than the other species. Lowering the activation energy can be justified by previous studies that report the activation energy will decrease at higher surface concentrations. (5, 6) At this lower value of the activation energy for CO desorption, the model results adequately matched the experimental data.

After comparing the model results to the fixed bed experiments, a parametric sensitivity study was conducted. The study indicated that an increase in methane conversion requires and increase in the rate of methane adsorption and a decrease in oxygen adsorption. The sensitivity study also indicated that CO desorption is one of the rate determining steps and that the dry and steam reforming reactions have little effect on conversion and selectivity at these conditions.

The model also predicts that most of the reaction occurs in a very narrow region near the entrance of the bed, with the rest of the bed contribution being relatively small. In addition, all of the oxygen is consumed by the midpoint of the bed. This would explain the lack of sensitivity of the fixed bed experimental results to changes in operating variables.

Although the model results are for a fixed bed reactor, certain conclusions about the membrane reactor can be drawn. A reasonable assumption is that the profiles near the membrane tube wall are similar to the entrance of the fixed bed reactor. This would indicate that all of the oxygen is consumed near the membrane wall and most of the reaction occurs in this region. This would explain why varying the operating conditions would not result in an increase in methane conversion. All of the oxygen is consumed near the membrane wall and therefore any methane that flows near the outer portion of the reactor will not be converted. To further study the profiles and performance of the membrane reactor, a two dimensional reactor model is now under development.

In summary, very promising results have been achieved in this study. High conversions and selectivities to syngas have been achieved in the membrane reactor. In addition, the reaction is carried out in safe and economical environment without the explosive problems which exist in previous reports. Future possibilities involve the study of the oxidative dehydrogenation of alkanes, which is a very important reaction at the industrial level.

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**Table 1. Effect of Total Feed Rate.**

Total Feed Rate (cc/min)	Temperature (°C)	Methane Conversion (%)	Oxygen Conversion (%)	CO Selectivity (%)	Hydrogen Selectivity (%)
235	401	54	100	76	34
525	558	58	100	88	77
750	564	70	100	89	70
1130	629	65	100	90	64
1500	641	68	100	90	50

**Table 2. Effect of Total Feed Rate Using the Membrane Reactor.**

Total Feed Rate (cc/min)	Temperature (°C)	Methane Conversion (%)	Oxygen Conversion (%)	CO Selectivity (%)	Hydrogen Selectivity (%)
300	419	64	100	75	62
450	494	75	100	88	72
600	520	64	100	86	76
750	515	64	100	90	82
900	607	52	100	86	69
1080	680	35	100	81	90

**Table 3. Effect of Methane/Oxygen Feed Ratio Using the Membrane Reactor.**

Methane/Oxygen Feed Ratio	Temperature (°C)	Methane Conversion (%)	Oxygen Conversion (%)	CO Selectivity (%)	Hydrogen Selectivity (%)
1	710	64	100	67	22
1.33	757	64	100	81	35
1.5	702	63	100	85	45
2	515	64	100	90	82
2.6	510	52	100	90	82
3.3	410	44	100	84	80

**Table 4. Effect of Second Bed Temperature Using the Double Bed Reactor.**

Second Bed Temperature (°C)	First Bed Temperature (°C)	Methane Conversion (%)	Oxygen Conversion (%)	CO Selectivity (%)	Hydrogen Selectivity (%)
300	516	73	100	87	83
400	596	74	100	77	60
500	627	75	100	78	61
600	682	78	100	81	64
700	759	83	100	85	64