

Novel Catalytic Reforming Using Microtechnology with Advanced Separations Technology

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Abstract

InnovaTek is combining microreactor technology with advanced catalysts and separations technology to create a portable-sized hydrogen generator. The ultimate goal of this 4-year cooperative project is the development of a microchannel catalytic reactor for the production of clean hydrogen by the catalytic reforming of methanol. Advanced membrane technology will be incorporated to remove carbon dioxide and water from the output stream. Our technology will provide a pure output stream of hydrogen that can be used in a compatibly sized PEM fuel cell for electrical generation. Work accomplished during the first year of the program is summarized. Achievements include catalyst testing, computational model development, micro reactor design, fabrication and testing, and preliminary membrane evaluation.

Introduction

InnovaTek is applying the advantages of microtechnology in the development of catalytic fuel reforming. The specific problem being addressed is a chemical conversion and separation process to provide clean hydrogen from methanol that is produced from renewable biomass energy sources. This approach to fuel processing provides a revolutionary breakthrough in terms of system size, weight, and dynamic response when compared to more conventional processing carried out in standard packed bed reactors.

This year's objectives and rationale were the following.

1. On the basis of catalyst testing, design and construct a computational model for the basic thermal and chemical component systems required for integration into a multi-component catalytic micro-reaction process unit for methanol reforming. The results of this analysis and modeling will provide a sound basis for proceeding with reactor design, fabrication and testing.

2. Based on results of catalyst testing and systems modeling, design, fabricate and test an integrated microreactor system for methanol reforming and hydrogen separation. The process feasibility of each individual system component will be tested evaluated and demonstrated.

Experimental

Laboratory Catalyst Testing

Several sets of experiments were conducted during the project to assess catalyst performance. One set of tests consisted of longer-term experiments in a fixed bed, plug flow reactor (PFR) while other work involved reduction and reforming experiments carried out in in-situ DXRD apparatus. Ultimately the catalysts were tested in micro channel reactor configurations.

In the tests, a liquid mixture of methanol and water was vaporized in pre-heated tubing and entered the reactor at near atmospheric pressure. The exit stream cooled and separated into liquid and gaseous phases which were both analyzed by gas chromatography. The reactor was a 4 mm diameter quartz tube with a catalyst loading of typically 50-200 mg of 40 μm catalyst particles. These were mixed with 100 mg of powdered quartz wool to produce an active bed volume of about 0.34 cm^3 . The catalyst was a Cu/Zn/Al methanol reforming catalyst supplied in the oxide form by United Catalyst and with a nominal composition of 50-60 % copper oxide and 25-35% zinc oxide.

The Dynamic X-ray Diffraction (DXRD) experiments were carried out, using 100 mg of catalyst while a gaseous methanol-water feed mixture flowed over the catalyst. The feed was diluted 50% with ultra high purity helium in order to avoid condensation within the DXRD hot stage. The gases exiting the hot stage were analyzed via gas chromatography. Simultaneous x-ray diffraction spectra were recorded as a function of time. In this mode, experiment measurements were taken during catalyst reduction as well as during actual reforming. Because of the helium dilution, the flow rates of the methanol-water feed were adjusted to approximate the conversions observed in the PFR experiments.

Tests were also performed in several micro-channel reactor configurations to determine optimal channel geometry. Figure 1 is a photo of one of our micro-channel reactors. Catalyst particle size was based on the width of the micro channels and ranged from 100-300 μm . The reactors were operated at temperatures between 240°C and 285°C and space velocities between 12-24 g feed per hour per gram catalyst. Conversion efficiency was determined using gas chromatography analysis of the reactor output stream.

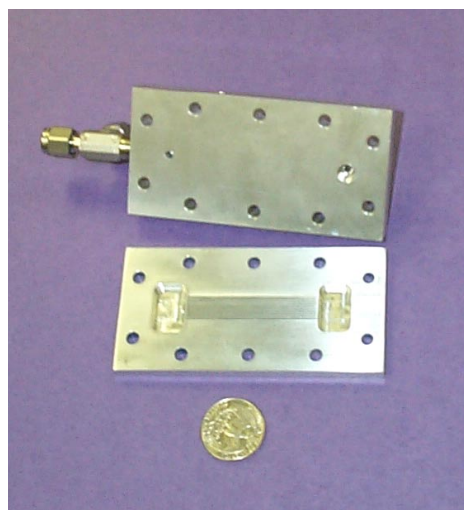


Figure 1. InnovaTek's Micro Channel Reactor for Methanol Reforming.

Results and Discussion

System Modeling

An initial set of process flow models for the microreactor system has been completed for reforming of methanol fuel using HYSYS simulation (Figure 2). The flow model incorporates chemical and thermal equilibrium equations for each major chemical reactor and heat exchanger in the system. It will help project input and output budgets for thermal and chemical reactions, providing information that will aid in system design, such as reactor geometry, flow rate requirements, materials needs, catalyst choices, etc.

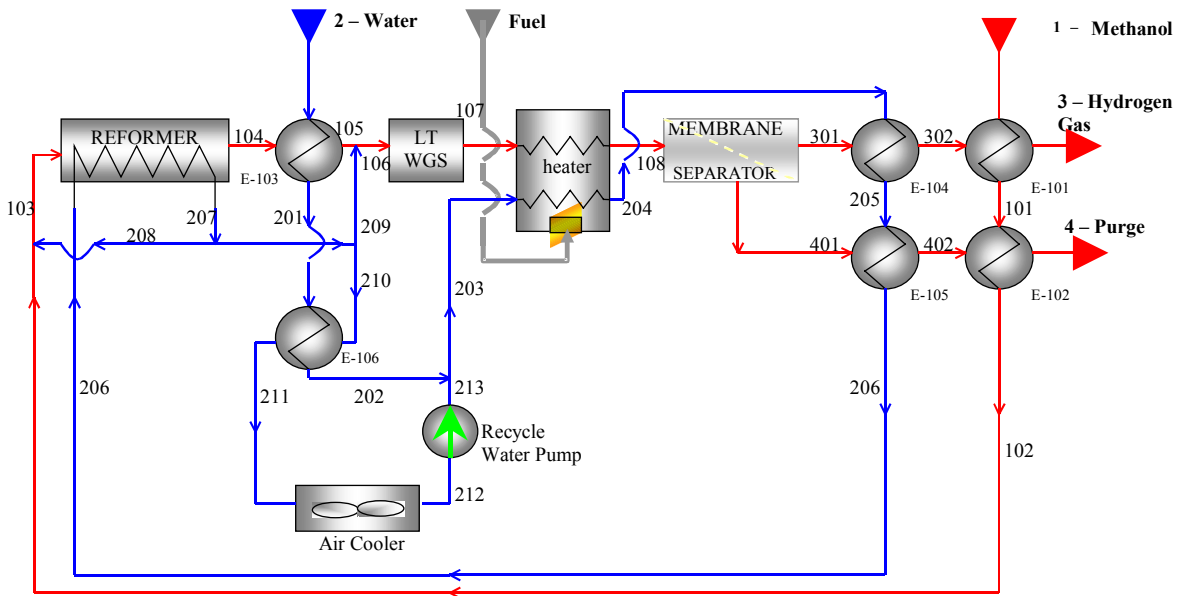


Figure 2. Simulation of Methanol Reforming Using Membrane Separation for CO Cleanup.

HYSYS simulation of a methanol reformer with membrane purification (Figure 2) shows the anticipated output of both a pure hydrogen product and the reject purge gas from the operation (Table 1). From this projection, a feed rate of 1.176 moles of methanol and 1.710 moles of water will produce a pure hydrogen stream at 1201 sccm. Similar simulations were accomplished to project output using water gas shift reactions to clean up CO from the system. These analyses are used to compare approaches for CO removal.

Table 1. HYSYS Projections for Methanol Reforming Using Membrane Separation

	1-methanol	2-water	3-hydrogen gas	4-purge
Vapor Fraction	0.0	0.0	1.0	1.0
Temp, °C	25	25	50	123
Pressure, bar	4	4	1.5	4
mole/hr	1.176	1.710	3.214	2.021
g/hr	37.69	30.81	6.48	62.01
ppm CO	0	0	0	20313
sccm H2	0	0	1201	100

Catalyst Evaluation

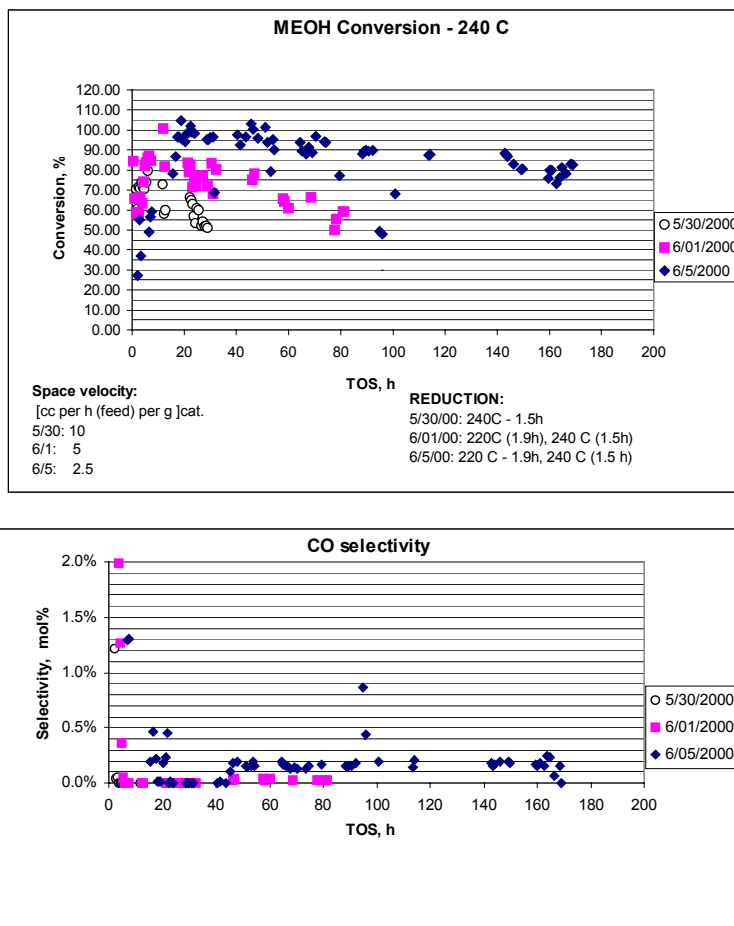
The parameters affecting reaction efficiency include the reaction temperature, the space velocity and the H₂O/MEOH feed ratio. The presentation of the results is divided into two parts: a section dealing with the results obtained in the PFR, followed by the results of in-situ DXRD experiments.

Plug Flow Reactor (PFR) Experiments

In the PFR experiments, temperatures were varied between 240 C and 300 C, space velocities were varied between 40 and 2.5 ml/h-g, and the H₂O/MEOH feed ratio was varied between 1.0 and 1.5.

Figure 3 shows the effect of space velocity (defined as the liquid mixture feed rate (mass/h) divided by the catalyst loading (in grams), at a reaction temperature of 240 C. As can be seen, there is an "induction time" for these runs that is a direct function of the space velocity, with shorter induction times at higher space velocities. This induction period appears to be the result

**Figure 3. Effect of Space Velocity on Methanol Conversion
240° C; H₂O/MEHO = 1.3**



further catalyst reduction caused by the methanol feed. Nevertheless, high conversions were obtained and, in the run with the lowest space velocity, conversions in excess of 90% were achieved for up to 100 hours on stream time. In all cases, deactivation occurred, and the onset of deactivation was an inverse function of space velocity. As shown in Figure 3, CO concentrations were high very early in each experiment, where methanol conversions were also high. After this initial period, the CO concentrations were below the detectable limit (~ 1500 ppm), even though conversions were still in excess of 90%.

The effect of temperature of reaction at constant space velocity of 40 ml/h-g. is shown in Figure 4. Interestingly, the initial conversion in both experiments is very high. Note also that the highest CO concentrations are about the same as those in Figure 3. Figure 5 shows the results when the H₂O/MEOH feed ratio was varied between 1.5 and 1.0 at a reaction temperature of 240 and the lowest space velocity of 2.5 ml/h-g. As can be seen, a ratio of 1.3 appears to be optimum, producing methanol conversions which are significantly higher than those observed at either higher or lower ratios.

In-Situ Reduction/Reforming

Although high methanol conversions were obtained and could be maintained for time on streams in excess of 100 hours, deactivation was observed in all of the PFR experiments. This, and the fact that there was a considerable induction time before high conversions were reached, are indications that the catalyst undergoes chemical changes during exposure to the methanol-water mixture. Consequently, a number of DXRD experiments were conducted in order to observe changes in crystallinity during reduction and reaction. Simultaneous measurements of XRD spectra and exit gas concentrations provide a correlation of catalyst activity with crystalline changes in the bulk catalyst.

As a result of the DXRD studies, we conclude that:

- the active catalyst is a mixture of amorphous Cu₂O and crystalline copper
- deactivation takes place when the amorphous Cu₂O crystallizes
- it is necessary to maintain the proper ratio of amorphous Cu₂O:Cu.

Figure 4. Effect of Temperature on Methanol Conversion (Space Velocity = 40 ml/hr per g catalyst, H₂O/MEHO = 1.3)

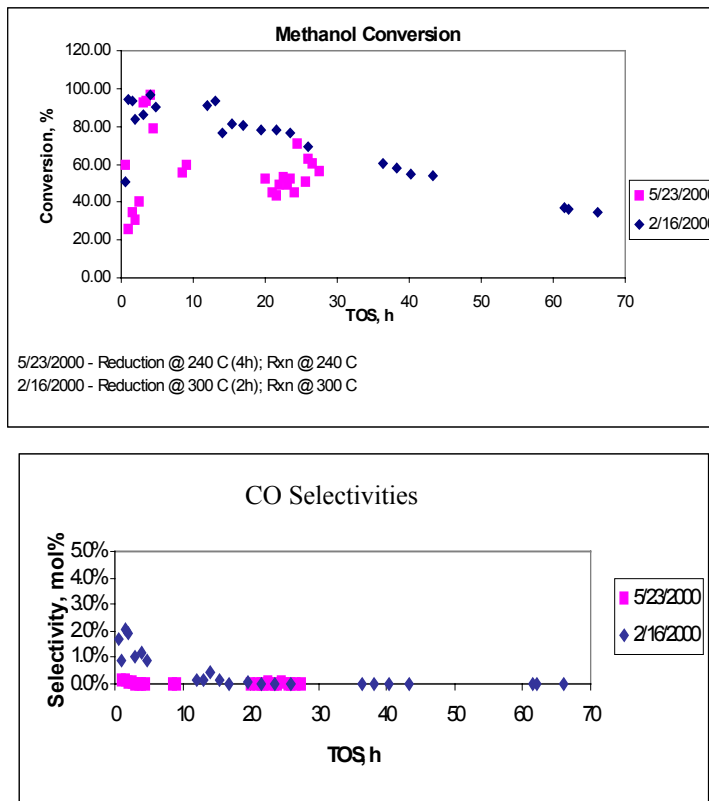
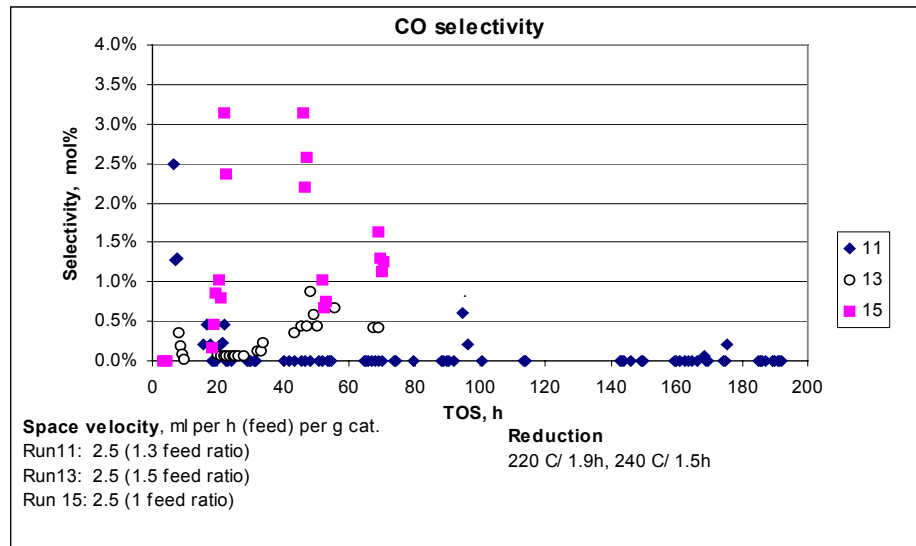
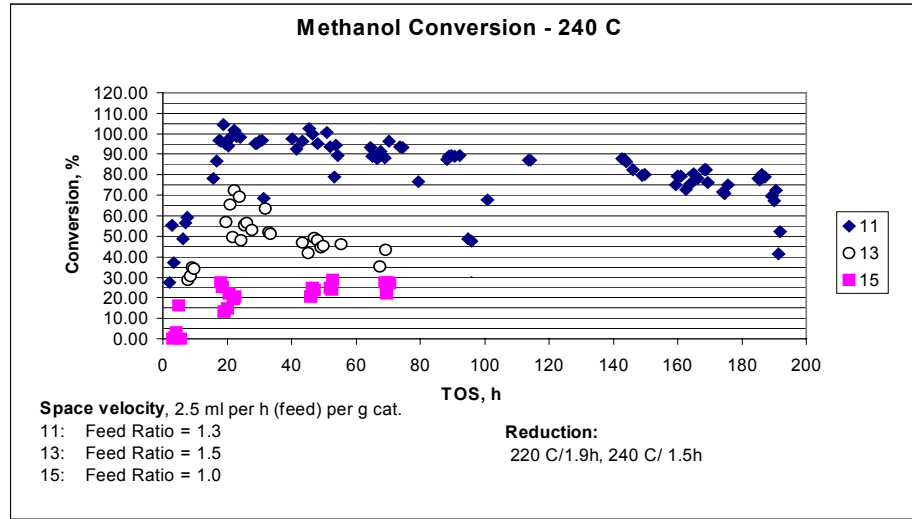
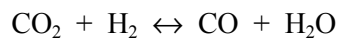


FIGURE 5 - Effect of Feed Ratio on Methanol Conversion
 [240 C, Sp. Vel. = 2.5 ml/h-g]



CO Production

One of the advantages of methanol reforming is that the product gas has minimal CO. Of course, any CO concentration greater than about 50 ppm, is still too high for a fuel cell. The CO produced during methanol reforming is generally higher, the higher the conversion and the higher the temperature. This is generally attributed to the reverse water gas shift reaction

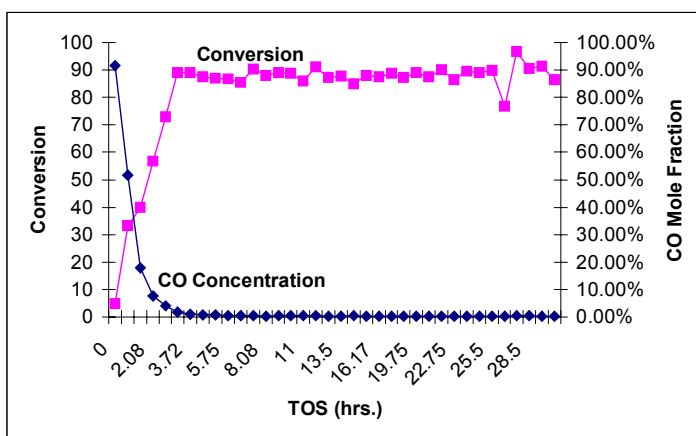


which would tend to occur at high CO₂ concentrations (high conversions) and high temperatures (thermodynamically favored). However, our results indicate that the high CO concentrations observed early in the runs, are more likely due to other factors.

Figure 6 is the result from an in-situ experiment showing CO concentration along with methanol conversion once the mildly reduced catalyst (5% H₂, 240 C, 1.5h) was exposed to the 1.3:1 water/methanol mixture. The initial CO concentration is very high, even at very low methanol conversions. However, once the catalyst becomes fully reduced, the methanol conversion reaches 90% but the CO concentration drops below the detectable limit of 1500 ppm.

Figure 6. Methanol Conversion vs CO Concentration

[Reduction: 5% H₂, 240C, 1.5h; Reaction: 300C, at TOS=0, H₂O/MeOH=1.3]



Micro Channel Reactor Testing

An initial set of experiments to evaluate the effects of space velocity and catalyst longevity was conducted using a micro-channel reactor. The results showing the effects of space velocity are presented in Figure 7. The use of micro channels improves performance with respect to space velocity. High conversions (> 80 percent) are maintained with space velocities up to 24 g feed/h per gram catalyst. The initial test for longevity shows a rapid decrease in activity at about 100 hours, which is consistent with earlier lab results (Fig. 8). These tests were performed with a micro-channel reactor with channels 500 microns wide and loaded with 0.5 grams of catalyst with a size distribution of 150-300 microns. This reactor was operated at 285° C.

The stability and longevity of the catalyst has been examined more thoroughly through additional duration runs. Using the 500 micrometer reactor loaded with 0.5 grams of 150-300 micron sized catalyst, 285° C, and a space velocity of 12 g feed/h per gram catalyst, 100

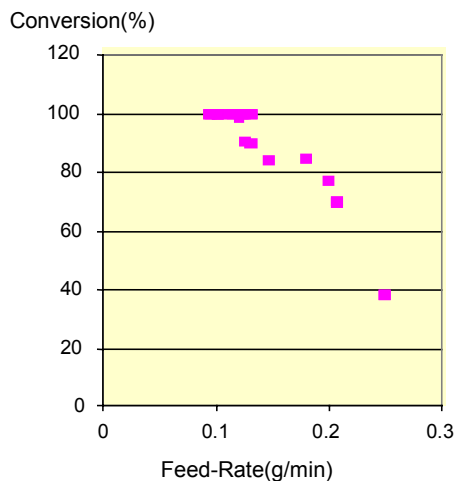


Figure 7. Effects of Space Velocity on Methanol Conversion

percent conversion was maintained for over 200 hours (Figure 9). Deactivation occurred quickly at about 200 hours and the conversion had dropped to below 20 percent at 300 hours.

It has not been possible up to this point to regenerate the catalyst after deactivation. The observed physical condition of the deactivated catalyst has shown great diversity. In some instances the catalyst's appearance is that of being in an extremely reduced condition (metal copper obvious) while in other instances it has an overly oxidized appearance (green copper oxide). The explanation for this may be that the catalyst deactivates similarly in each case, however, the prevailing conditions within the reactor after the catalyst deactivated affected the final physical appearance.

A number of experiments were conducted with the following variables to examine their effect of catalyst activity: feed compositions, operating temperatures, reduction times and temperatures, regeneration with air, regeneration with H₂O, regeneration with varying concentrations of H₂, and reduced vs. oxidized catalyst. The result of all these experiments is that no noticeable improvement in catalyst lifetime has been observed.

Preliminary XRD results performed on spent (deactivated) catalyst indicated possible sintering of the catalyst. This would explain the inability to regenerate the catalyst. The sample that was examined however, had been tested under more extreme conditions than normal. Operating temperatures were 300 C for extended periods, reductions were extreme (pure H₂ at >285 C) and multiple attempts made to regenerate and test this particular sample. Catalyst that had not been as severely utilized i.e. operating temperatures under 250 C and mild reduction of 2 hours in 20 percent hydrogen have not exhibited any better tendency towards regeneration.

The issues of catalyst longevity and reactivation will be studied further during Year 2.

Membrane Testing

A commercially available membrane unit was tested as a possible hydrogen purifier. The unit was rated at 750 sccm at 450° C and 120 psi. The specifications described it as a noble metal coated over a porous stainless steel tube. This unit was attached to the microchannel catalytic

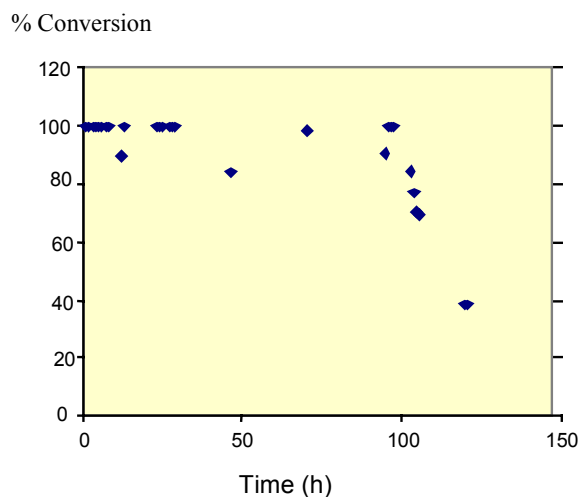


Figure 8. Methanol Conversion vs Time

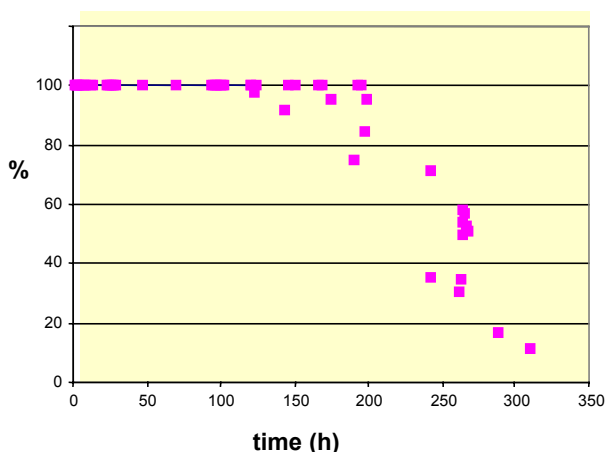


Fig. 9 Conversion vs time (500 micrometer aluminum reactor with 0.5g catalyst)

reactor. Because our system did not achieve the high pressure requirement for separation the flow rate was quite low. However, hydrogen output was 100% pure. Further work is needed in Year 2 to match the reformer with a suitable membrane, possibly one with lower pressure requirements.

Conclusions

- A thermal and process system model that was developed as a system simulator can be used to optimize the design of a micro channel reactor. The active length and inlet cross section of catalytic methanol reforming is optimized through temperature control and throughput rate for a specific catalyst. With iterative testing and further refinement, the base model will be used to provide a sound basis for improved reactor and process engineering.
- Hydrogen production is maximized and CO production is minimized by proper selection of 1) temperature-dependent reaction equilibria, 2) ratio of methanol to steam, and 3) catalyst activity. Through the innovative use of sensors and controls, the reformer operating system can be controlled to respond to different load requirements while maintaining optimum performance. Such a control system can be used to control volume of active catalyst bed, methanol to steam ratio, and catalyst reactivation (through hydrogen flushing).
- Long term, detailed steam reforming tests using a copper-zinc-oxide catalyst revealed fundamental information on the catalytic process, including method of deactivation. As a result, we have formulated a possible mechanism for catalyst action in the process. We will use this mechanism to design catalyst forms for appropriate action in the process.
- The combination of a burner to heat fluid in the heat exchangers with layers of co-current and counter-current flow against the reaction components will yield temperature zones in the reactor to achieve optimum performance.
- As a result of reactor and burner assembly and testing, a laminar sealing and gasketing process was discovered that provides ease of assembly, temperature and feed stream compatibility, and strong sealing capability.

References

W. Lloyd Allen, Patricia M. Irving and William J. Thomson, "MICROREACTOR SYSTEMS FOR HYDROGEN GENERATION AND OXIDATIVE COUPLING OF METHANE", in Proceedings of the 4th International Conference on Micro Reaction Technology, AIChE Spring National Meeting, March 2000, Atlanta, GA, USA.

Patricia M. Irving and W. Lloyd Allen, "MICRO FUEL PROCESSOR FOR HYDROGEN PRODUCTION" in Proceedings of the 2000 Conference on Small Fuel Cells, April 2000, sponsored by The Knowledge Foundation, Brookline MA.

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