

HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

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Principal Author: Paul A. Erickson

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The Regents of the University of California, Davis

One Shields Avenue

Davis, California 95616

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ABSTRACT

Hydrogen can be produced from many feedstocks including coal. The objectives of this project are to establish and prove a hydrogen production pathway from coal-derived methanol for fuel cell applications.

This progress report is the sixth report submitted to the DOE reporting on the status and progress made during the course of the project. This report covers the time period of January 1 – March 31, 2005. This quarter saw progress in four areas. These areas are:

1. Autothermal reforming of coal derived methanol,
2. Catalyst deactivation,
3. Steam reformer transient response,
4. Catalyst degradation with bluff bodies.

All of the projects are proceeding on or slightly ahead of schedule.

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EXECUTIVE SUMMARY

Hydrogen can be produced from many feedstocks including coal. The objectives of this project are to establish and prove a hydrogen production pathway from coal-derived methanol for fuel cell applications.

This progress report is the sixth report submitted to the DOE reporting on the status and progress made during the course of the project. This report covers the time period of January 1 – March 31, 2005.

Much progress has been made on the project funded by the Department of Energy during this reporting period. All of the projects are proceeding on or slightly ahead of schedule. This quarter saw progress in four areas. These areas are:

1. Autothermal reforming (ATR) of coal derived methanol,
2. Catalyst deactivation,
3. Steam reformer transient response,
4. Catalyst degradation with bluff bodies.

Preliminary experiments of ATR entry length have been performed for coal-derived methanol. The ATR research including investigation of the entry length required for fully mixing of fuel with oxygen at different flow conditions and O₂/C ratios was initiated. Reactant mixing was found to change the ATR performance and further research is planned to quantify this effect.

Data investigating the role of temperature in catalyst deactivation has been collected. There is a narrow temperature band where catalyst deactivation is slowest. Below the optimal temperature range, deactivation occurs due to fouling caused by accumulation of carbon compounds on the catalyst surface. Above the optimal temperature range, deactivation is very much greater due to rapid sintering. Surface analysis will be needed to precisely determine the processes causing the deactivation. This reinforces the idea that minimizing temperature gradients within the reactor can be as important to the steam reformation process as fuel purity, if not more so. Further experiments will look at the effect of flow rate and reactant/product concentration on catalyst deactivation. The reactor will also be run in a differential mode in order to collect data suitable for use in a catalyst deactivation model.

Steam reforming catalyst degradation experiments were performed with chemical grade methanol and the use of bluff bodies to quantify the effect of bluff bodies on catalyst deactivation. The results showed that the bluff body experiments had a higher temperature increase rate, which implies a higher catalyst degradation rate. More experiment runs are still needed to make the statistical analysis. In addition to chemical grade methanol, experiment runs using coal-based methanol are also scheduled to compare the catalyst degradations level.

Experiments investigating the transient response of steam reformation have been performed. Both coal-derived and chemical grade methanol was used. The chemical grade methanol had slightly higher conversions, but the response of the different fuels to the transient experiments was similar. The addition of acoustic mixing to the experiments also proved to increase conversion but had no direct effect on the transient response.

Several projects are scheduled for the next quarter including further ATR reactor development and testing of reactant mixing, continued evaluation of coal-based methanol in the steam reformers, further transient testing and measuring catalyst degradation using the various methanols. We also are evaluating various clean-up options for the reformate and studying how to direct the clean hydrogen stream to the PEM fuel cell. Additionally the research team will be participating in the 2005 Hydrogen Program Review at Washington DC.

Several research publications showing the results of using coal-derived methanol in steam reformation have been accepted and are now in press. Results will be presented at the 2005 ASME Heat Transfer Conference and the 2005 AIAA 3rd International Energy Conversion Engineering Conference. The reviewed publications will be sent shortly to the DOE.

EXPERIMENTAL

The following section describes the experimental methods used and developed during the reporting period for the following areas: autothermal reforming of coal derived methanol, catalyst deactivation, steam reformer transient response, and catalyst degradation with bluff bodies.

Autothermal Reforming of Coal-Derived Methanol

Mixing effects in steam reforming have already been shown to be of great significance to the effectiveness of a reformer. Coal-derived methanol has been set up for autothermal reformation (ATR). Mixing in ATR is much more significant than in steam reformation (SR) because of the addition of oxygen inside the reactor, which through Partial Oxidation (POX) supplies heat, by means of combustion, for the steam reforming reaction. To figure out the effects of mixing as well as find out the optimal location for the placement of the ATR catalyst within the reactor, what we call, “urban catalyst” (catalyst used in vehicle catalytic converters) was put in different locations inside the reactor for preliminary set-up of ATR of coal-derived methanol.

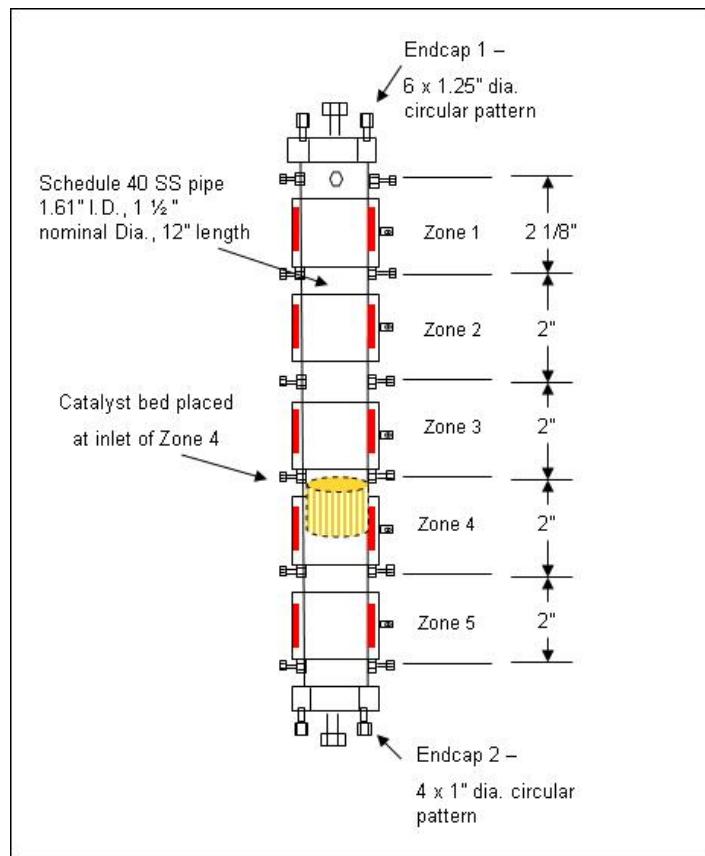


Figure 1: Schematic of ATR Reactor

Urban catalysts wafers 3.5cm in diameter by 3.4cm in length (1.38" x 1.34") were placed in zone 1 and zone 4 during different runs. Zone 1, as can be seen in Figure 1, is located at top of the reactor so that there is approximately 2.54cm (1") of entry length for mixing of the gases leaving the superheater. On the other hand, zone 4 is located below the middle of the reactor (approximately 17.8cm (7") entry length), which should be enough entry length for complete mixing of the fuel with oxygen, supplying heat through combustion. The Steam/Carbon Ratio was held constant at 1.5:1 for the entire experiment. The Oxygen/Carbon ration was varied from 0.2 up to 0.35. Liquid hourly space velocity was constantly set at 2.

Catalyst Deactivation

In the previous quarterly report, an outline for a study on catalyst deactivation in a methanol-steam reformer was described. This quarter, the first set of experiments in this study was performed and the results are presented herein. All experiments were performed on reactor A filled with crushed catalyst.

Steam Reformer Transient Response

For practical applications of small-scale reformers, transient response is just as important to reactor performance as steady-state conversion. Steam reformation is known to have a relatively slow transient response due to heat transfer limitations, so it is beneficial to understand the behavior of steam reformers under transient flow conditions and find ways to improve the response time. During the last quarter of the year preliminary experiments were run to evaluate the transient response of a steam reformer using chemical grade methanol.

In this quarter experiments were performed both with chemical grade methanol as well as coal-derived methanol. Our initial studies which were taken as the reactant flow rate through a steam reformer was cycled between 2.5 ml/min and 5 ml/min (0.0845 and 0.169 oz/min) were fairly close in conversion percentage making it difficult to clearly see the transient response, so for the second round of experiments the flow rate was varied from 2.5 ml/min to 7.5 ml/min (0.0845 oz/min to 0.254 oz/min), alternating every 10 minutes, which allowed the reactor to just reach steady state before the next change in flow rate. The steady-state conversion at 2.5 ml/min (0.0845 oz/min) was expected to be 100%. However, the high flow rate of 7.5 ml/min (0.254 oz/min) would not be, so a series of baseline steady-state runs were taken to give a benchmark. Since steam reforming is an endothermic reaction the temperature profiles within the reactor tell a good story of how the reactor is responding. By comparing the actual transient conversions to an idealized step function of conversions we can also see how well the reactor responds.

It has been shown that the addition of an acoustic standing wave promotes better heat transfer and thus yields higher conversions [1]. Since the transient response is directly related to heat transfer limitations it was expected that the introduction of a standing wave during the transient experiments would result in a shorter recovery time constant. All of the studies performed include conversions taken with 30 watts of acoustic enhancement, 15 watts of acoustic enhancement as well as with out any acoustic enhancement at all.

Catalyst Degradation With Bluff Bodies

Previous experiment results have demonstrated that introducing bluff bodies can significantly improve the steam reforming performance. Therefore, it was expected that bluff bodies might also affect the catalyst degradation rate. This experiment was initiated to investigate and compare the catalyst degradation rates between reactors with bluff body packages and without bluff body packages.

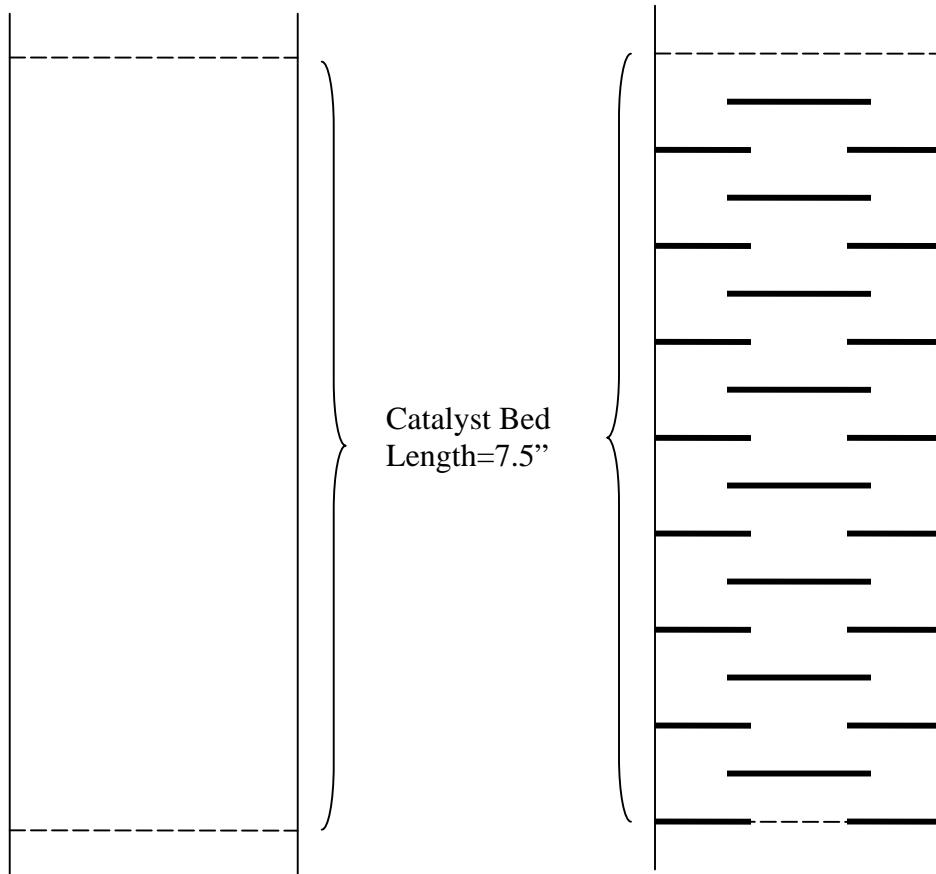


Figure 2: Catalyst bed housing for reactor B, without bluff bodies (left), With 8 bluff body packages (right)

Reactor B was used as a base reactor (see Figure 2) to investigate the catalyst degradation rate under a passive flow in the catalyst bed. Eight packages of bluff bodies using a crushed copper-based catalyst. Chemical-grade methanol was used as the reforming fuel for this degradation experiment. Reactor B with no bluff body packages was tested with the same conditions to compare the bluff body effect on the catalyst degradation rate. The crushed catalyst had an average length of 0.25 cm (0.098 in). A 30-hour experiment was conducted with an 80-minute data point interval to measure the real time methanol conversion. The mass of the catalyst used in the experiment was 250 grams (0.551 lb) packed in Reactor B.

RESULTS AND DISCUSSION

The following section presents results from the reporting period from the following areas: autothermal reforming of coal-derived methanol, catalyst deactivation, steam reformer transient response, and catalyst degradation with bluff bodies.

Autothermal Reforming of Coal-Derived Methanol

Figure 3 represents the methanol conversion associated with different O₂/C ratios. The conversion of methanol using urban catalyst located at zone 4 was higher than when it was placed at zone 1. This indicates that mixing effects of fuel with oxygen should be significantly considered especially for ATR experiments. These preliminary results can lead us to find the optimal location of catalyst placement to enable complete mixing in our ATR reactor. Catalyst placement in different reaction zones will be repeated to compare with the current initial results

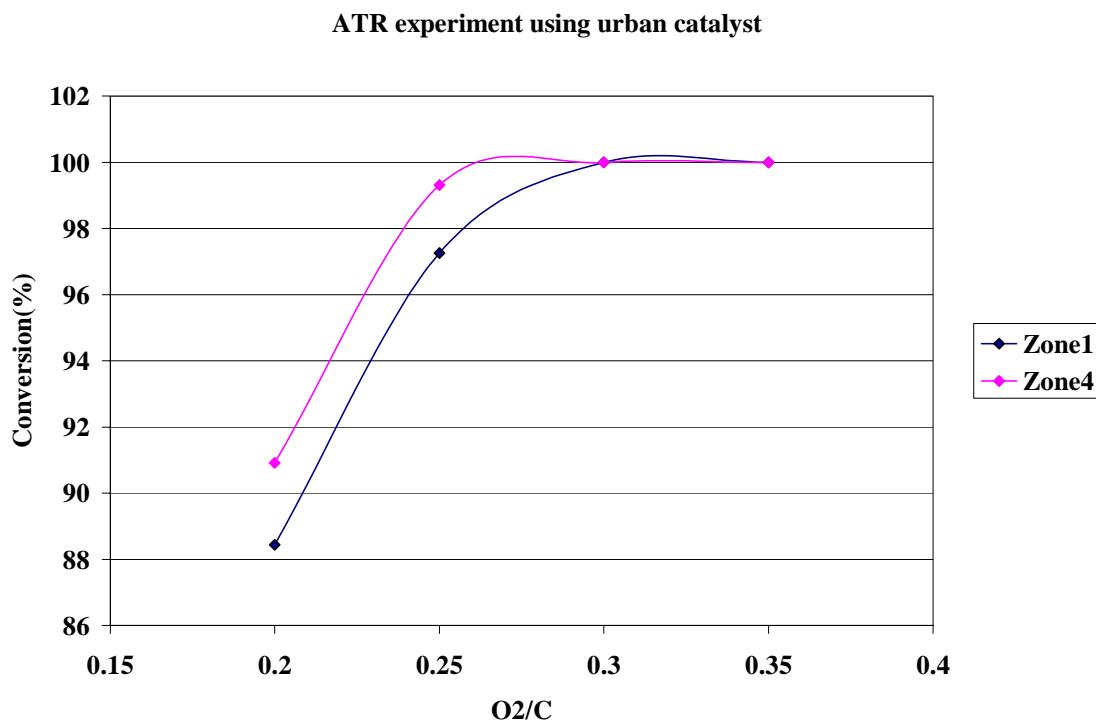


Figure 3: Methanol conversion associated with different O₂/C ratio

Figure 4 represents hydrogen concentrations at O₂/C ratios of 0.2 and 0.25. SR hydrogen concentrations that have been performed in the lab are consistently above 70%. However, due to the combustion wave from the oxygen and fuel, hydrogen concentrations fluctuated $\pm 10\%$ from the average in ATR. Moreover, ATR hydrogen concentrations were always below 50%, because nitrogen from the air, which is left after combustion, dilutes the gas concentration. A portion of fuel is also used up for

combustion in order to sustain a deflagration wave. As expected, Zone 4, which has a greater mixing area for the fuel and oxygen, shows much higher concentrations of hydrogen than zone 1 in the case of $O_2/C = 0.2$. At $0.25 O_2/C$, the difference of hydrogen concentrations decreased because the increment of oxygen flow rate as well as partial pressure of oxygen gases enhances the mixing of the fuel with oxygen.

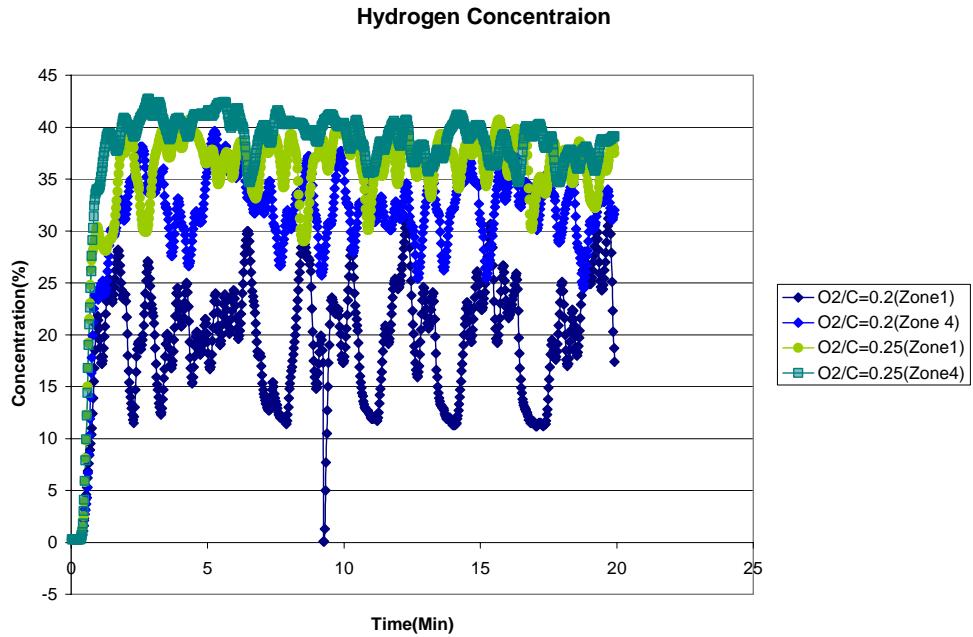


Figure 4: Hydrogen concentration differences for variance in O_2/C ratios and zones

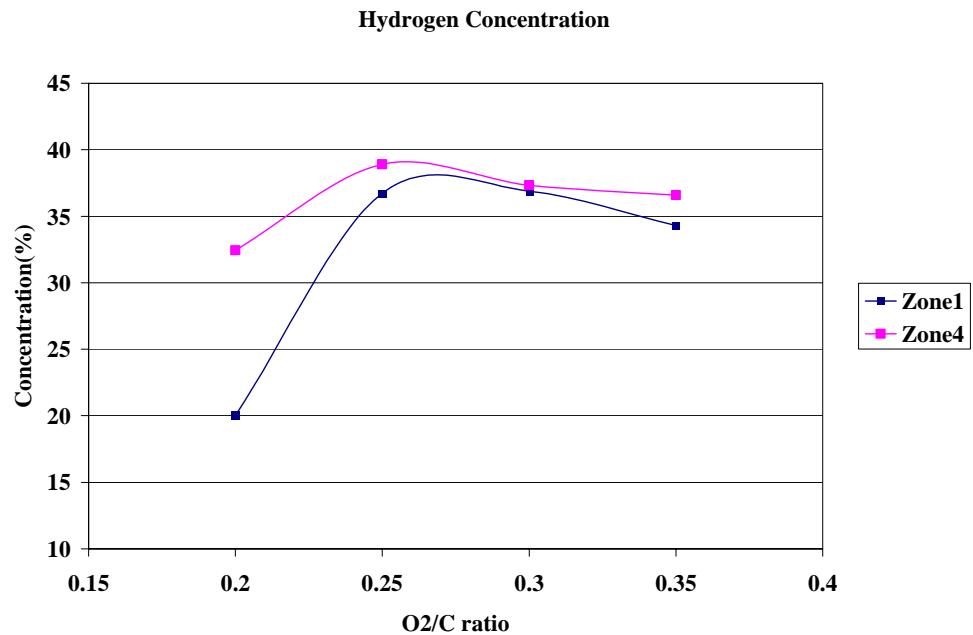


Figure 5: Averaged hydrogen concentration differences for variance in O_2/C ratios and zones

Figure 5 represents the averaged hydrogen concentration differences in the case of varying both O₂/C ratio and zone placement of the catalyst. Theoretically, the optimal O₂/C ratio in the case of equilibrium is around 0.23. There is always the possibility of carbon formation below 0.2 O₂/C ratio. Mixing effects should be considered to find out the optimized O₂/C because maximum averaged hydrogen concentration at different zones shifted a little bit left when urban catalyst moved from zone 1 to zone 4. In the case of Zone 1 placement, the averaged maximum hydrogen concentration was shown at an O₂/C of around 0.275. For Zone 4 placement, the averaged maximum hydrogen concentration was shown around 0.25 O₂/C. Therefore, the effects of mixing fuel with oxygen can significantly affect the overall efficiency of ATR.

Catalyst Deactivation

Although the catalyst deactivation study is still in progress, data has already been collected which shows some interesting trends.

Table 1: Experimental conditions

Temperature (°C)	Catalyst loading (g)	Premix flow rate (ml/min)
210	28.3	2.6
250	14	2.6
270	13	3.2
290	5.4	2.6
310	3.6	2.6
350	2.7	2.6

Table 2: Conversion vs. time online at various reactor temperatures

Time online (hrs)	Conversion at given temperature					
	210°C	250°C	270°C	290°C	310°C	350°C
0	61.87%	88.03%	83.79%	67.63%	71.47%	65.86%
1.5	60.65%	86.05%	82.03%	68.63%	69.21%	58.22%
3	59.05%	84.12%	81.15%	68.96%	68.16%	53.01%
4.5	57.84%	82.75%	80.11%	67.66%	66.36%	48.69%
6	56.20%	80.72%	79.15%	67.83%	64.96%	45.48%
7.5	56.76%	79.05%	78.01%	65.72%	63.30%	42.56%

Table 3: Initial activity and change in activity at different reactor temperatures

Temperature (°C)	Initial activity (ml/min premix per g catalyst)	Decrease in activity (ml/min premix per hr online)	Decrease in activity relative to initial rate (%/hr online)
210	0.06	0.0007	1.20%
250	0.16	0.0022	1.35%
270	0.21	0.0018	0.88%
290	0.33	0.0012	0.37%
310	0.52	0.0075	1.45%
350	0.63	0.0292	4.60%

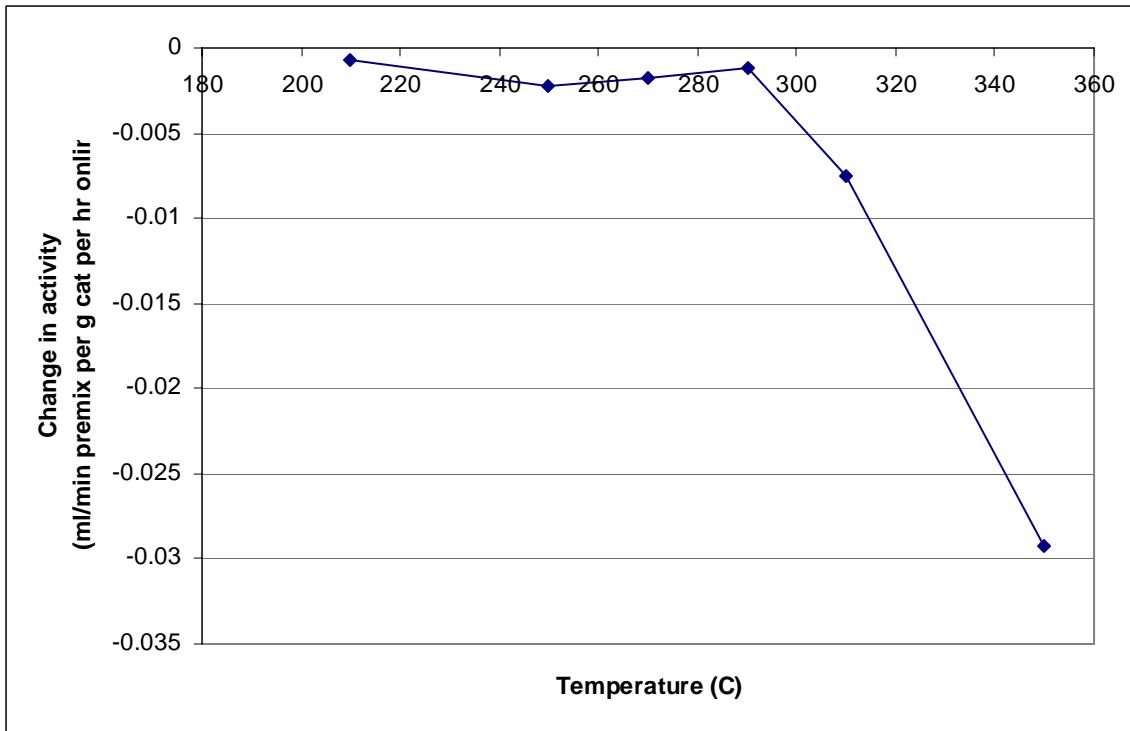


Figure 6: Change in activity vs. temperature

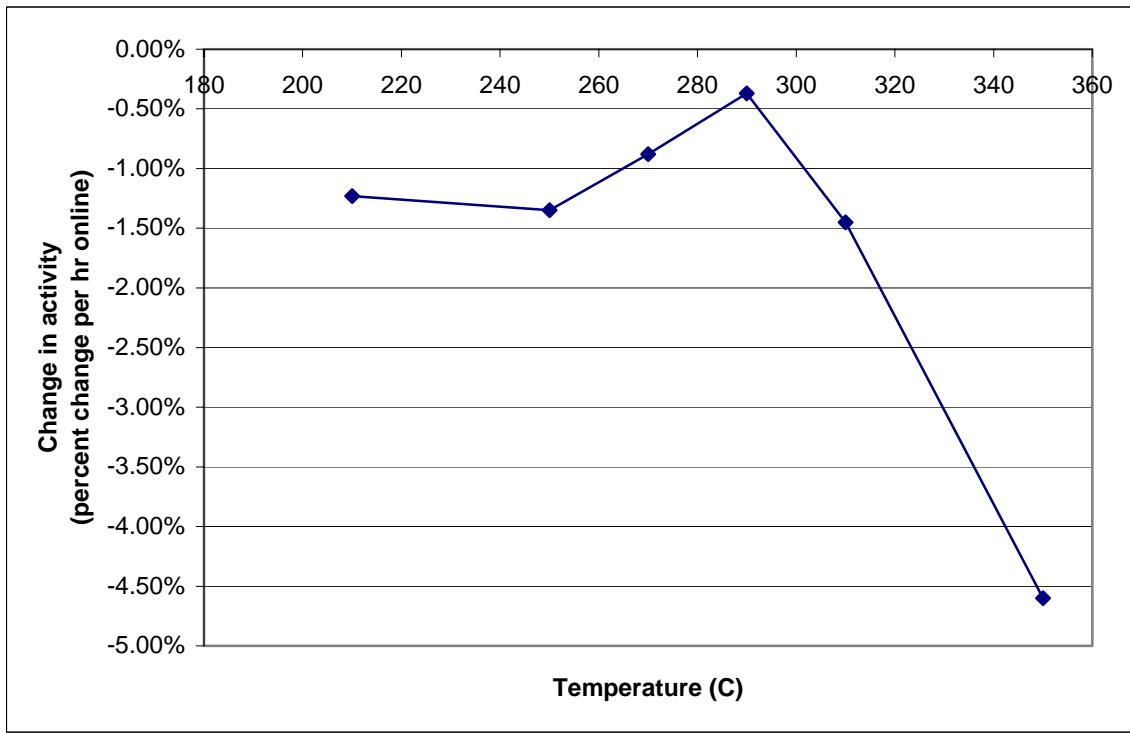


Figure 7: Relative decrease in activity from initial rate

As expected, initial catalyst activity is highly dependent on temperature. In fact, based on these measurements, only 31 grams (0.068 lb) of catalyst should be necessary for full conversion at 250°C (482°F) and 5 ml/min (0.169 oz/min) of premix. Compare this to the 250 grams (0.551 lb) that are required for full conversion in a non-isothermal reactor. Furthermore, there is a narrow temperature band where catalyst deactivation is slowest. Below the optimal temperature range, deactivation relative to the initial activity is somewhat greater. This is likely due to fouling caused by accumulation of carbon compounds on the catalyst surface. Above the optimal temperature range, deactivation is very much greater. This is likely due to rapid sintering, where the catalyst surface area decreases due to agglomeration of metal catalyst particles and degradation of catalyst support material. Surface analysis is needed to precisely determine the processes causing the deactivation. These initial results emphasize the need for better temperature control of the reactor and reduced temperature gradients within the catalyst bed. Further experiments in this area will look at the effect of flow rate and reactant/product concentration on catalyst deactivation. Additionally, the reactor will be run in differential mode in order to collect data suitable for use in a catalyst deactivation model.

Steam Reformer Transient Response

The experimental set up of the packed reactor with the acoustic equipment can be seen below in Figure 8. An acoustical driver, sealed in an explosion-proof enclosure, was mounted to the bottom of the reactor. The mounting adapter has a cooling water jacket, and a small nitrogen purge to protect the diaphragm of the driver from overheating. A high temperature pressure transducer was mounted near the top of the catalyst bed housing.

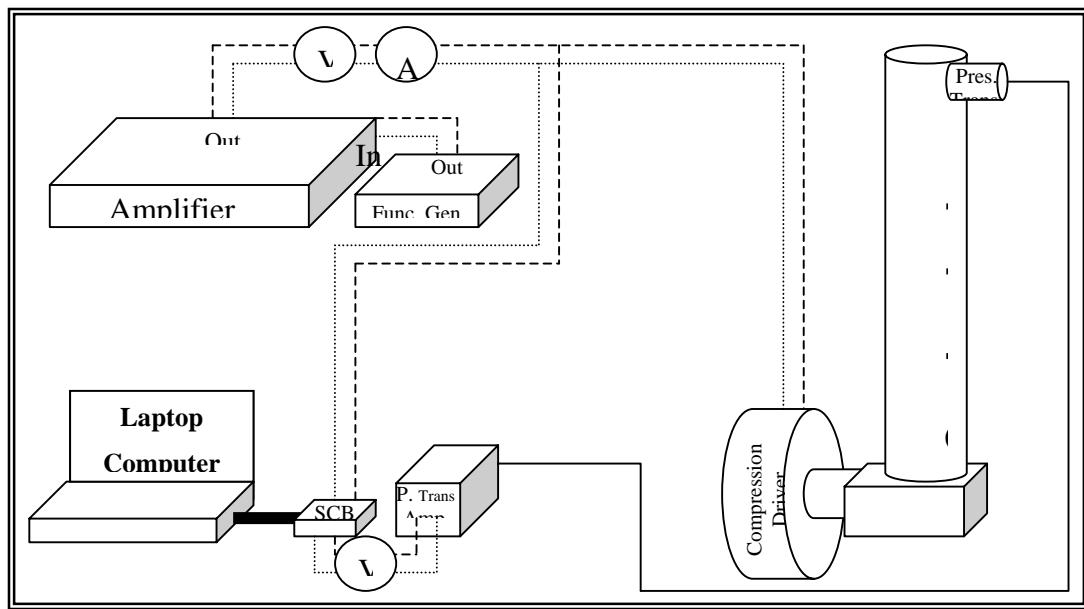


Figure 8: Experimental set up

To determine the dominant mode in the catalyst bed housing a swept sine wave was introduced into the reactor, and the transfer function taken. An FFT of the transfer function was taken, so that the dominant frequency could be determined. Figure 9 is a plot of the Transfer function magnitudes of Reformer B at room temperature with pelletized catalyst, crushed catalyst, no catalyst, as well as packed with crushed catalyst and bluff bodies.

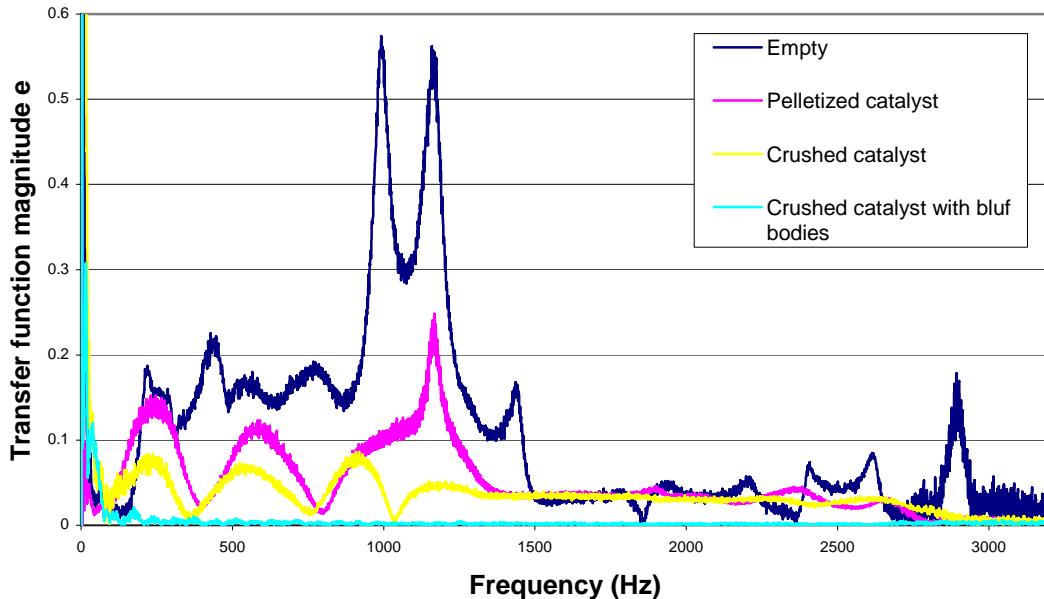


Figure 9: Transfer function magnitude vs. frequency for catalyst bed housing B

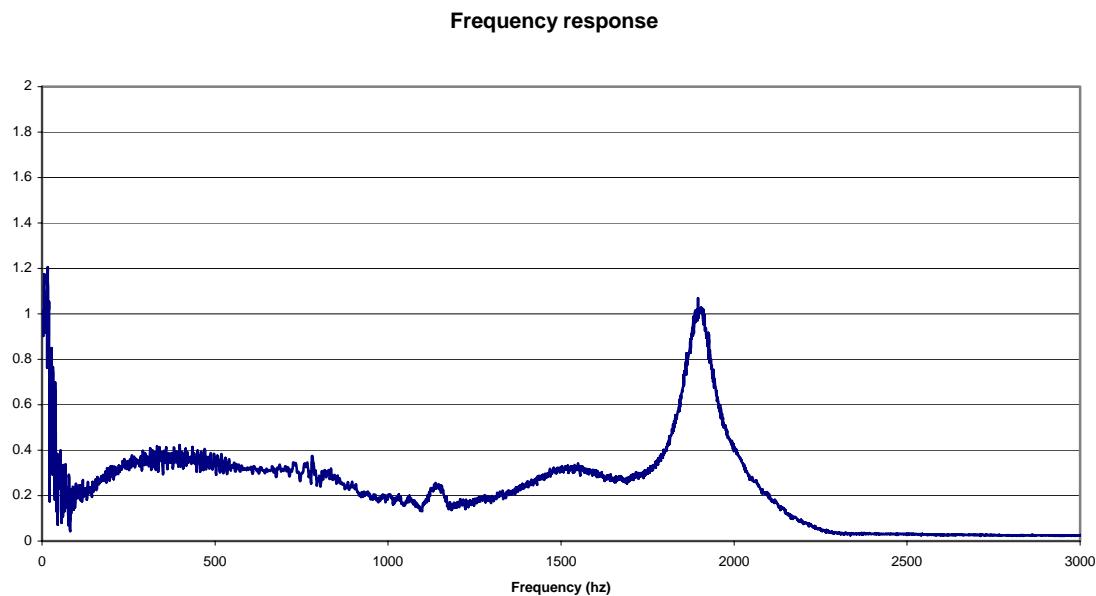


Figure 10: Transfer function magnitude vs. frequency while reforming coal-derived methanol

Since the speed of sound varies with temperature and gas composition the optimal frequency was redetermined at operational temperature and while reforming. Figure 10 below is a plot of the Transfer function magnitude while reforming coal-derived methanol.

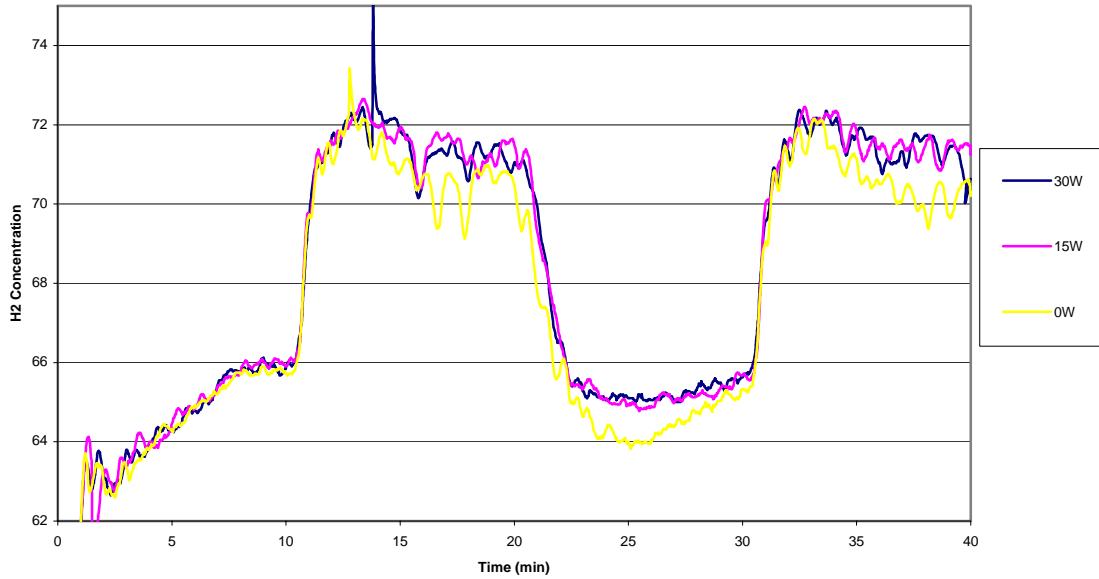


Figure 11: Hydrogen Concentration in product stream from chemical grade methanol

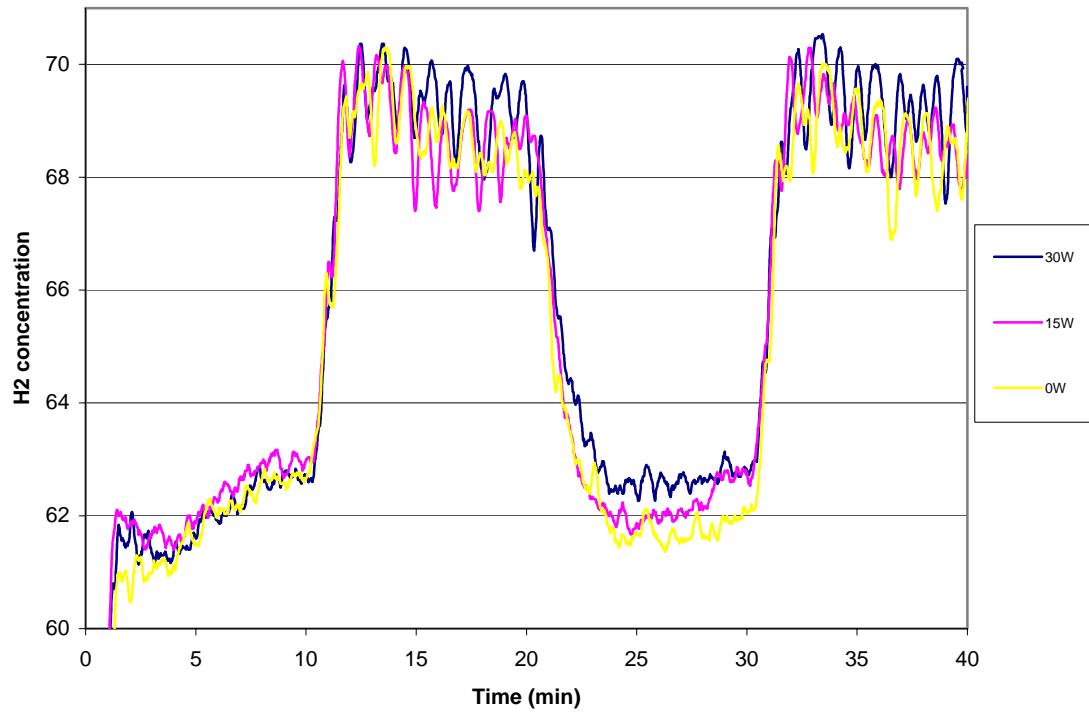


Figure 12: Hydrogen Concentration in product stream from coal-derived methanol

We can see in Figures 11 and 12 that the chemical grade methanol gives a slightly higher concentration of hydrogen, with minimal increases due to the addition of acoustical power. Figures 13 and 14 show the reactor temperature as the flow rate changes from low flow to high flow. When the flow rate increases and the centerline temperatures drop immediately we notice that the Zone 4 temperature rises for about a minute before dropping. It has been determined that this is due to the increased flow rate pushing the exothermic water-gas-shift reaction down to Zone 4 from Zone 3.

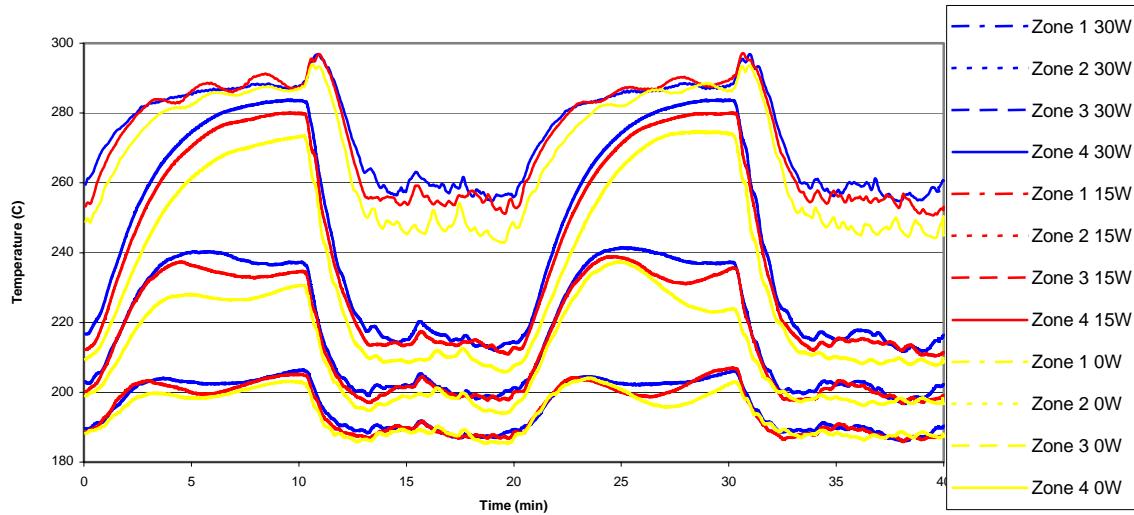


Figure 13: Reactor temperature during two cycles from low flow to high flow with chemical grade methanol (average of 4 runs)

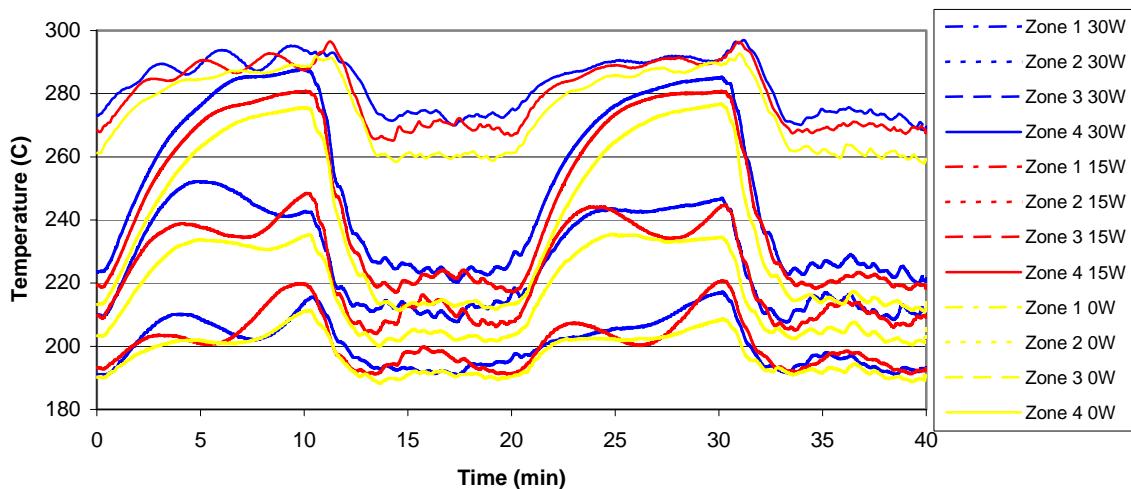


Figure 14: Reactor temperature during two cycles from low flow to high flow with coal-derived methanol (average of 4 runs)

Methanol conversion was also measured during this experiment as shown in Tables 4 and 5. An idealized conversion percentage is estimated based on the conversion percentages from 30 minutes of steady state operation at low flow plus 30 minutes of steady state operation at high flow.

Table 4: Methanol conversion during the experiment

Chemical Grade MeOH					
Power level (W)	Conversion (%)	Average conversion (%)	Standard Deviation	Idealized conversions	Difference
0	95.48				
0	95.4				
0	95.75	95.565	0.156	95.512	-0.053
0	95.63				
15	96.34				
15	96.35				
15	96.31	96.315	0.040	96.820	0.505
15	96.26				
30	97.03				
30	96.82				
30	96.87	96.905	0.090	96.312	-0.593
30	96.9				

Table 5: Methanol conversion during the experiment

Coal Derived MeOH					
Power level (W)	Conversion (%)	Average conversion (%)	Standard Deviation	Idealized conversions	Difference
0	96.58				
0	95.66	95.527	1.126	96.195	0.668
0	94.34				
15	96.67				
15	95.28	96.017	0.699	97.132	1.115
15	96.1				
30	97.86				
30	97.17	97.163	0.700	97.877	0.713
30	96.46				

By comparing the idealized conversion to the measured conversion, and taking the difference we can get a value from which the transient response can be evaluated. In Table M.1 the difference comes up as negative in two of the three cases. This is due to the baseline conversions from which the idealized conversions were calculated. The

baseline conversions for the chemical grade methanol showed drastic catalyst deactivation, which is currently being investigated. Table 5 gives a better picture of the transient response, and from this data it can be concluded that although the acoustic enhancement does improve conversion overall it does not appear to have a strong influence on shortening the transient response time. The coal-derived methanol showed slightly lower conversions, but the difference was insignificant compared to the increase obtained through the acoustical enhancement.

Catalyst Degradation With Bluff Bodies

Two 30-hours runs without bluff bodies and one 30-hour run with bluff body packages have been taken to compare the catalyst degradation rates. The fuel conversions versus experiment running time are shown in Figures 15 and 16. Figure 15 indicates the catalyst inside the reactor B without bluff body packages degraded 0.14 and 0.1503 conversion percents per hour for two runs. Comparing to the 0.1449 conversion percents per hour shown in Figure 16 with eight bluff body packages inside the reactor, the experiment result showed that the bluff body packages did not have a significant effect on the catalyst degradation rate in conversion percentage.

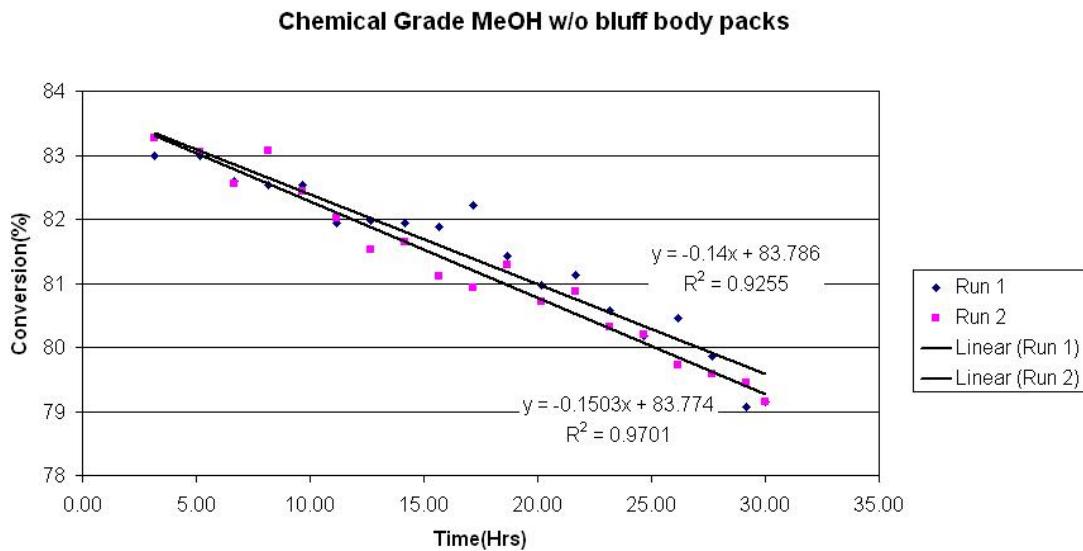


Figure 15: Conversion vs. time without bluff body in reactor B

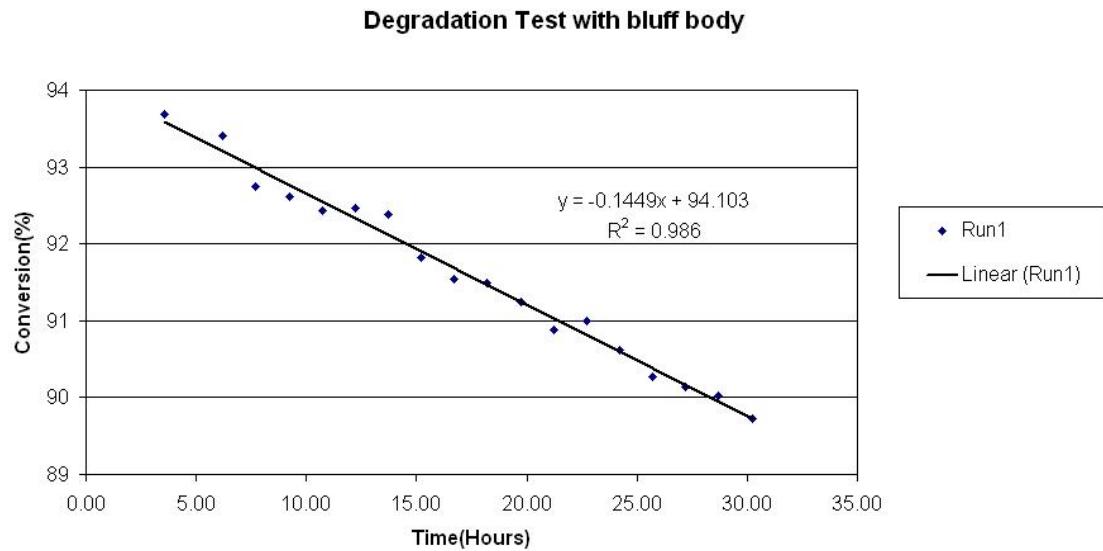


Figure 16: Conversion vs. time with 8 packs of bluff bodies in reactor B

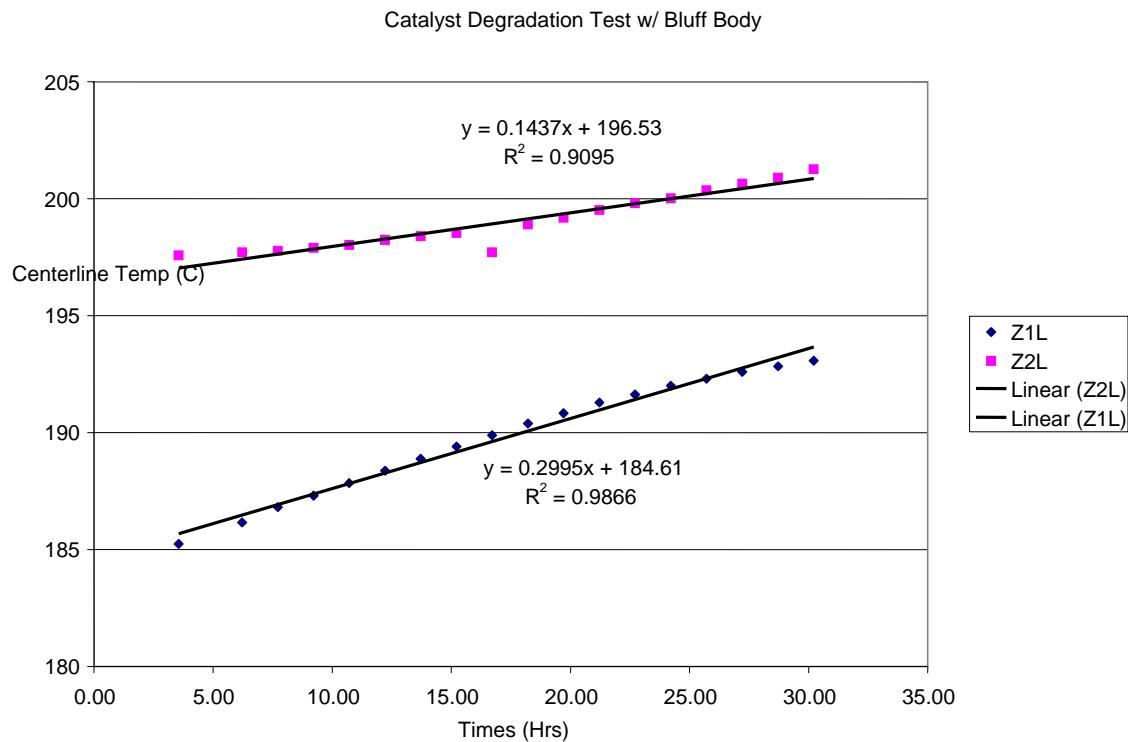


Figure 17: Centerline temperatures at Zone1 and Zone2 vs. time, with bluff bodies

However, by showing the centerline temperatures at Zone 1 (upstream) versus experiment time, the bluff bodies' effect on catalyst degradation rate can be seen. The catalyst degradation can be represented in the temperature increase of the catalyst due to the endothermic nature of the reaction process. In Figure 17 the slope of the linear

regression line shows that the temperature increase rate of the condition with bluff bodies is 0.2995°C per hour. In Figure 18, the average temperature increase rate of the two runs is 0.1897°C per hour (0.2055 and 0.1739 °C/hr respectively). This result shows that the bluff body experiment had a higher temperature increase rate, which implies a higher catalyst degradation rate.

The catalyst degradation might not be shown in the conversion vs. time chart because the catalyst degradation starts from upstream in the reactor. As time goes by, the degradation moves downstream inside the reactor, but the overall catalyst reforming capacity still overrides the catalyst degradation level.

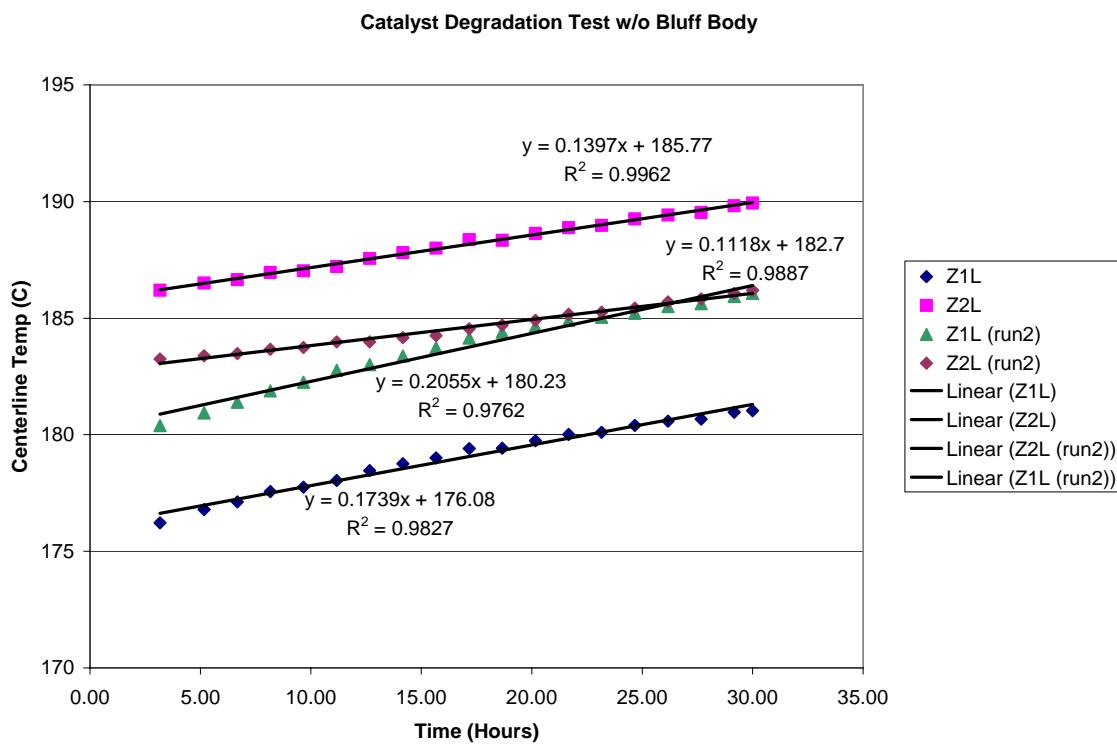


Figure 18: Centerline temperatures at Zone1 and Zone2 vs. time, without bluff bodies

More experiment runs are still needed to make the statistical analysis. In addition to chemical grade methanol, experiment runs using coal-based methanol are also scheduled to compare the catalyst degradations level.

CONCLUSION

Preliminary experiments of ATR entry length have been performed for coal-derived methanol. The ATR research of the entry length required for fully mixing of fuel with oxygen at different conditions such as different liquid hourly space velocity and O₂/C ratio was initiated.

Data investigating the role of temperature in catalyst deactivation has been collected. There is a narrow temperature band where catalyst deactivation is slowest. Below the optimal temperature range, deactivation occurs due to fouling caused by accumulation of carbon compounds on the catalyst surface. Above the optimal temperature range, deactivation is much greater due to rapid sintering. Surface analysis will be needed to precisely determine the processes causing the deactivation. This reinforces the idea that minimizing temperature gradients within the reactor can be as important to the steam reformation process as fuel purity, if not more so. Further experiments will look at the effect of flow rate and reactant/product concentration on catalyst deactivation. The reactor will also be run in differential mode in order to collect data suitable for use in a catalyst deactivation model.

Steam reforming catalyst degradation experiments were performed with chemical grade methanol and the use of bluff bodies to quantify the effect of bluff bodies on catalyst deactivation. The results showed that the bluff body experiments had a higher temperature increase rate, which implies a higher catalyst degradation rate. More experiment runs are still needed to make the statistical analysis. In addition to chemical grade methanol, experiment runs using coal-based methanol are also scheduled to compare the catalyst degradations levels.

Further experiments investigating the transient response of steam reformation have been performed. Both coal-derived and chemical grade methanol was used. The chemical grade methanol had slightly higher conversions, but the response of the different fuels to the transient experiments was similar. The addition of acoustics to the experiments also proved to increase conversion but had no direct effect on the transient response.

Several projects are scheduled for the next quarter including further ATR reactor development and testing, continued evaluation of coal-based methanol in the steam reformers, further transient testing and measuring catalyst degradation using the various methanols. We also plan to evaluate various clean-up options for the reformat, and how to direct the clean hydrogen stream to the PEM fuel cell. Additionally, the research team will be participating in the 2005 Hydrogen Program Review at Washington.

Several research publications showing the results of using coal-derived methanol in steam reformation have been accepted and are now in press. Results will be presented at the 2005 ASME Heat Transfer Conference and the 2005 AIAA 3rd International Energy Conversion Engineering Conference. The reviewed publications will be sent shortly to the DOE.

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