HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

41850R07.pdf

Quarterly Technical Progress Report
Reporting Period Start Date: April 1, 2005
Reporting Period End Date: June 31, 2005
Principal Author: Paul A. Erickson
Report Issue Date: July 2005
DOE Award Number: DE-FC26-03NT41850
Submitting Organization:
The Regents of the University of California, Davis
One Shields Avenue
Davis, California 95616

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 seventh 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 April 1 – June 31, 2005. This quarter saw progress in four areas. These areas are:

1. Steam reformer transient response,
2. Heat transfer enhancement,
3. Catalyst degradation,
4. Catalyst degradation with bluff bodies,
5. Autothermal reforming of coal-derived methanol.

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

TABLE OF CONTENTS

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 seventh 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 April 1 – June 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 five areas. These areas are:

1. Steam reformer transient response,
2. Heat transfer enhancement,
3. Catalyst degradation,
4. Catalyst degradation with bluff bodies,
5. Autothermal reforming of coal-derived methanol.

Work with quantifying the transient response has been recently completed and analyzed. During the last quarter, the transient response of coal-derived methanol was analyzed and compared to the fuel cell grade methanol results found previously.

We have continued to investigate the role of temperature in catalyst deactivation in order to understand how geometry can play such a large role in this important parameter. Tests with quasi-isothermal reactors quantify the large dependence of catalyst degradation on temperature. 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. Work continues on investigating the role of temperature. This quarter we have specifically investigated ways to improve heat transfer and to analyze the affect of heat transfer on percent convergence. Different geometries and the affect of an internal cartridge heater were specifically investigated this quarter.

Degradation tests have begun using the flow disturbance disks and rings sets referred to as bluff bodies. As the bluff body set up has shown increased conversion of fuel as noted in past reports, it is expected that the flow disturbers will also have an effect in decreasing catalyst degradation rates. The second set of data has been collected regarding the use of coal-based methanol with the bluff body set up. The degradation rates are much higher in Reactor B than with the previous smaller reactors used for testing catalyst deactivation. In comparison to catalyst degradation due to the differences in fuel type (fuel cell grade vs. coal derived methanol) as reported previously, it appears that the effect of reactor geometry on catalyst degradation far outweighs the effect of fuel type. This is an encouraging result for those eager to use coal-derived methanol as a hydrogen feedstock. Future work is necessary to further quantify the effect of geometry in catalyst degradation.

Autothermal reforming of coal-derived methanol has taken place with a low-grade catalyst. Initial findings show that reactor performance was similar to fuel cell grade methanol. Analysis of the results is continuing and further tests will be made with a specialty catalyst.

Several projects are scheduled for the next quarter including further ATR reactor development and testing, such as the affect mixing of air fuel and water has on ATR. Next quarter bluff body enhancement of ATR is going to be investigated. An evaluation of coal-based methanol steam reformers and measuring catalyst degradation using coal based and chemical grade methanol will continue. We also plan to evaluate various clean-up options for the methanol reformate for use in a PEM fuel cell next quarter.

EXPERIMENTAL

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

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 the final experiments and analysis in regard to transient response and acoustic enhancement were performed both with chemical grade methanol as well as coal-derived methanol. For a complete summary of work done on improving transient response with acoustic enhancement, please reference the master's thesis completed in May 2005 [1]. The thesis completed using research done at the Hydrogen Production and Utilization Lab at UC Davis supported by this grant.

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 [2]. 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.

Heat Transfer Enhancement

The following setup was used to determine the preliminary experimental results of heat transfer enhancement via internal cartridge heater. The purpose of heat transfer enhancement is to increase the percent convergence of coal-derived methanol. The ideal case would be 100 % convergence. Reactor A is shown below in Figure 1 and reforms methanol using eight band heaters. Reactor C is shown below in Figure 2 and reforms using two band heaters and an internal cartridge heater. Reactor A and Reactor C have the same ¾" nominal diameter but differ in length. Reactor C, which has an internal cartridge heater, was loaded with 39g of crushed catalyst. Reactor A was loaded with 250g of pelletized catalyst and a second experiment was conducted using 250g of crushed catalyst. For the three previously described cases, contact time has been defined in terms of space velocity and packing density to enable comparison with different experimental results. The same set point was applied in the case of reactor A regardless of different flow rates. However, the set point of reactor C had been changed to minimize thermal gradients inside the reactor.

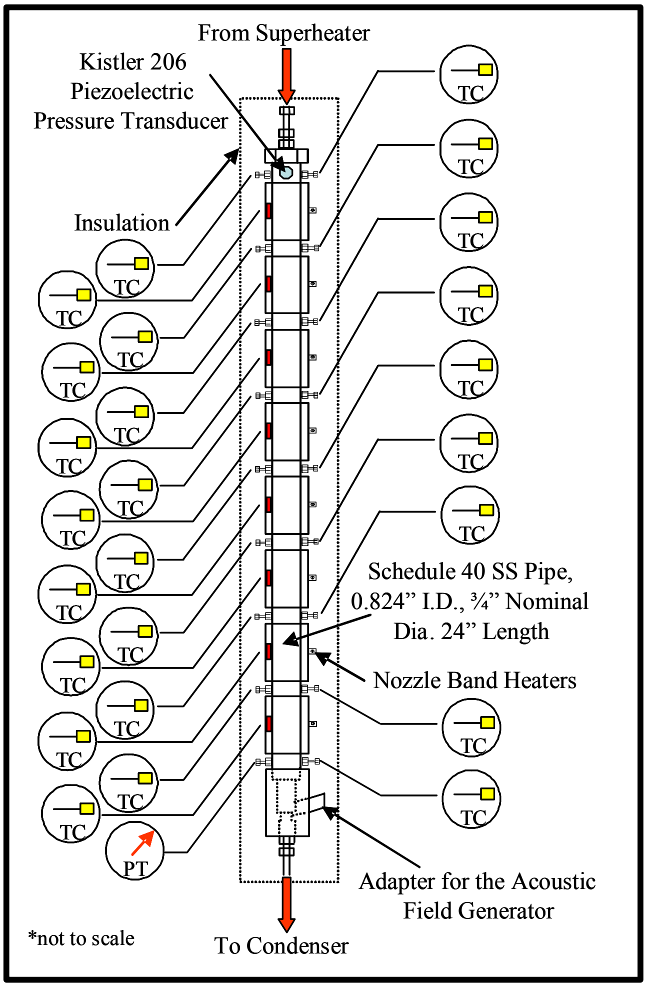


Figure 1: Reactor A Schematic

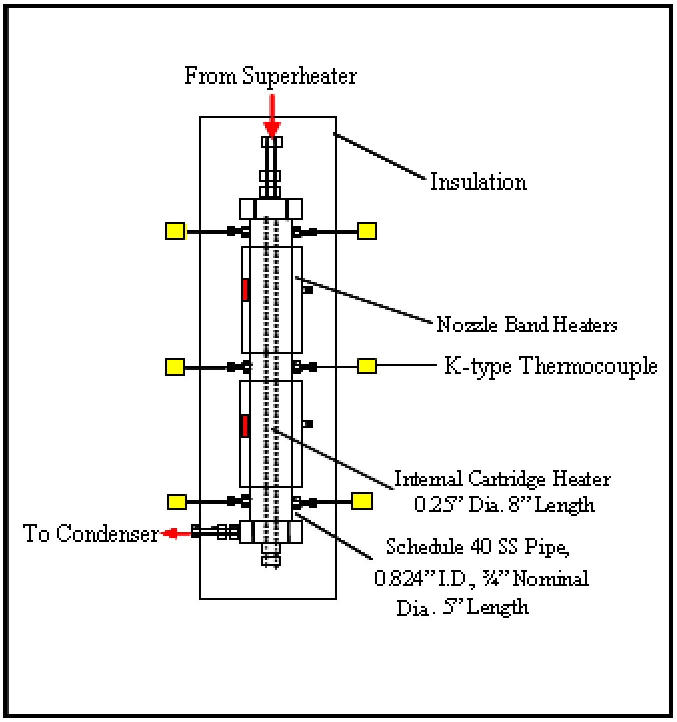


Figure 2: Reactor C Schematic

Catalyst Degradation

Both chemical grade and coal-derived methanol was tested using different reactor geometries. As mentioned in previous reports, reactor geometry significantly affects catalyst aging regardless of using the same operating conditions (same space velocity and inlet temperature). Reactor geometry dominates catalyst aging because heat and mass transfer can be severely limited as reactor size increases. To analyze the affect geometry has on chemical grade and coal-derived methanol two reactors with different geometries were used. Reactor B is an example of a long reactor and has been set up with eight bluff body packages. The outer diameter and length of Reactor B is 1.66" and 10" respectively. Reactor C was used as smaller sized reactor. The outer diameter and length of Reactor C is 1.05" and 5" respectively. Reactor B was loaded with 250g of crushed catalyst, while Reactor C was loaded with 39g. The steam to carbon ratio was maintained at a constant 1.5:1 molar ratio. For all the experiments, a 2.5 liquid hourly space velocity associated with premix flow rate was maintained.

Catalyst Degradation with Bluff Bodies

As described in the previous quarterly report, a catalyst degradation test with and without bluff bodies has been completed using chemical grade methanol. The results indicated that the degradation phenomena did not have a significant effect on conversion percentage, but did increase reactor centerline temperature.

This quarter, the experiment using coal-derived methanol and eight bluff body packages was completed to compare the difference in catalyst degradation using chemical grade methanol.

Autothermal Reforming of Coal-Derived Methanol

Mixing effects in steam reforming has 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.

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 3, 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.

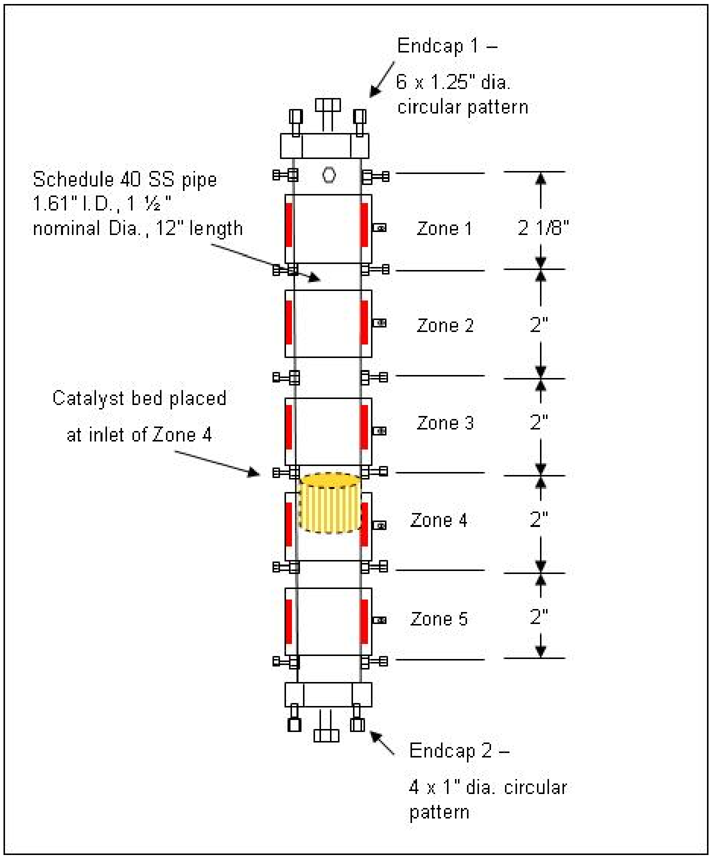


Figure 3: Schematic of ATR Reactor

RESULTS AND DISCUSSION

Steam Reformer Transient Response

In that the acoustics of the reactor varies slightly each time the catalyst bed housing is packed, the dominant frequencies were revaluated for each packing. Figure 4 below shows an example of the transfer function magnitude vs. frequency for the reactor during reduction. Figure 5 shows the transfer function magnitude vs. frequency for the reactor during the reformation of coal-derived methanol.

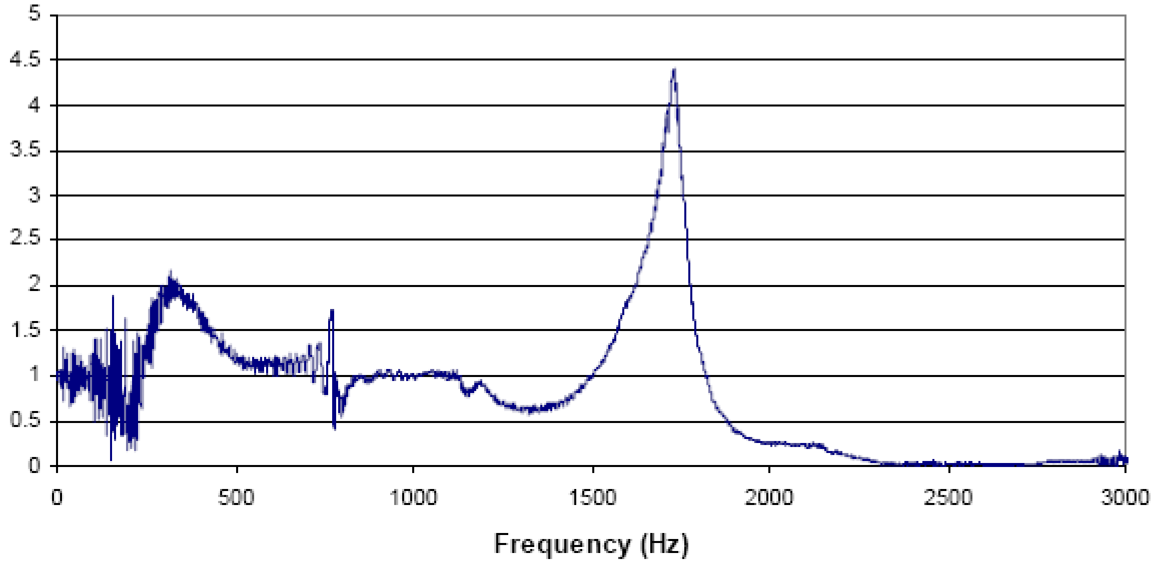


Figure 4: Transfer function magnitude of catalyst bed housing while reducing catalyst

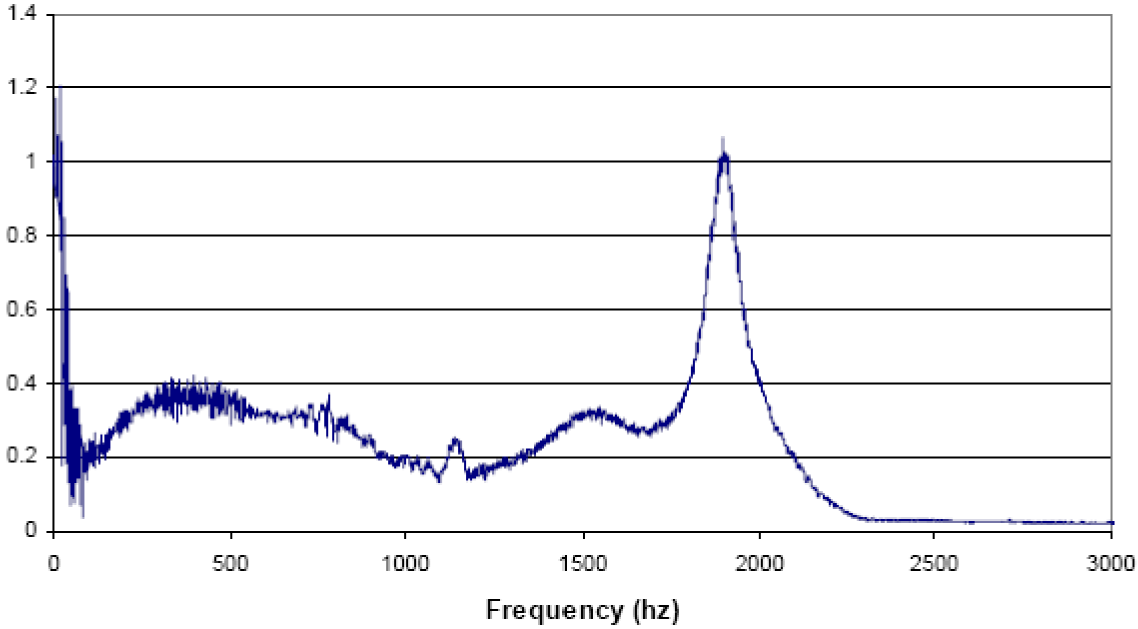


Figure 5: Transfer function magnitude of catalyst bed housing while reforming coal-derived methanol

During reduction the catalyst bed is heated to 200 °C (392 °F) and is filled with 98.5% nitrogen, and 1.5% hydrogen by mass. While reforming the catalyst bed is at a temperature of around 260 °C (500 °F), and is filled with hydrogen, carbon monoxide, carbon dioxide, methane, as well as unreacted water and methanol. It is clear that the peak between these two operations shifts in frequency due to an increase in temperature and a change in the gas composition by a comparison of the plots below.

For the catalyst bed housing used the dominant mode frequency for the case of the chemical grade methanol was 1935 Hz while reforming. When the coal-derived methanol was used the dominant mode frequency was found to be 1898 Hz. During operation the temperature and gas compositions do fluctuate. To optimize the influence of the acoustic enhancement a feed back control system would be required to periodically recalculate the optimal frequency and adjust the input.

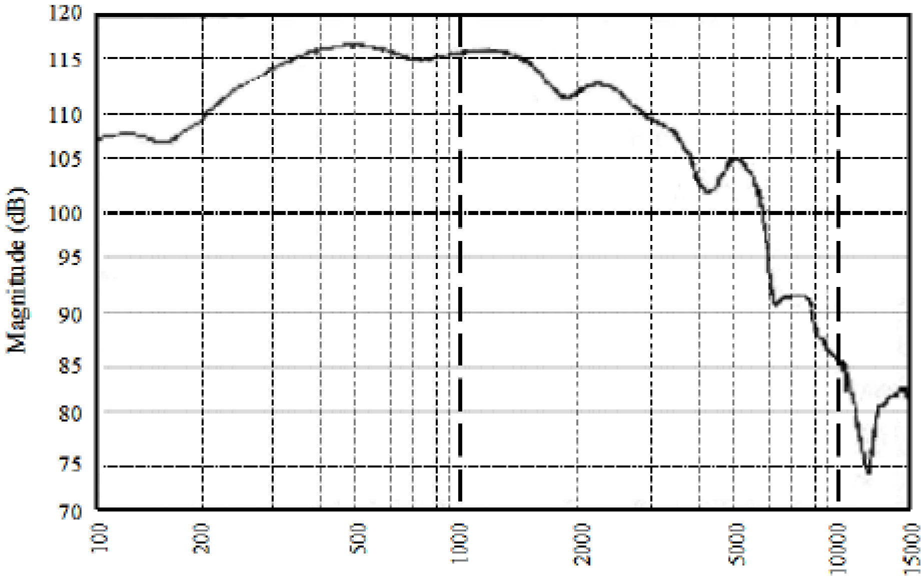


Figure 6: Frequency response of the Atlas PD-60A Driver (Courtesy of Atlas)

In addition to variances in the changing condition of the catalyst bed there is a limitation to the response that can be achieved by a swept sine from the driver while determining the dominant modes. Figure 6 presents the frequency response of the compression driver indicating that tones below 200 Hz, and above 50000Hz will be produced with less power. Although there is a limitation as to the range of the modes that can be examined it is not believed that tones outside of this range would yield higher sound pressure levels.

CONVERSION DATA

The primary output from the experiments was the fuel conversion. The fuel conversions calculated from the transient experiments are tabulated below in Table 1 along with the overall averages and standard deviations. After completion of the initial experiments using the chemical grade methanol it was determined that four data points was not necessary and thus for all remaining reformer settings only three points were collected.

Table 1: Conversions of transient experiments

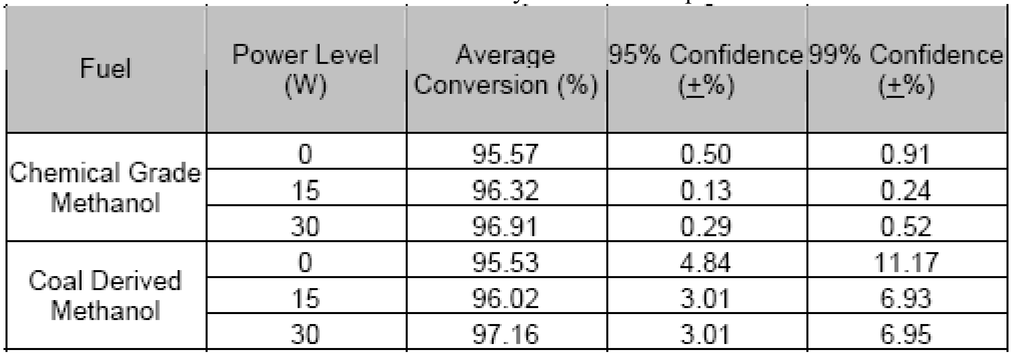
Fuel	Power Level (W)	Conversion (%)				Average Conversion (%)	Standard Deviation
		Run 1	Run 2	Run 3	Run 4		
Chemical Grade Methanol	0	95.48	95.4	95.75	95.63	95.57	0.156
	15	96.34	96.35	96.31	96.26	96.32	0.040
	30	97.03	96.82	96.87	96.9	96.91	0.090
Coal Derived Methanol	0	96.58	95.66	94.34	-	95.53	1.126
	15	96.67	95.28	96.1	-	96.02	0.699
	30	97.86	97.17	96.46	-	97.16	0.700

As expected we see higher standard deviations for the coal-derived methanol, which is attributed to higher rates of degradation. However, it is apparent that the addition of acoustics to the reformer resulted in greater overall conversion, and created less deviation in the case of both fuels most likely due to lessened thermal gradients. The statistical accuracy of the measured conversions was derived using the student-t distribution. The 95% and 99% confidence range was calculated using Equation 1, where C% is the percent conversion $t_{v,p}$ is the student-t distribution, and S_x is the standard deviation.

$$C\% = \overline{C}\% \pm t_{v,p} S_x \tag{1}$$

Results of the two confidence levels for the transient experiments can be seen in Table 2 below.

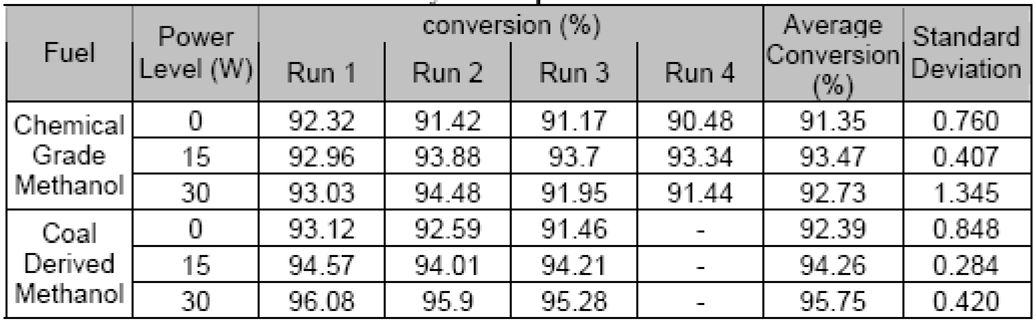
Table 2: Statistical accuracy of transient experiments



Fuel	Power Level (W)	Average Conversion (%)	95% Confidence (±%)	99% Confidence (±%)
Chemical Grade Methanol	0	95.57	0.50	0.91
	15	96.32	0.13	0.24
	30	96.91	0.29	0.52
Coal Derived Methanol	0	95.53	4.84	11.17
	15	96.02	3.01	6.93
	30	97.16	3.01	6.95

As stated previously in order to provide a comparison for improvements in the transient response steady state runs were performed to yield a base line of comparison. It was expected that the steady state conversions at a flow rate of 2.5 ml/min would be 100%. Two runs were performed at a flow rate of 2.5 ml/min without acoustics and verified this assumption. The addition of acoustics can only improve the process so no further runs were performed. A series of runs using a flow rate of 7.5 ml/min with each of the fuels, and at each of the various acoustical settings were performed. The conversions derived from the steady-state experiments as well as their collected averages and standard deviations are displayed below in Table 3.

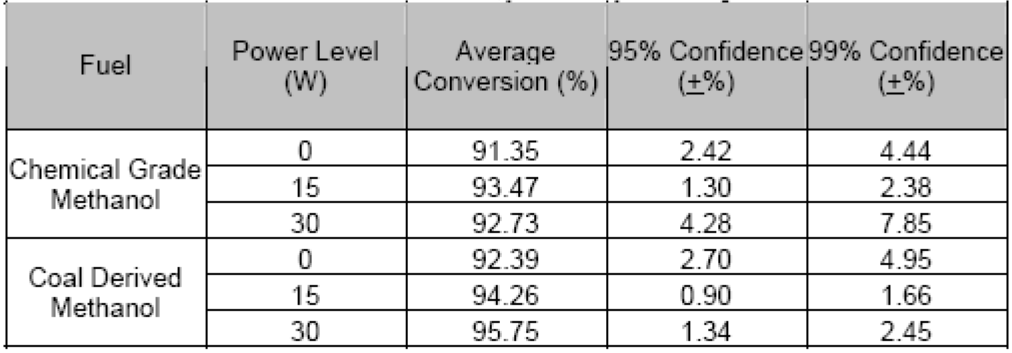
Table 3: Conversions of steady state experiments at a flow rate of 7.5 ml/min



Fuel	Power Level (W)	conversion (%)				Average Conversion (%)	Standard Deviation
		Run 1	Run 2	Run 3	Run 4		
Chemical Grade Methanol	0	92.32	91.42	91.17	90.48	91.35	0.760
	15	92.96	93.88	93.7	93.34	93.47	0.407
	30	93.03	94.48	91.95	91.44	92.73	1.345
Coal Derived Methanol	0	93.12	92.59	91.46	-	92.39	0.848
	15	94.57	94.01	94.21	-	94.26	0.284
	30	96.08	95.9	95.28	-	95.75	0.420

There was a severe and unexplainable drop in the conversion of the chemical grade methanol with 30 Watts of acoustical power. Runs two through four were taken directly after one another as dictated by the randomization of experiment order. It is possible that this drop is due to a sound pressure level drop in the reactor brought on by a shift in the catalyst bed. The statistical accuracy of the measured conversions of the steady-state experiments was also calculated using the student-t distribution as described above. The results of the accuracy calculations can be seen in Table 4 below.

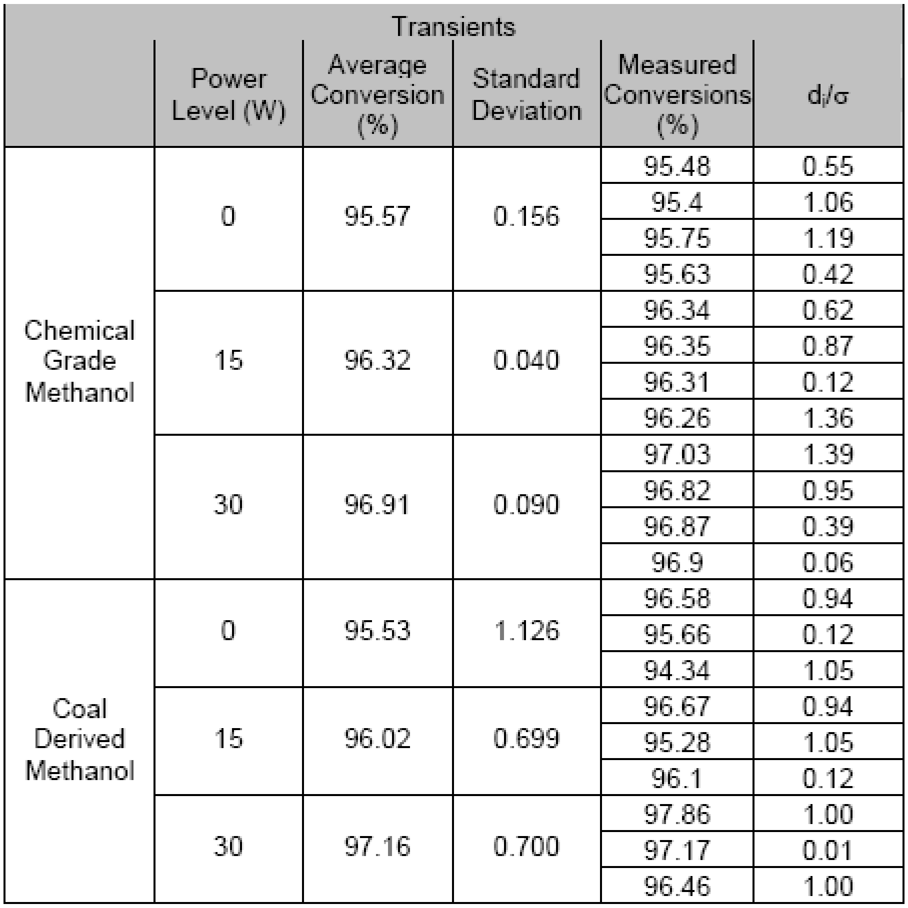
Table 4: Statistical accuracy of steady state experiments



Fuel	Power Level (W)	Average Conversion (%)	95% Confidence (±%)	99% Confidence (±%)
Chemical Grade Methanol	0	91.35	2.42	4.44
	15	93.47	1.30	2.38
	30	92.73	4.28	7.85
Coal Derived Methanol	0	92.39	2.70	4.95
	15	94.26	0.90	1.66
	30	95.75	1.34	2.45

After evaluating the standard deviation and statistical accuracy of the steady state and transient conversion data the validity of the data was questioned due to a larger standard deviation than had been expected. Chauvenet's criterion was thus used to test the validity of the measured data. The criterion specifies that a reading may be rejected if the probability of obtaining the particular deviation from the mean is less than 1/2n, where n is the number of data samples. For the data series where four data points were collected the ratio of the maximum acceptable deviation to standard deviation is 1.54, and for three data point sets that ratio would be 1.38. Table 5 shows the calculated ratios of the variance in the percent conversion from the mean to the standard deviation (d_i/σ) for the transient experiments.

Table 5: Calculation of the ratio of variance of conversion to standard deviation for transient experiments



Transients					
	Power Level (W)	Average Conversion (%)	Standard Deviation	Measured Conversions (%)	d_i/σ
Chemical Grade Methanol	0	95.57	0.156	95.48	0.55
				95.4	1.06
				95.75	1.19
				95.63	0.42
	15	96.32	0.040	96.34	0.62
				96.35	0.87
				96.31	0.12
				96.26	1.36
	30	96.91	0.090	97.03	1.39
				96.82	0.95
				96.87	0.39
				96.9	0.06
Coal Derived Methanol	0	95.53	1.126	96.58	0.94
				95.66	0.12
				94.34	1.05
	15	96.02	0.699	96.67	0.94
				95.28	1.05
				96.1	0.12
	30	97.16	0.700	97.86	1.00
				97.17	0.01
				96.46	1.00

TRANSIENT RESPONSE EVALUATION

To provide a baseline of comparison for the transient response an approximated average conversion that would be expected from a perfectly responding reformer was calculated. This was done for each of the acoustical and fuel purity settings using Equation 1 the baseline data presented above, where t is the time between changes in flow (10 min), $\overline{\%C}_{2.5,SS,a}$ is the percent conversion at a steady state flow rate of 2.5 ml/min for each of the individual acoustical settings (determined to be 100%), and $\overline{\%C}_{7.5,SS,a}$ is the percent conversion at a steady state flow rate of 7.5 ml/min for each of the individual acoustical settings (taken from Table 3).

$$\overline{\%C}_{ideal} = \frac{2t\overline{\%C}_{2.5,SS,a} + 2t\overline{\%C}_{7.5,SS,a}}{4t}$$

These idealized conversions are displayed in Table 6 where the difference between the idealized conversions and the actual conversions is also tabulated. It was expected that the difference between the actual and idealized averages would decrease incrementally as acoustical power was added. However, from the data presented below this is not the case.

Table 6 Comparison of actual conversions to idealized conversions

Fuel	Power Level (W)	Average Conversion (%)	Idealized Conversions	Difference
Chemical Grade Methanol	0	95.57	95.67	0.11
	15	96.32	96.74	0.42
	30	96.91	96.36	-0.54
Coal Derived Methanol	0	95.53	96.20	0.67
	15	96.02	97.13	1.12
	30	97.16	97.88	0.71

The importance of further advancements in fuel reformer technology was set forth if fuel cell vehicles are to see commercial use. Improvements in the transient response of steam reformers was identified as an important goal that will aid in bridging the gap between traditional IC engine and fuel cell powered vehicles. The use of acoustic pressure waves as a method of enhancing transient response time was investigated. In order to evaluate the improvement gained an adapter was fitted to the bottom of a catalyst bed housing which connected an acoustic compression driver to the system. The flow rate of the reformer was varied from 2.5 ml/min to 7.5 ml/min as a square wave with a period of 20 minutes. The frequency of the dominant standing wave was determined and introduced into the reformer at two different power levels. Fuel purity was also evaluated to determine if methanol derived from coal would have varied transient effects. The data collected evaluated the response by a comparison of averaged conversion over two cycles, which was then compared to the calculated average conversion of a perfectly responding reformer. In addition to an evaluation of the conversions, analysis of the catalyst bed temperature fluctuations were made.

The addition of a resonating acoustic standing wave proved to enhance overall conversion of the fuel, but was inconclusive with respect to an increase in transient response for either methanol grade. However, an analysis of the temperature fluctuations inside the catalyst bed shows lessened thermal gradients across the diameter of the catalyst bed indicating an increase in the heat transfer rate coefficient. Upon further analysis of the temperature readings of the exterior and interior catalyst bed walls it was determined that the temperature slope set point of the controls scheme was limiting the heat flux into the catalyst bed thus hindering the improved response that was expected.

From the data collected it is evident that the addition of a resonating acoustic wave inside of the catalyst bed of a steam reformer does result in increased heat transfer and thus should shorten the time constant of the transient response. Although the acoustic enhancement causes an increase in heat transfer it is important that the temperature controls scheme of the steam reformer be adjusted to take full advantage of the improvement. The experiments utilizing coal-derived methanol showed a similar transient response to that of the chemical grade methanol. There were larger temperature fluctuations observed inside the catalyst bed during the experiments with coal-derived methanol, and an increased rate of catalyst deactivation that made it difficult to show the improvements in response time accomplished by the addition of the acoustic standing wave.

RECOMMENDATIONS

The results of this study suggest that acoustics can be one method for improving transient response times of steam reformers, but there is much more work that needs to be done if small scale reformers are to become widely used. As explained in chapter 2 it is believed that the dominant effect of the acoustic wave is that of an increased, and oscillatory, flow velocity yielding better heat transfer. In addition to heat transfer the pressure wave may also have a substantial impact on the mass transfer of the system moving reactants and reformate in and out of catalyst sites. Experiments should be run to quantify the contribution of both of these mechanisms of acoustic enhancement to steam reformation. Since the frequency and length of the reformer is known the pressure and velocity nodes and antinodes can be easily determined. By comparing conversions with catalyst alternately placed at these nodes or antinodes, the magnitude of the contributions can be observed.

Just as important as the heat transfer within the catalyst bed is the heat supplied externally to the wall. Too much heat at the wall can sinter the catalyst; whereas too little heat in the center of the bed can cause coking. Improved heat transfer helps to reduce these gradients and simplify controls. Also observed was that during low flow operation the catalyst bed temperatures rose driving the water-gas shift reaction in the opposite direction. Further work needs to be done on temperature control schemes for steam reformers to optimize heat flux during transients, and optimize the wall temperatures so that sintering at the wall and coking in the center is avoided. The current catalyst bed employs the use of 14 thermocouples for the thermal controls although a commercialized reformer might only be afforded one or two. Therefore it is important that the operation of the reformer be well characterized with respect to the heat requirements per location for a given reactor geometry and flow rate.

Fluctuations in the sound pressure level of the catalyst bed were observed during reforming with the addition of acoustics. This was due to changes in temperature and gas composition. It is expected that a greater impact from the acoustics could be achieved if a feed back control were employed to periodically calculate the transfer function magnitudes with respect to the catalyst bed conditions and adjust the frequency accordingly. Aside from the active method of increasing heat transfer by the super-position of an acoustic wave there are other passive forms that should be evaluated under transient operation. Work has been performed in the Hydrogen Production and Utilization Lab using bluff bodies (alternating disk and rings) as a passive method of increasing conversion. There are also studies planned for evaluating operation of the steam reformer with the placement of a twisted tape down the central axis of the catalyst bed. It has been shown that by crushing the catalyst pellets and increasing the available surface area that greater conversion is achieved due to the greater availability of catalyst sites. These simple methods could all serve to greatly improve the transient response.

Further transient analysis of the coal derived methanol is called for to determine why the temperature fluctuations are greater (albeit slightly) than those observed by the chemical grade methanol. In particular it would be interesting to analyze the reformate gas composition to determine if there are any other reactions taking place that might contribute to the temperature change. With the contribution from this and ongoing research it is expected that we will see fuel cell vehicles come to commercialization more expeditiously.

Heat Transfer Enhancement

From a quick observation of the results shown in Figure 7, conclusions can be made about heat transfer enhancement and percent conversion. Reactor C, loaded with crushed catalyst, obviously reached greater conversion than Reactor A, loaded with pelletized catalyst. In the lower flow rate case, Reactor A, loaded with crushed catalyst, had better conversion than Reactor C. However, after around 0.0025 contact time, the conversion of Reactor C showed much greater conversion percentage than Reactor A. .

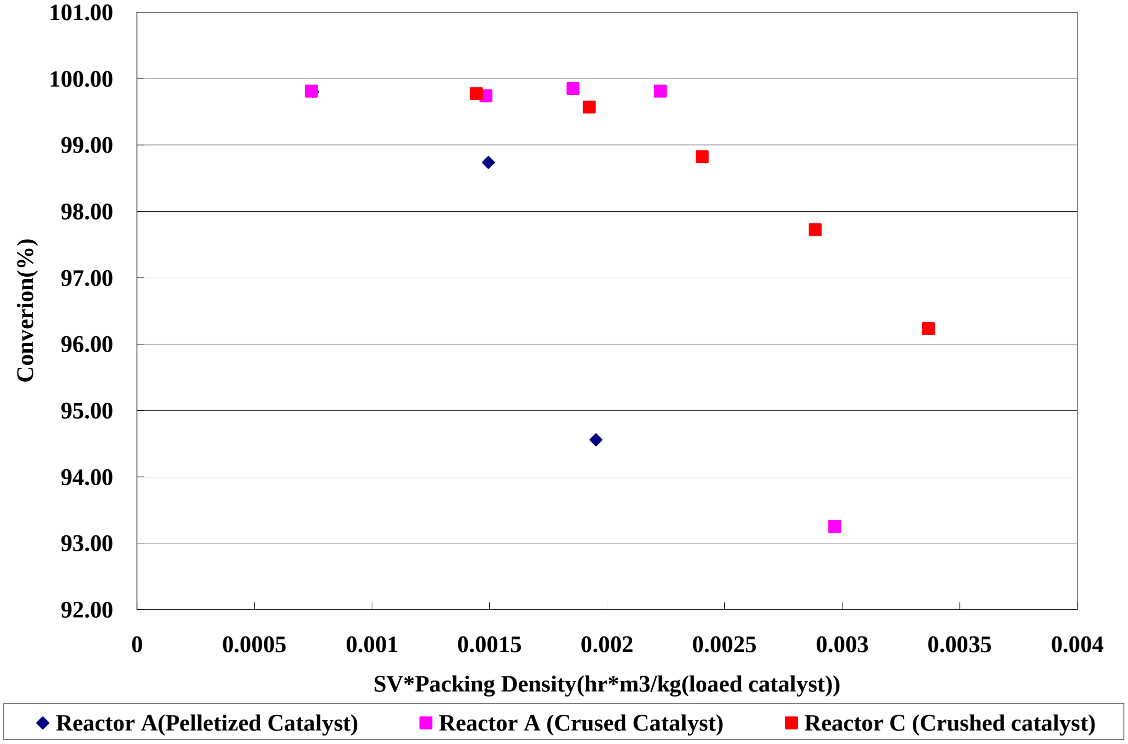


Figure 7 Conversions of methanol in case of Reactor A and Reactor C

Heat and mass transfer limitations are well-known drawbacks occurring from hydrogen production via steam reformation. Another significant problem is the condensation of bulk gas onto the solid phase catalyst. This effect of condensation can grow gradually as flow rate increases. It can also develop severe thermal gradients inside the reactor. For example, when LHSV-M increased, the cold region along the centerline due to the condensation of bulk gas increased in length, as shown in Figure 8. Additionally, the cold region can be formed from the endothermic methanol reduction. However, condensate formation due to heat transfer limitations had a much greater effect than the endothermic chemical reaction on the cold region formation.

1.02-LHSV-M 99.8% 2.05 LHSV-M 98.65% 3.07 LHSV-M 92.71% 4.09 LHSV-M 89.39%

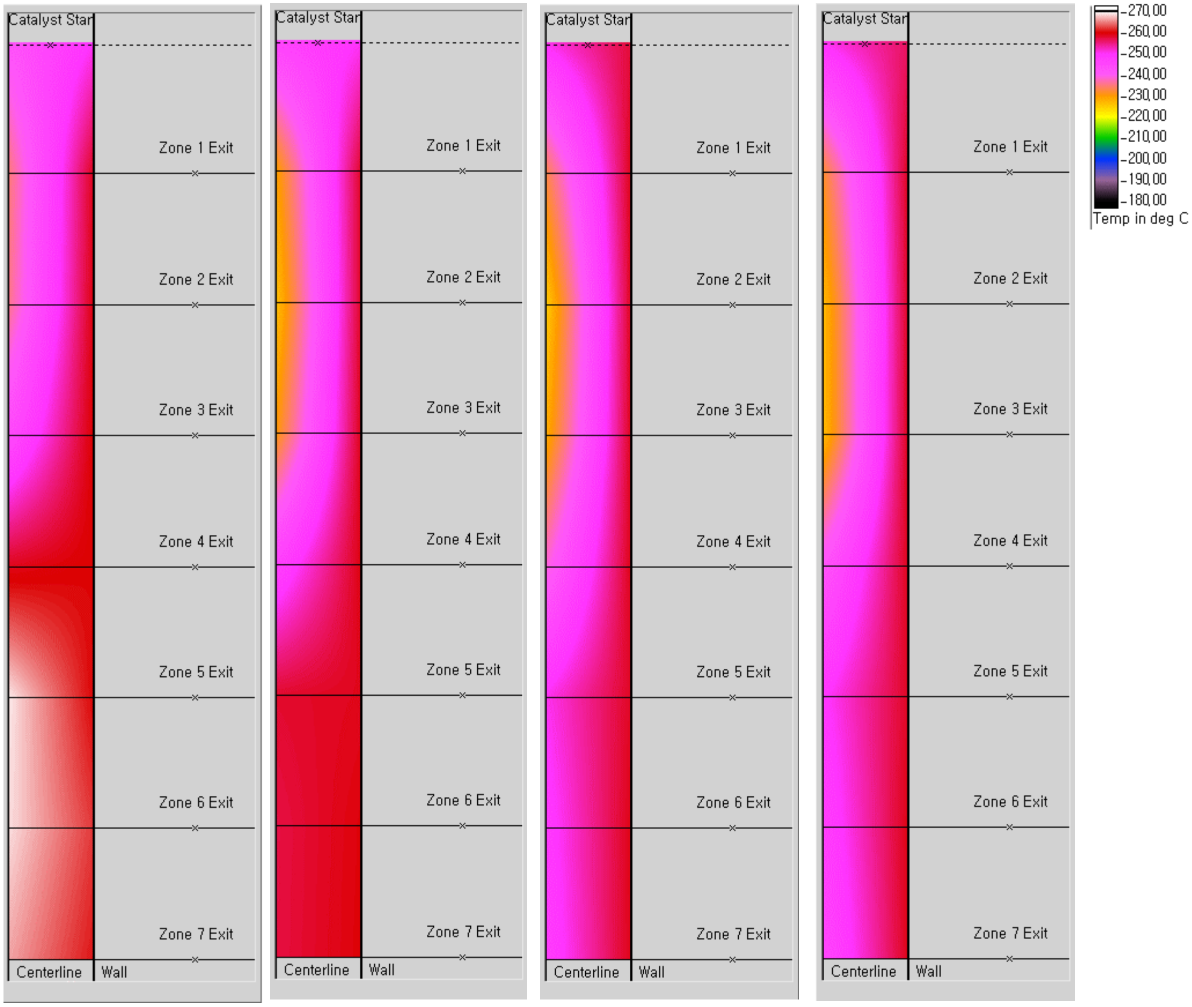


Figure 8: Temperature profile in the Reactor A with pellitized catalyst

Thermal and concentration gradients also developed proportionally inside Reactor A. The concentration of hydrogen is much greater along the reactor centerline due to the endothermic nature of methanol reformation and heat is supplied externally from outside the reactor. For the 1 and 2 LHSV-M cases, the centerline temperature become closer to the wall temperature after zone 3 and 4, respectively. The previously described result occurred from mass transfer. In the

1 LHSV-M case, the centerline temperatures of zone 6 and 7 are much hotter than the inside of the wall. Hydrogen mass transfer (i.e. products) due to the hydrogen concentration gradients in the reactor caused this result, because mass transfer can directly affect heat transfer. However, heat transfer cannot directly affect mass transfer.

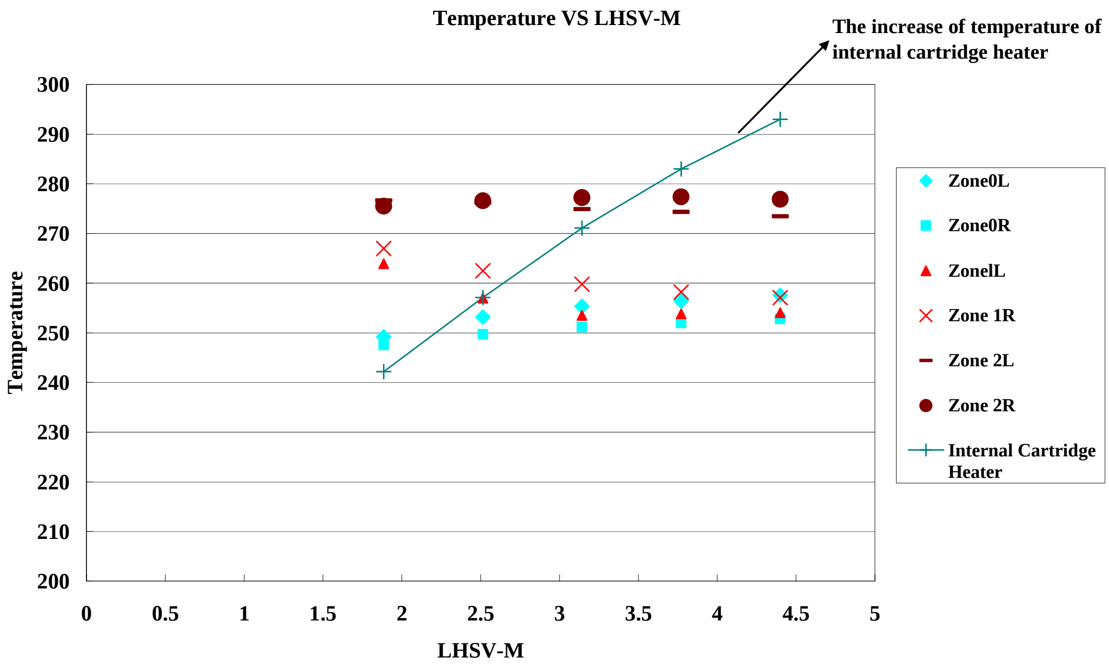


Figure 9: Averaged temperatures of different zones in Reactor C

As shown in Figure 9, the bulk gas condensation affected the internal cartridge heater temperature. To maintain a temperature difference of less than 5 C^{o} between the inside wall and centerline, the internal cartridge heater set-point temperature was intentionally increased as LHSV-M was increased.

Catalyst Degradation Test Results

As shown in Figure 10, the degradation rate of coal-derived methanol was greater than that of chemical grade methanol for both reactors, in terms of fuel. However, reactor geometry apparently has a much greater affect on percent convergence than the affect of fuel type. Even though Reactor B has been loaded with nearly six times more crushed catalyst than Reactor C, the degradation rate of Reactor B was much larger than Reactor C. Consequently, it can be concluded that reactor geometry has a greater affect on catalyst aging than fuel impurities.

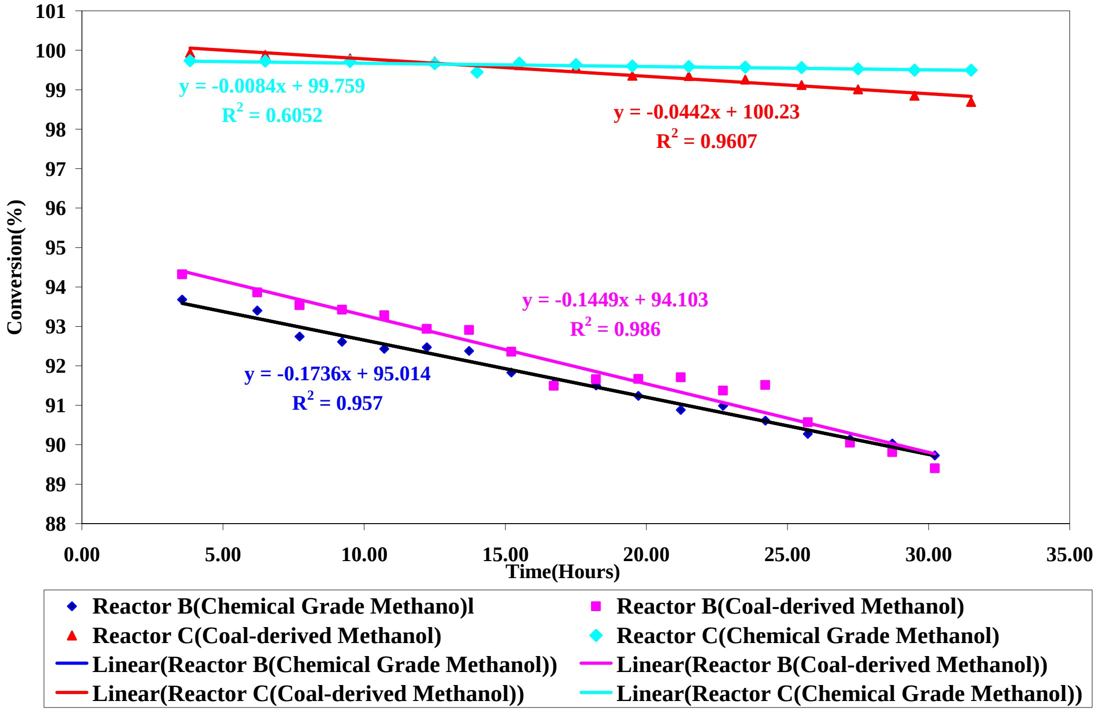


Figure 10: catalyst degradation both coal-derived and chemical grade methanol for different geometries.

Catalyst Degradation with Bluff Bodies

A 30-hour run with a premix flow rate of 12.5 ml/min (2.5 LHSV-M) was conducted using the coal-derived methanol and eight bluff body packages. The fuel conversion vs. running time data was collected and shown in Figure 11.

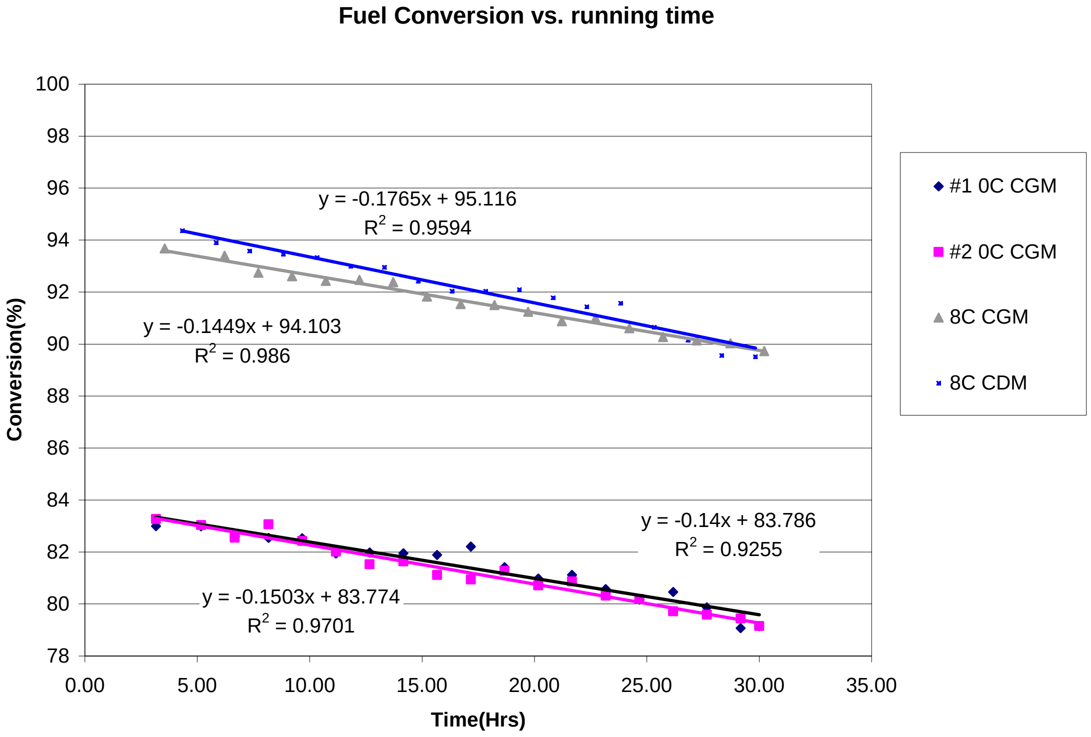


Figure 11: Fuel conversion percentage vs. running time with and without bluff bodies using chemical-grade methanol (CGM) and coal-derived methanol (CDM)

The initial fuel conversion of coal-derived methanol was larger than that of chemical grade methanol due to different hydrocarbon concentrations in the two methanol fuels. More detail of the different hydrocarbon concentrations in the two fuels was discussed in the first annual report. As expected, the degradation rate for coal-derived methanol (-0.1765 %/hr with blue line) is larger than that for chemical grade methanol (-0.1449 %/hr gray line).
Table 7 shows the degradation rates for the two methanol fuels and reactor geometries:

Table 7: degradation rates (conversion % per hour) with different methanol fuels and reactor geometries

	Chemical Grade Methanol	Coal Derived Methanol
Reactor B (0C)	-0.1452	N/A
Reactor B (8C)	-0.1449	-0.1765
Reactor C (internal cartridge heater)	-0.02196	-0.1065

The data showed the degradation rate of Reactor B loaded with eight bluff body packages was 6.6 times larger (0.1449/0.02196) than the degradation rate of Reactor C with chemical grade methanol. The degradation rate of Reactor B (8C) using coal-derived methanol was 1.2 times (0.1765/0.1449) greater than Reactor B (8C) using chemical grade methanol. Again the reactor geometry was demonstrated to outweigh the fuel option effects on catalyst degradation. In contrast, the fuel option had a larger effect on the degradation rate (0.1765/0.1449=1.22) of Reactor (8C) than that of bluff bodies (0.1452/0.1449=1.002) on Reactor B.

In Figure 12, the centerline temperature inside the reactor again shows the catalyst degradation rate difference between CGM and CDM.

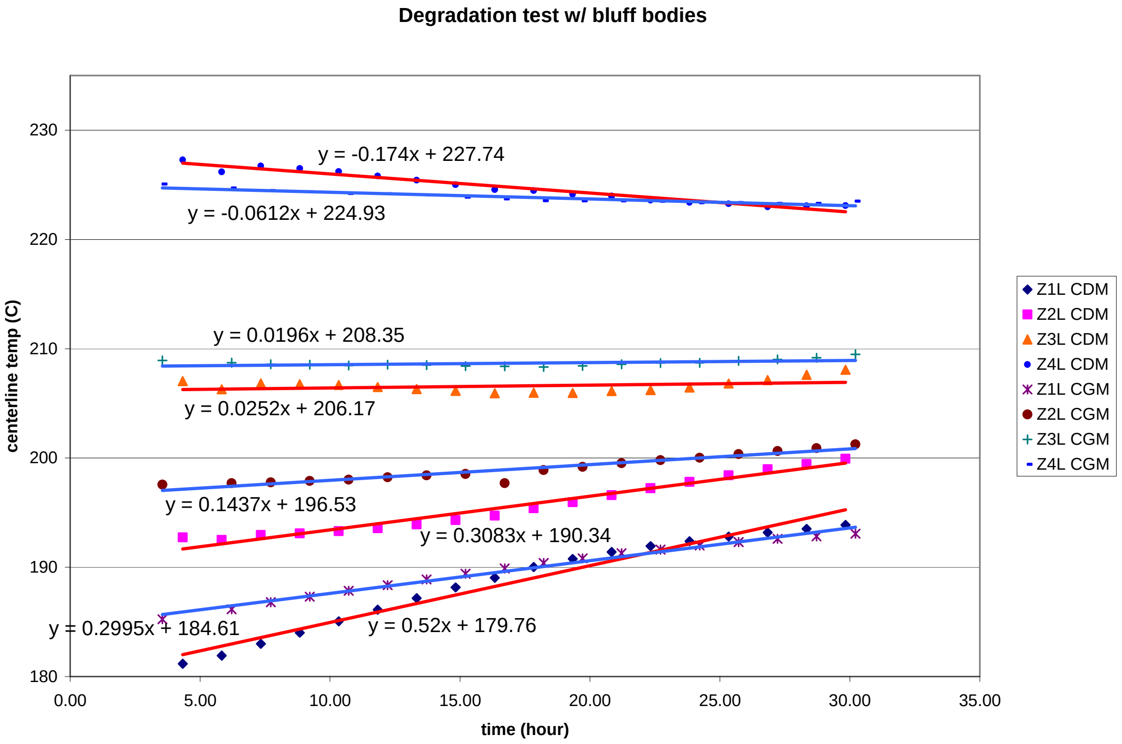


Figure 12: Centerline temperatures vs. running time at different axial positions with 8 packs of bluff bodies using CGM and CDM.

The red lines represent the data trend line for coal-derived methanol and the blue lines represent the data trend lines for chemical grade methanol. As expected, the slopes of the red lines at zone 1 and zone 2 are about 1.5 to 2 times greater than that of the blue lines. This again indicates that the higher hydrocarbon concentrations in the coal-derived methanol might cause a faster deactivation rate compared to chemical grade methanol.

The experiment with reactor B (0C) using coal derived methanol will be taken in the next quarter to give a more comprehensive comparison among the effects of different methanol fuels and reactor geometry. Additionally, the reactor operating temperature is expected to have an important influence on degradation rate. To investigate the effect, the set-point temperature will be set at higher value.

Autothermal Reforming of Coal-Derived Methanol

Progress was made in preparing for Autothermal reformatting of coal derived methanol through mixing. The goal of the mixing procedures is to determine how oxygen, water and fuel play a role in the reformation of coal derived methanol. The three mediums will be mixed at different points in the reformation process. The conversion percentage from each mixing will reveal the most efficient way to reform coal derived methanol. The additional infrastructure was completed and the facilities at the Hydrogen Utilization and Production Lab are prepared complete the experiments.

This quarter initial experiments were conducted using coal-derived methanol in the new infrastructure. Unfortunately the initial experiments led to large carbon deposits on the stainless steel piping when pure coal-derived methanol was used for mixing. Currently research is underway to investigate the cause of the large amount of carbon deposits. The current hypothesis is that pure methanol may react with the stainless steel at high temperatures to form carbon deposits. This effect has not occurred before, because before the ATR mixing experiments the methanol was premixed with water to maintain a steam to carbon ratio at a constant 1.5:1 molar ratio. If pure methanol reacts with the stainless steel infrastructure and a premix of water and methanol does not, the minimum amount of water to be added to the methanol water premix will be determined to prevent the carbon deposits from forming.

CONCLUSION

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.

From the conversion data it does not appear that the addition of acoustics had a significant effect on the transient response of steam reformation. However, the information presented in this chapter shows that the improvement in heat transfer is evident and that a restriction by the control program was the limiting factor restricting the amount of heat supplied to the reformer. The coal-derived methanol had a similar transient response to that of the chemical grade methanol, and the overall conversion of both fuels was increased by the addition of the acoustics as expected.

Coal-derived methanol can serve as a clean form of coal use, and afford the introduction of indirect liquid fuelled fuel cell vehicles that could also serve as a path to consumer acceptance of fuel cell vehicles in general. The transient experiments using coal-derived methanol had a very similar response to that of the chemical grade methanol. The only differences observed were higher catalyst deactivation rates; slightly larger temperature variations and a small amount of reformate stream dilution. Further experiments need to be performed to evaluate the source of the temperature variations, although it could be due to the higher order hydrocarbons reacting under some unknown conditions.

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 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. This quarter reactor geometry was investigated as a possible means to improve heat transfer. From the analysis, the addition of an internal cartridge heater improved methanol convergence and decreased catalyst degradation. When LHSV-M increased, the cold region along the centerline due to the condensation of bulk gas increased in length, as shown in Figure 8. Additionally, the cold region can be formed from the endothermic methanol reduction. However, condensate formation due to heat transfer limitations had a much greater effect than the endothermic chemical reaction on the cold region formation. Further research will be done on reactor geometry, heat transfer and how catalyst degradation can be reduced.

Further analysis of catalyst degradation with bluff bodies was completed. The data showed degradation rate of Reactor B loaded with eight bluff body packages was 6.6 times larger than the degradation rate of Reactor C with chemical grade methanol. The degradation rate of Reactor B (8C) using coal-derived methanol was 1.2 times greater than Reactor B (8C) using chemical grade methanol. Again the reactor geometry was demonstrated to outweigh the fuel option effects on catalyst degradation. In contrast, the fuel option had a larger effect on the degradation rate (1.22 time lager) of Reactor B (8C) than that of bluff bodies (1.002 time larger) on Reactor B. The bluff bodies are able to increase the conversion rate of methanol and at the same time have limited affect on catalyst degradation rate. The use of bluff bodies in a reactor could compensate for the noted decrease in methanol convergence of coal-based methanol compared to chemical grade methanol. Research will continue next quarter to further investigate the relationship between degradation and bluff bodies.

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 O_2/C ratio was initiated. The current ATR research involving mixing of air, fuel and water is currently stalled as we are investigating the causes of the carbon build up inside the fuel vaporizer fuel train. The current hypothesis is that the fuel is reacting with the stainless steel. We have not observed this before, because a methanol and water premix is normally used. We plan to correct the problem and to continue on with the research as planned. Next quarter we are planning on investigating the affect of bluff bodies on ATR.

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, and measuring catalyst degradation using the various methanols. We also plan to evaluate various clean-up options for reformate and how to direct the clean hydrogen stream to the PEM fuel cell.

REFERENCES

[1] Beerman, M.J., Evaluation Of The Use Of Acoustic Waves For Improving The Transient Response Of Steam Reformers, masters thesis, University of California, Davis, CA, 2005

[2] Erickson, P.A., Enhancing the Steam-Reforming Process with Acoustics: An Investigation for Fuel Cell Vehicle Applications, doctoral dissertation, University of Florida, Gainesville, FL, 2002

[3] Davieau, D.D., An Analysis of Space Velocity and Aspect Ratio Parameters in Steam-Reforming Hydrogen Production Reactors, masters thesis, University of California, Davis, CA, 2004

[4] Dorr, J.L., Methanol Autothermal Reformation: Oxygen-to-Carbon Ratio and Reaction Progression, masters thesis, University of California, Davis, CA, 2004

[5] Dorr, J.L., and Erickson, P.A., Preliminary Modeling and Design of an Autothermal Reformer, 2004 International Mechanical Engineering Congress and Exposition, Anaheim, CA, November 2004, IMECE2004-5989