

HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

41850R10.pdf

Quarterly Technical Progress Report

Reporting Period Start Date: January 1, 2006

Reporting Period End Date: March 31, 2006

Principal Author: Paul A. Erickson

Report Issue Date: April 2006

DOE Award Number: DE-FC26-03NT41850

Submitting Organization:

The Regents of the University of California, Davis

One Shields Avenue

Davis, California 95616

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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 tenth 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, 2006. This quarter saw progress in six areas. These areas are:

1. The effect of catalyst dimension on steam reforming,
2. Transient characteristics of autothermal reforming,
3. Rich and lean autothermal reformation startup,
4. Autothermal reformation degradation with coal derived methanol,
5. Reformate purification system,
6. Fuel cell system integration.

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

TABLE OF CONTENTS

DISCLAIMER	2
ABSTRACT.....	3
TABLE OF CONTENTS.....	4
EXECUTIVE SUMMARY	5
EXPERIMENTAL.....	7
The Effect of Catalyst Dimension on Steam Reforming	7
Transient Characteristics of Autothermal Reforming.....	8
Rich and Lean Autothermal Reformation Startup	9
Autothermal Reformation Degradation with Coal-Derived Methanol	9
Reformate Purification System.....	11
Fuel Cell System Integration	14
RESULTS AND DISCUSSION.....	17
The Effect of Catalyst Dimension on Steam Reforming	17
Transient Characteristics of Autothermal Reforming.....	18
Rich and Lean Autothermal Reformation Startup	20
Autothermal Reformation Degradation with Coal-Derived Methanol	21
Reformate Purification System.....	22
Fuel Cell System Integration	24
CONCLUSION.....	25
REFERENCES	26

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 tenth 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, 2006.

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 six areas. These areas are:

1. The effect of catalyst dimension on steam reforming,
2. Transient characteristics of autothermal reforming,
3. Rich and lean autothermal reformation startup,
4. Autothermal reformation degradation with coal derived methanol,
5. Reformate purification system,
6. Fuel cell system integration.

The investigation regarding the effect of catalyst dimension on steam reforming performance has continued this quarter. The pelletized, or original sized catalyst was compared to crushed catalyst of 0.25 cm average diameter, and catalyst powder. For each case, 250 grams of catalyst was used with and without eight bluff body packages. The results show that the powdered catalyst can increase the methanol conversion by almost 10% over crushed catalyst, and 20% over pelletized catalyst at 4.0 LHSV-M. This shows the importance of the diffusion limitation in reforming coal derived methanol. If expecting to maximize the conversion one must have as small a catalyst particle as possible.

To optimize the methanol to hydrogen pathway via autothermal reformation, fundamental studies such as light-off (transient behavior) and the effects of steam to carbon and oxygen to carbon ratios should be investigated. Heat loss due to radiation from the oxidation region is significant for autothermal reformation. To reduce radiation loss, an inert material was inserted into the autothermal reformer. A 1.0 inch long, circular monolithic material, mainly composed of Al_2O_3 , was used as the inert material for the tests and was located above the autothermal catalyst surface. The transient response with the inert material was compared to the reformer transient response without the inert material. The results show that catalyst surface temperature without inert material is close to the catalyst surface temperature with inert material at O_2/MeOH ratios equal to 0.27. Consequently, a 0.27 O_2/MeOH ratio would be the optimal operating condition in the case without inert material. On the other hand, a 0.22 O_2/MeOH ratio could be the optimized operating condition with inert material. Gas analysis is needed to confirm these results.

To examine the effect of O₂/MeOH ratio on autothermal reformation transients, two different ATR start up processes which are fuel rich and fuel lean start up were defined. In the case of fuel lean startup, premix vapor (~250°C) flows into the reactor one minute after hot air (~250°C) is introduced so fuel can be oxidized in an air rich environment. On the other hand, in the case of fuel rich start up, air was introduced into the reactor one minute after premix fuel gas enters the reactor so oxidation takes place in a fuel rich environment. The transient time of lean fuel startup was shorter than that of fuel rich startup. The results indicate that fuel lean startup would be preferred over fuel rich startup in that deposited components on the surface of catalyst, such as carbon, can be burnt off during a fuel lean startup process. Removing the deposits off the surface of the catalyst could improve catalyst activity, and reduce catalyst degradation.

Previous reports have shown steam reformation catalyst degradation. The degradation presents limited lifetime issues. To determine the lifetime of the autothermal catalyst, degradation tests similar to those performed previously for steam reformation were completed. Results were confirmed from previous indications in the ninth quarterly report (October-December 2005) that autothermal reforming of coal-derived methanol has lower degradation rates than steam reforming of coal-derived methanol due to the higher operating temperature attained in autothermal reformation.

Since PEM fuel cells require high quality hydrogen as its fuel, a clean up system is necessary to purify the hydrogen rich reformat after exiting a reformer. One purifying process for hydrogen production includes a water-gas-shift reaction, and a palladium membrane separation. In this quarter, a palladium membrane separation unit was purchased and has been integrated into a purifying system to produce 99.95% pure hydrogen reformed from coal-derived methanol.

The purified hydrogen stream will be used to fuel a PEM fuel cell. The Hydrogen Production and Utilization Lab is using a Ballard Nexa® stack from the Hybrid Vehicle Propulsion Systems Laboratory at UC Davis. The fuel cell will demonstrate a hydrogen production pathway from coal-derived methanol for fuel cell applications.

While the main thrust of the work is progressing toward the demonstration of the fuel cell operating from coal derived methanol as outlined in the original proposal, further work on previous topics has expanded as well. Once the whole pathway is running the data will be compared against a steam and autothermal reforming model which has been developed.

EXPERIMENTAL

The following section describes the experimental methods used and developed during the reporting period for the following areas: the effect of catalyst dimension on steam reforming, transient characteristics of autothermal reforming, rich and lean autothermal reformation startup, autothermal reformation degradation with coal-derived methanol, reformat purification system, and the fuel cell system integration.

The Effect of Catalyst Dimension on Steam Reforming

The investigation regarding the effect of catalyst dimension on steam reforming performance has continued this quarter. The pelletized, or original sized catalyst was compared to crushed catalyst of 0.25 cm average diameter, and catalyst powder. The crushed catalyst went through a series of two screens: a large mesh (64 squares per inch, 0.03 in wire dia.) and a small mesh (256 squares per inch, 0.015 in wire dia.) The catalyst powder was separated from the larger catalyst pieces after being crushed. This quarter the catalyst powder was compared with pelletized and crushed catalyst with eight packs of BB1 type bluff body (small ring and large disk, in annual report). Figure 1 shows the dimensions of the small, medium and large rings and disks. Since the powder particle was smaller than the mesh supporting the catalyst in the reactor, 10 grams of crushed catalyst was packed before the powder to prevent the powder from falling down through the mesh. In each case 250 grams of catalyst was used. In the ninth technical report (October-December 2005), the experimental configuration of a smaller dimension catalyst (referred to as powder catalyst) with eight packages of bluff bodies was tested to investigate the effect of catalyst dimension and its' contribution to increased mass transfer.

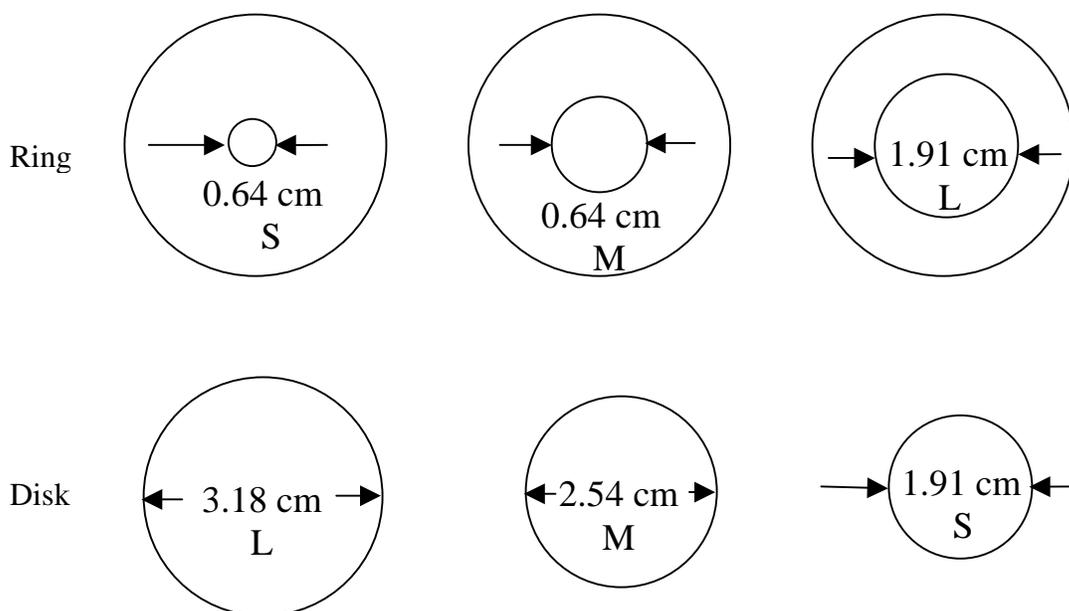


Figure 1: Ring and Disk Dimensions

Transient Characteristics of Autothermal Reforming

To optimize the methanol to hydrogen pathway via autothermal reformation, fundamental studies such as light-off (transient behavior) and the effects of steam to carbon and oxygen to carbon ratios should be investigated. Heterogeneous catalytic combustion light-off is a function of inlet gas temperature and oxygen to carbon ratio. Zone 3L and Zone 4L indicate the centerline temperatures above the monolithic catalyst surface. Heat loss due to radiation from the oxidation region was significant for autothermal reformation. To reduce the radiation loss, an inert material was inserted into the autothermal reformer. A 1.0 inch long, circular monolithic material, mainly composed of Al_2O_3 , was used as the inert material for the tests and was located above the autothermal catalyst surface. The transient response with the inert material was compared to the reformer transient response without the inert material.

The catalyst wafer (high grade autothermal washcoated) with a 3.5cm diameter by 3.4cm in length (1.38" x 1.34") was placed in the autothermal reformer shown in Figure 2. The reformer design allows various positions for the catalyst. The temperatures can be monitored in the defined zones as well.

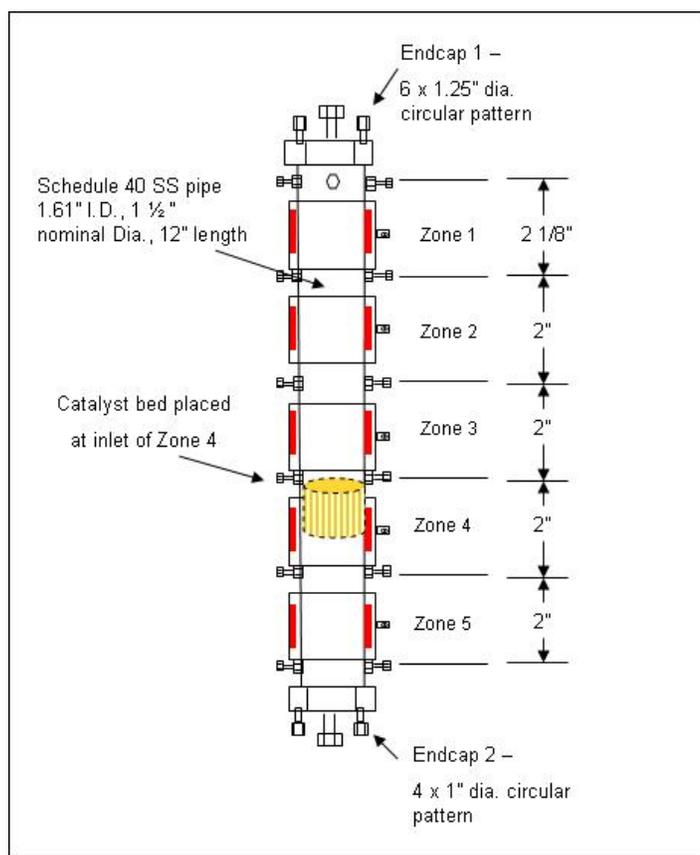


Figure 2: Schematic of ATR Reactor

Figure 3 shows the location of the three thermocouples monitoring the catalyst temperatures. One thermocouple monitors the catalyst surface temperature, the next monitors the temperature at the midpoint and the third monitors the catalyst temperature $\frac{3}{4}$ of the way through the catalyst.

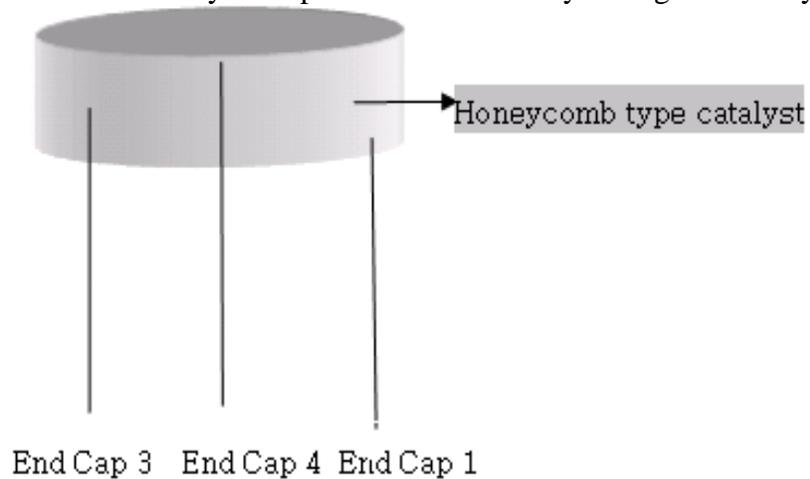


Figure 3: The location of end-cap thermocouples

Rich and Lean Autothermal Reformation Startup

To examine the effect of $O_2/MeOH$ ratio on autothermal reformation transients two different ATR startup processes which are fuel rich and fuel lean startup can be defined. In the case of fuel lean startup, premix vapor ($\sim 250^\circ C$) flows into the reactor one minute after hot air ($\sim 250^\circ C$) is introduced so fuel can be oxidized in an air rich environment. On the other hand, in the case of fuel rich start up, air is introduced into the reactor one minute after premix fuel gas enters the reactor so oxidation takes place in a fuel rich environment. These two ways of ATR startup can be done using the current autothermal reformation setup at the Hydrogen Production and Utilization Laboratory. The current setup allows the methanol premix to be heated by the vaporizer train and vented out the exhaust before entering the reactor, as well as letting the air be heated and vented before entering the reactor. This setup allows either the fuel or the oxidizer to enter the reactor first. The reactor shown in Figure 2 was used for the rich and lean autothermal reformation setup.

Autothermal Reformation Degradation with Coal-Derived Methanol

Previous reports have shown steam reformation catalyst degradation, which presents limited lifetime issues. To determine the lifetime of the autothermal catalyst, degradation tests similar to the ones performed for steam reformation were completed. It was confirmed in the ninth quarterly report (October-December 2005) that) that autothermal reforming of coal-derived methanol has lower degradation rates than steam reforming of coal-derived methanol due to the

higher operating temperature attained in autothermal reformation. Some of problematic chemical compounds found in coal-derived methanol can react with oxygen and can be also volatilized rather than deposit on the surface of catalyst. Reactor inlet temperature was maintained at approximately 250° C.

Reformate Purification System

Since PEM fuel cells require high quality hydrogen for fuel, a clean up system was necessary to purify the hydrogen rich reformat after exiting the reformer. Typical purifying process for hydrogen production includes water-gas-shift reaction, pressure swing absorption, and palladium membrane reaction. During this quarter, a palladium membrane was purchased and has been integrated into a purifying system to produce 99.95% pure hydrogen reformed from coal derived methanol. The palladium membrane reactor was chosen in this project for the potential to make the research theories presented during this grant more robust in the in the future. For example, we can investigate the effects of temperature and pressure on the overall system, and determine if the same trends are observed at higher pressures.

The membrane reactor needs a differential upstream pressure to drive pure hydrogen through the membrane, therefore it is necessary to increase the hydrogen rich reformat pressure before entering the clean up system. Considering the high cost and complexity to set up a vapor phase compressor and pressure swing absorption (PSA) system to pressurize reformat after the reforming reactor, we chose to pressurize the reforming system from the liquid premix side and operate the whole system at the desired pressure.

Two subsystems were added into the overall system to build the pressure required for the clean up system. These two systems include the pressurized system and the membrane reactor system.

Pressurized system

A schematic of the pressurized system is shown in Figure 4. To build the pressure from the liquid premix side, a pressurized sample cylinder with one-gallon capacity, which can sustain 1800 psi, replaced the plastic carboy as the premix reservoir. A nitrogen tank is connected to the cylinder as the pressure source to drive the premix liquid to the pump and then to the system at 200 psi. Because the micro gear pump can only handle 30 psi differential pressure between the inlet and outlet ports, the pressure has to be built up in the reforming system before slightly increasing the upstream liquid pressure. A 300 psi safety valve is connected before the cylinder for safety.

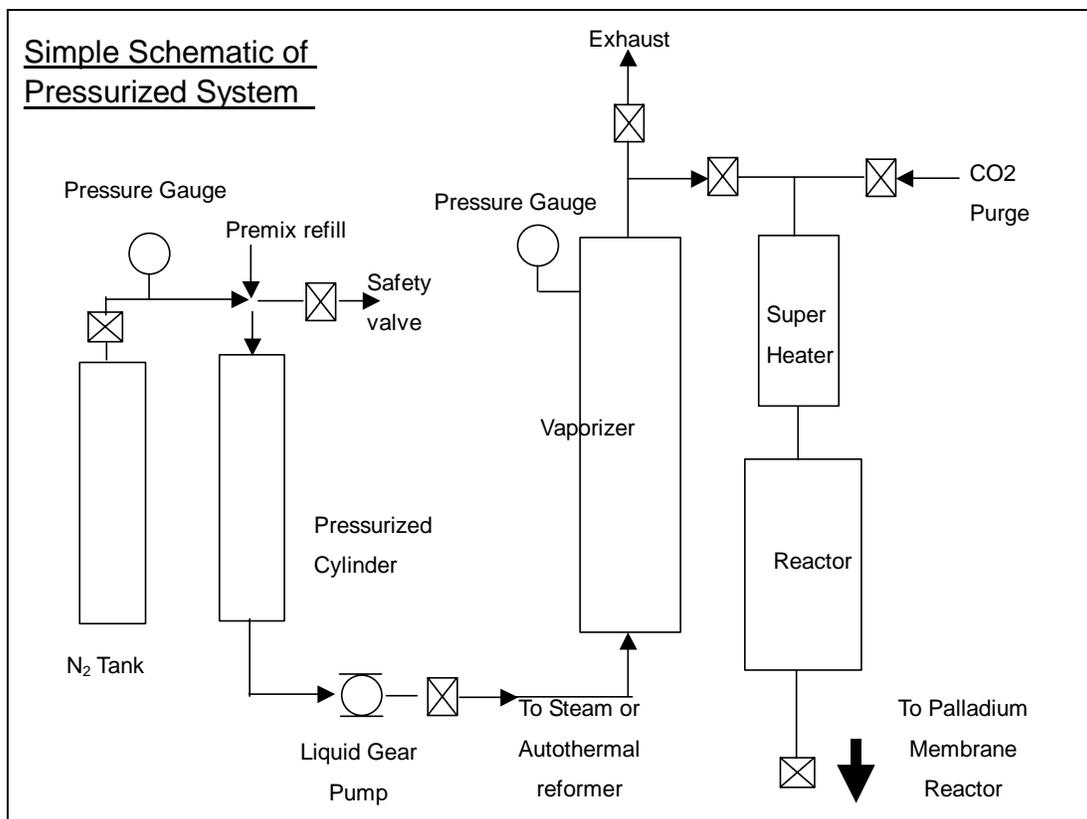


Figure 4: Clean up Unit Schematic

Membrane reactor system:

The schematic of the membrane reactor is shown in Figure 5. The palladium membrane reactor was manufactured by REB Research with a pure hydrogen output flow capacity of 1.0 std. L per minute (SLPM). The housing of the reactor is a 5/8 inch diameter by 9 inch long stainless tube which contains five palladium membrane tubes inside. The dimension of palladium membrane tubes is 0.2 cm diameter by 17.78 cm (7") long with wall thickness of 0.007 cm. The maximum operating condition of the upstream flow is 300 psi running at 400°C. The membrane reactor is heated by a six foot rope heater controlled by the Lab View VI coupled with the main program of the whole system. A needle valve connected at the sweep output tube serves as the flow control valve to control the pressure inside the whole system.

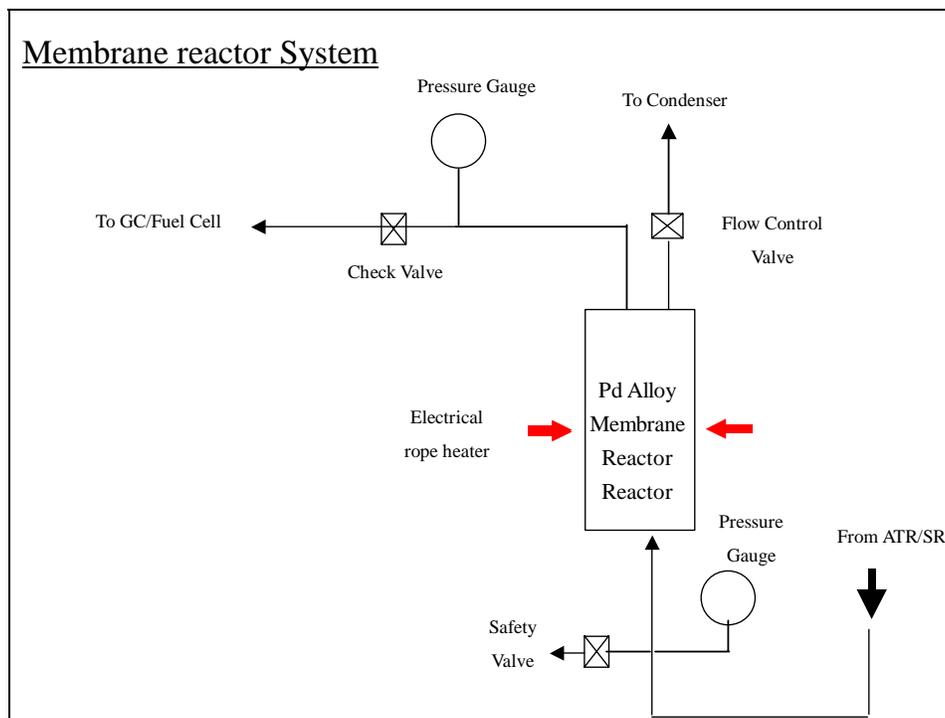


Figure 5: Membrane Reactor Schematic

Figure 6 shows a picture of the palladium membrane being used for the clean up unit in contrast to a 6" ruler. The picture on the right is the same palladium membrane wrapped in insulation and installed on the clean up unit. Figure 7 shows the built clean up unit on the left and the system integrated with the steam reforming reactor on the right.



Figure 6: Membrane Reactor

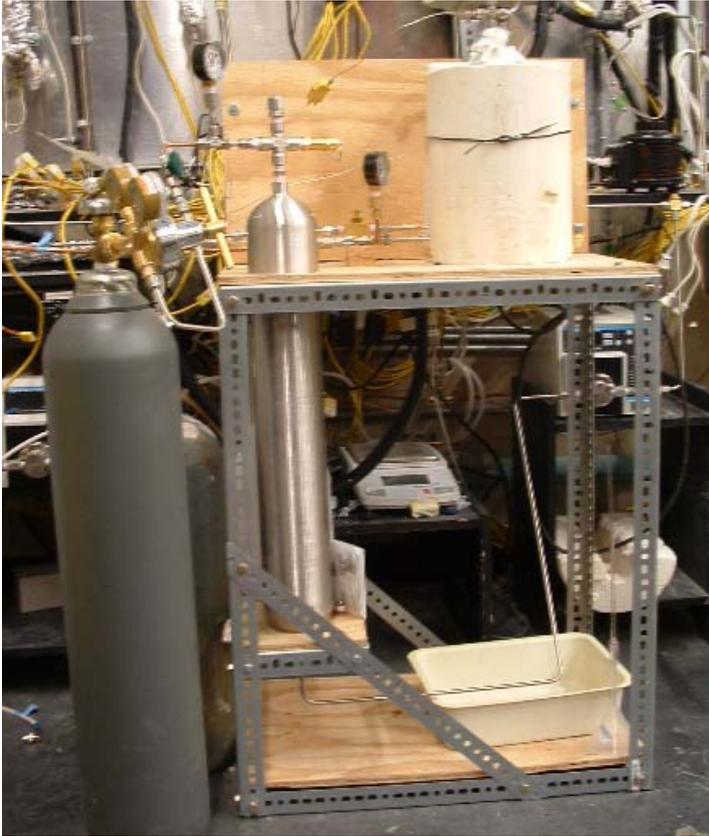


Figure 7: Purification Unit

Fuel Cell System Integration

One main objective of the current research is to establish and prove a hydrogen production pathway from coal-derived methanol to hydrogen for fuel cell applications. The previous two years of research have focused on reforming coal based methanol and comparing the results to chemical grade methanol. The third year of research integrates a clean up system to purify the reformed gas to be used in a hydrogen fuel cell.

A Ballard Nexa® stack from the Hybrid Vehicle Propulsion Systems Laboratory at UC Davis will be the fuel cell used for further research. The commercially available stack is shown in Figure 8. The fuel cell requires a fuel purity of 99.99% dry gaseous hydrogen. The fuel cell has a rated power of 1200 Watts and has a rated current of 42 Amps. The fuel cell conveniently uses air as a cooling medium and has a maximum water exhaust of 0.87 liters per hour. The maximum hydrogen usage is 18.5 SLPM, and the desired input pressure is 30 psi. Figure 9 shows the fuel cell stack and the slots used for air cooling. The NEXA power module is started by connecting a 24 V key on switch. Once the key on switch is initiated, the run switch starts the fuel cell system. Within a few seconds the fuel cell is in standby mode and will be ready to

generate power. The system requires no user input and generates enough power to follow the current draw from the system to “load follow”. The current and voltage can be monitored and recorded through a Lab View program.



Figure 8: 1.2 kW NEXA Fuel Cell Power Module

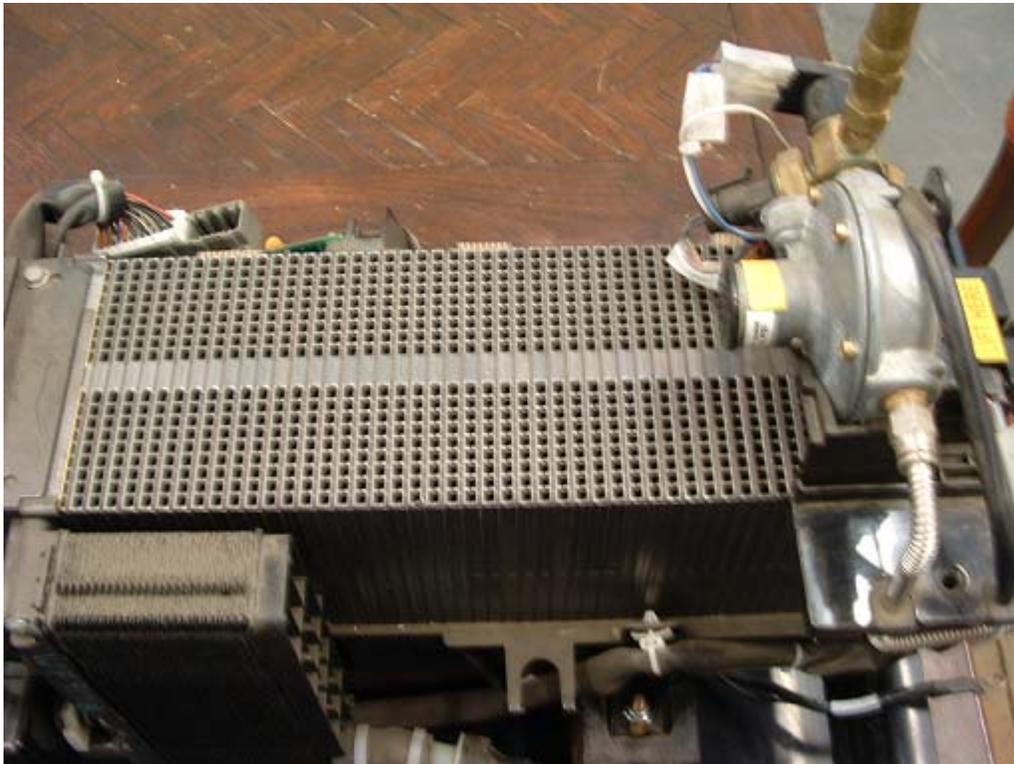


Figure 9: Fuel Cell Stack

The NEXA fuel cell will need a load or current draw once it is started up. To provide the load a current chopper system shown in Figure 10. The system is being borrowed from a small hybrid vehicle which uses capacitors and batteries. The current chopper uses a Mosfet switch that can be controlled using Lab View. The Curtis chopper can increase the load or current draw from the fuel cell and send it to the load bank shown in Figure 11.



Figure 10: Current Chopper



Figure 11: Load Bank

RESULTS AND DISCUSSION

The Effect of Catalyst Dimension on Steam Reforming

In the ninth technical report (October-December 2005), the experimental configuration of a smaller catalyst dimension (referred to as powder catalyst) with eight packages of bluff bodies was tested to investigate the effect of catalyst dimension. More specifically the relationship between catalyst diameter and its' effect on methanol conversion rate due to increased mass transfer was investigated. In this quarter, a powder catalyst experiment data run without bluff body packages was collected. A complete data set, which compares the catalyst dimension and bluff body's effects on steam reforming process, is shown in Figure 12 and Figure 13.

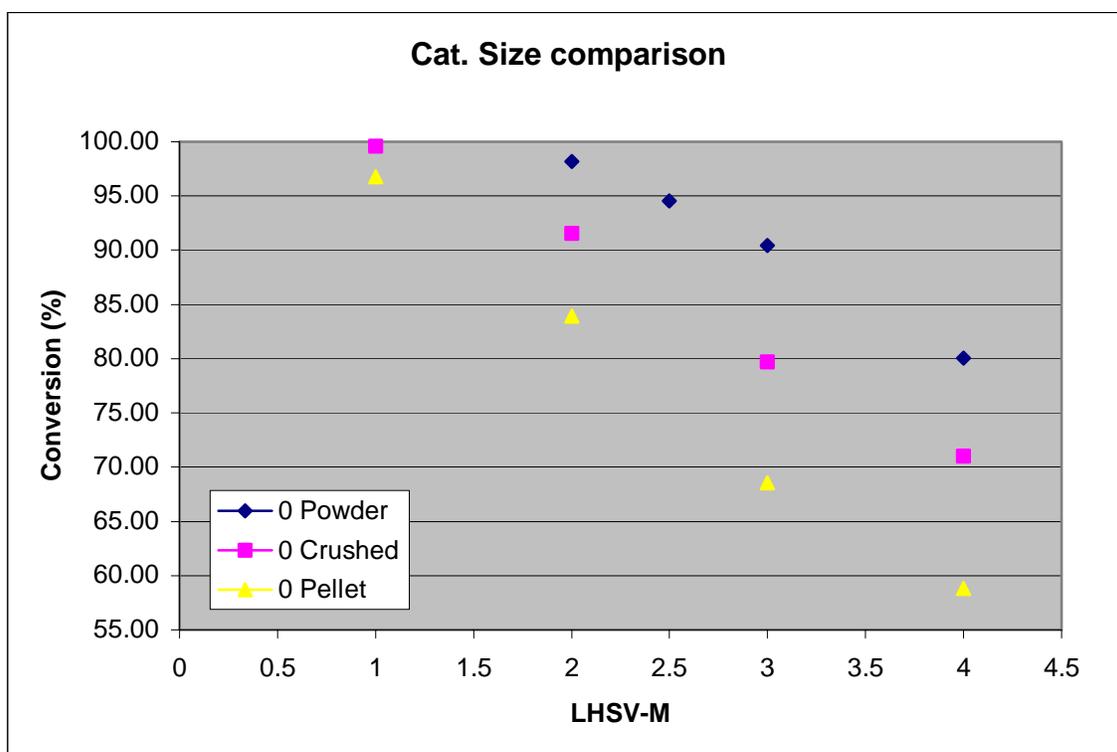


Figure 12: Catalyst Comparison without Bluff Bodies

The results from Figure 12 show that the powder catalyst can increase the methanol conversion by almost 10 % over crushed catalyst, and 20% over pelletized catalyst at 4.0 LHSV-M. Figure 13 doesn't show the dramatic increase in conversion over crushed or pelletized catalyst, but approximately shows a 15% increase over powder catalyst without eight bluff body packages. The conversion rate can be 94% at 3.75 LHSV-M. The pelletized catalyst case without bluff bodies had a 58% conversion at 4.0 LHSV-M.

During the powder catalyst experiment with eight packages of bluff a pressure drop up to 50 psi was created across the catalyst bed. The micro pump's flow rate was affected by the back

pressure since it can handle a maximum of 50 psi pressure difference, and would prefer 30 psi or less. Therefore, the LHSV-M (2.5, 3.0, 3.5, 4.0 LHSV-M) run needs to be re-corrected based on the mass of premix used instead of the flow rate shown on the micro pump. From these two figures, the effects of catalyst dimension and bluff body seems to couple together due to mass and heat transfer enhancement. This shows the importance of the diffusion limitation in reforming methanol. If expecting to maximize the conversion one must have as small a catalyst particle as possible. A further data analysis and theory investigation is planned for the following quarter based on these experiment results.

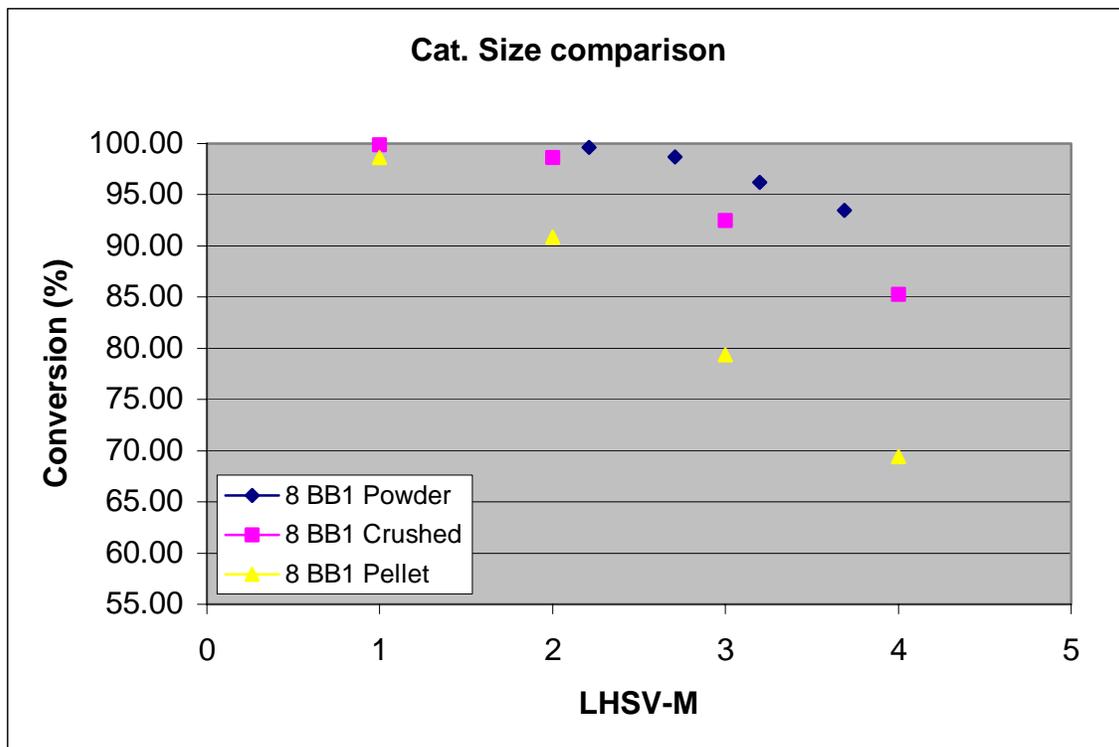


Figure 13: Catalyst Comparison with Bluff Bodies

Transient Characteristics of Autothermal Reforming

To optimize the methanol to hydrogen pathway via autothermal reformation, fundamental studies such as light-off (transient behavior) and the effects of steam to carbon and oxygen to carbon ratios should be investigated. Heterogeneous catalytic combustion light-off is a function of inlet gas temperature and oxygen to carbon ratio. As shown in Figure 14, Zone 3L and Zone 4L indicate the centerline temperatures above the monolithic catalyst surface. Heat loss due to radiation from the oxidation region is significant for autothermal reformation. To reduce radiation loss, an inert material was inserted into the autothermal reformer. A 1.0 inch long, circular monolithic material, mainly composed of Al_2O_3 , was used as the inert material for the tests and was located above the autothermal catalyst surface. As shown below in Figure 14, the circle plot indicated the average temperatures without inert material and the triangular plot

represents the average temperatures with inert material used as a radiation shield. Radiation heat loss from the catalyst surface propagates opposite the gas flow direction. The radiation causes the Zone 4L temperature to increase suddenly after light-off for a 0.22 oxygen to methanol ratio, with and without inert material. The inert material plays several important roles. It acts as a heat sink and radiation shield as well as increases mixing between fuel and air. The catalyst surface temperature with inert material was much higher than without inert material, even at lower $O_2/MeOH$ ratios. Figure 14 shows the temperature of Zone 3L with inert material to be constant over the $O_2/MeOH$ ratio (triangles) compared with the temperature of Zone 3L without inert material (circles).

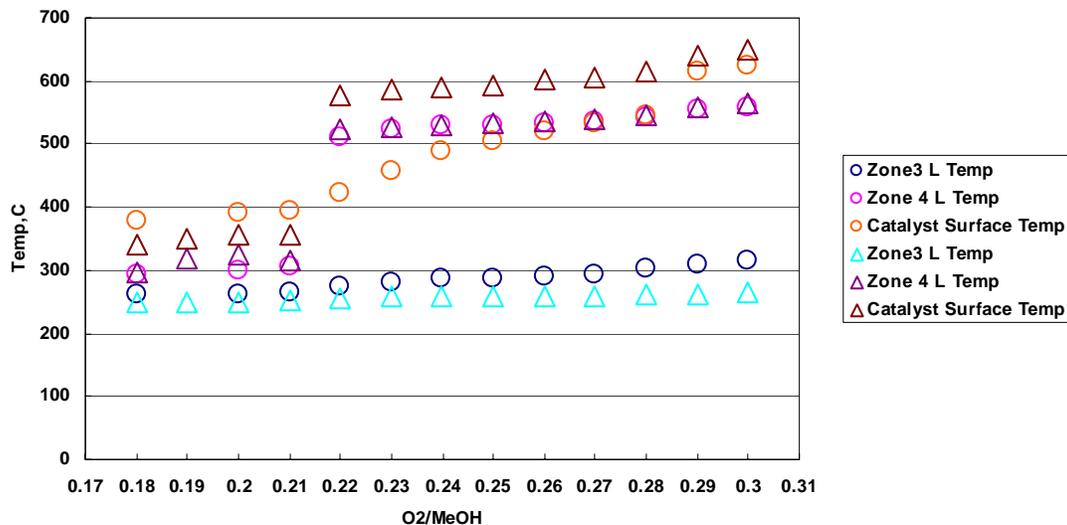


Figure 14: Average temperature catalyst surface and above catalyst surface in case of with inert material (Triangles) (Radiation Shield) and without inert material (Circles)

At $O_2/MeOH$ ratio equal to 0.27 without inert material, radiation losses from catalyst surface and heat generation by fuel combustion is balanced so the oxygen to methanol ratio would have greater autothermal reformation efficiency than other $O_2/MeOH$ ratios. If the $O_2/MeOH$ ratio is increased, fuel consumption by the oxidation reaction increases and likewise heat generation via fuel oxidation increases. The results show that catalyst surface temperature without inert material is close to the catalyst surface temperature with inert material at $O_2/MeOH$ ratios equal to 0.27. Consequently, a 0.27 $O_2/MeOH$ ratio would be the optimal operating condition in the case without inert material. On the other hand, a 0.22 $O_2/MeOH$ ratio could be the optimized operating condition with inert material. Gas analysis is needed to confirm the effect of the inert material. The lower $O_2/MeOH$ ratio would reduce the fuel required to exothermic reaction, and increase the overall reaction efficiency. Figure 15 shows the methanol conversion rate jumps up to over 99% from around 90% at $O_2/MeOH$ ratios of 0.22 and greater. The results show that enough heat can be generated from fuel oxidation to support the endothermic steam reforming reaction.

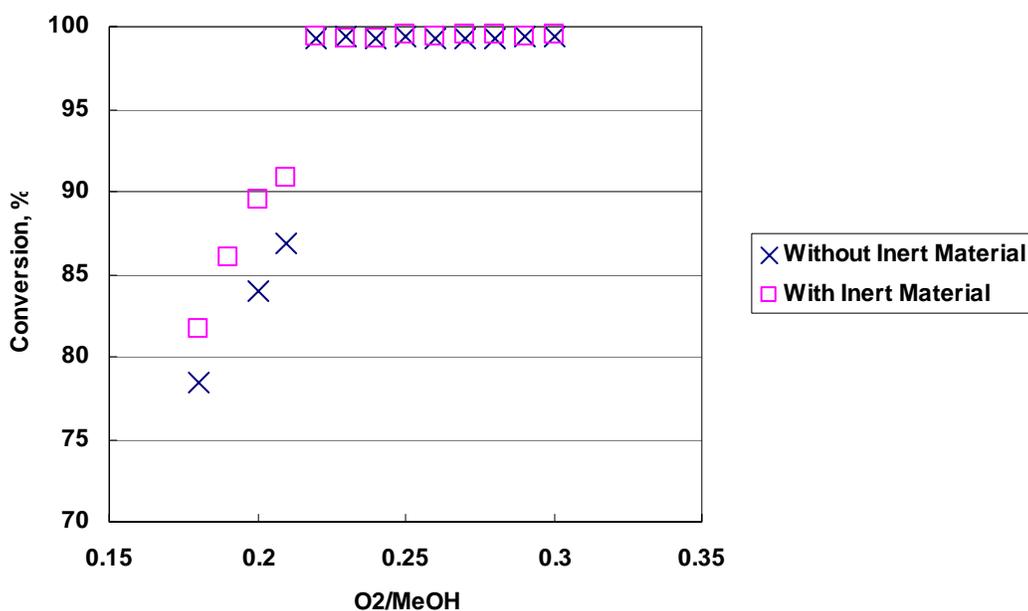


Figure 15: Conversion versus O₂/MeOH in case of without inert material and with inert material

Rich and Lean Autothermal Reforming Startup

To examine the effect of O₂/MeOH ratio on autothermal reforming transients two different ATR startup process which are fuel rich and fuel lean startup can be defined. In the case of fuel lean startup, premix vapor (~250C^o) flows into the reactor one minute after hot air (~250C^o) was introduced so fuel can be oxidized in an air rich environment. On the other hand, in the case of fuel rich startup, air was introduced into the reactor one minute after premix fuel gas enters the reactor so oxidation takes place in a fuel rich environment. As shown in Figure 16, end cap temperatures indicates monolithic catalyst top surface temperature, Zone 3L and Zone 4L indicate the centerline temperatures above the monolithic catalyst upper surface. Fuel lean startup shows higher temperature during transient warm-up time when compared with fuel rich startup. The transient time of lean fuel start up is shorter than that of fuel rich startup. The results mean that fuel lean startup would be preferred over fuel rich startup in that deposited components on the surface of catalyst, such as carbon, can be burnt off during a fuel lean startup process. Removing the deposits off the surface of the catalyst could improve catalyst activity, and reduce catalyst degradation.

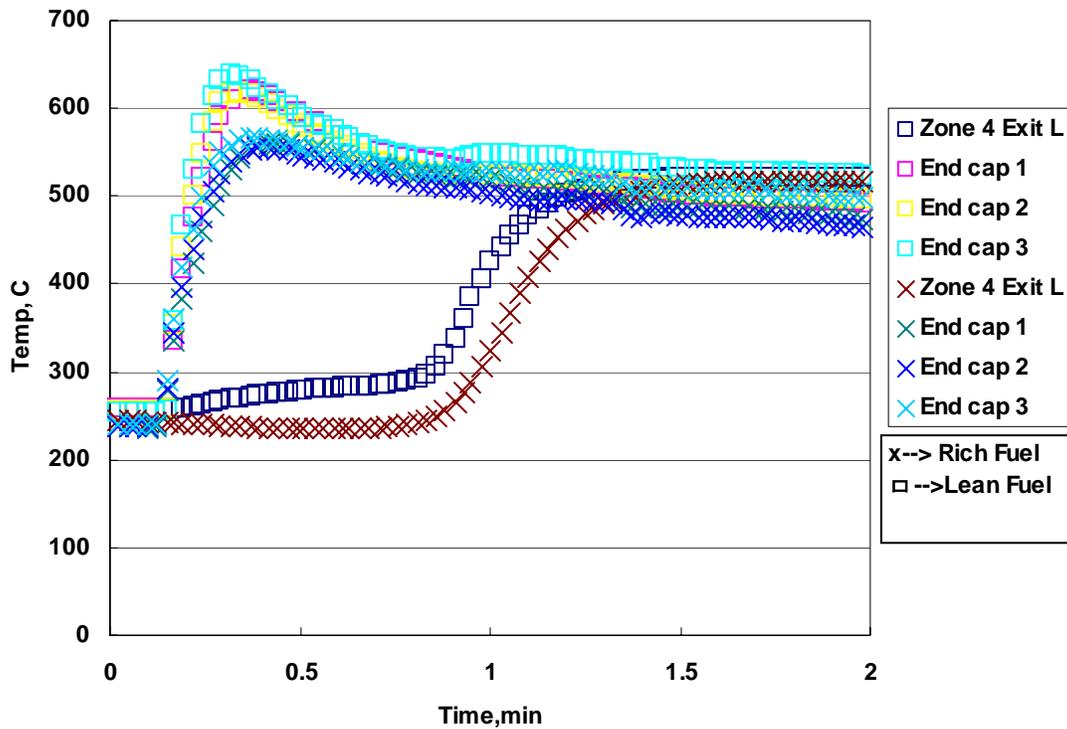


Figure 16: ATR Transient Rich Fuel Start up versus Lean Fuel Start Up at O₂/MeOH=0.22

Autothermal Reformation Degradation with Coal-Derived Methanol

It was confirmed in the ninth quarterly report (October-December 2005) that autothermal reforming of coal-derived methanol has lower degradation rates than steam reforming of coal-derived methanol due to the higher operating temperature attained in autothermal reforming. Some of problematic chemical compounds found in coal-derived methanol can react with oxygen and can be also volatilized rather than deposit on the surface of catalyst. Consequently, no degradation was observed during a 30 hour autothermal reforming degradation test.

However, such a high operating temperature might increase the thermal stress during startup and shut down process. Continuous steady state catalyst degradation test might not be a suitable test for ATR degradation for coal-derived methanol. Therefore, a new catalyst degradation test will be implemented for autothermal reformation degradation. It will consist of 60 startup and shut down processes during a 100 hour degradation test. The test has been initiated at 0.27 O₂/MeOH and lean fuel startup process. These results will be compared with the results of steam reforming methanol.

Reformate Purification System

The new clean up system has been tested on the steam reforming system using Reactor B. Several challenges have been encountered during the test including the uncertainty of the LHSV-M and the fluid's vaporizing characteristics in the pressurized reactor environment. Because the overall system operates under relatively high pressure (up to 200 psi), it is found that a high-pressurized liquid and a differential pressure between the inlet and outlet of the micro pump can affect the gear pump flow rate. This can cause an uncertainty in the LHSV-M while trying to maintain a fixed experimental condition. The LHSV-M value used in the original system depends on the flow rate set to the micro pump (or the mass of premix used during the run time). However, in the clean up system, it has become difficult to measure the mass of premix used for every experimental run. An alternative way to calculate the LHSV-M can be done by measuring the mass and the density of condensate for a given run time when methanol conversion can be confirmed for a certain value. The accuracy of this method can be affected by the condenser's working ability. By comparing the calculated LHSV-M values using this method and the previous method, the off set error is within 0.1 LHSV-M. To use this new method, the methanol conversion has to be confirmed; therefore, the experiment is run at low flow rates to make sure a 99% conversion is achieved. The 99% conversion at low flow rates is based on previous results.

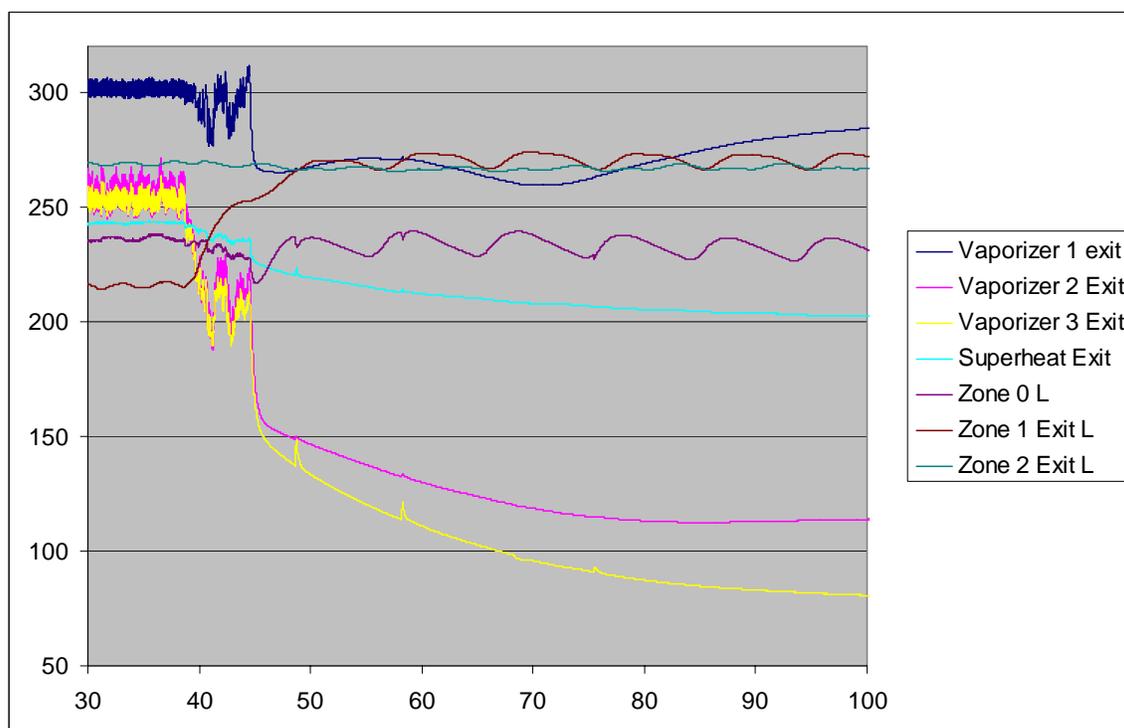


Figure 17: Temperature Profile of Reactor B with High Pressure using Ambient Pressure Set Points

New temperature set points for the three-stage vaporizer and super heater need to be determined for the pressurized system. Figure 17 is the temperature profile collected during the first test run using the temperature set points for ambient pressure. After 38 minutes, the system was

pressurized. One can see while the pressure started to build up, the three vaporizers' exit temperatures immediately dropped off thus drawing the super heater exit temperature down. This temperature drop off inside the vaporizer might be due to the differential pressure between the inlet and outlet of the micro pump squeezing large amounts of liquid premix into the system. It might also result from the pressure effect on the fluid's thermal properties such as changing the latent heat of vaporization and increasing the boiling point temperature. Because a needle valve connected at the sweep tube of the membrane reactor serves as a flow control valve, an uncertain flow rate might have caused the temperature drop as well.

By raising the temperature set point and increasing the heat flux into the system in the following test run, the fuel temperature before entering into the catalyst bed can be stabilized above 250°C as shown in Figure 18. More effort will be taken to find a best temperature set point for running the pressurized system. The pure hydrogen sample coming out from the reactor will be analyzed using the gas chromatograph (GC) system in the laboratory before using the gas in the PEM fuel cell in the coming experiment schedule as the clean up system reaches its stable and optimum function.

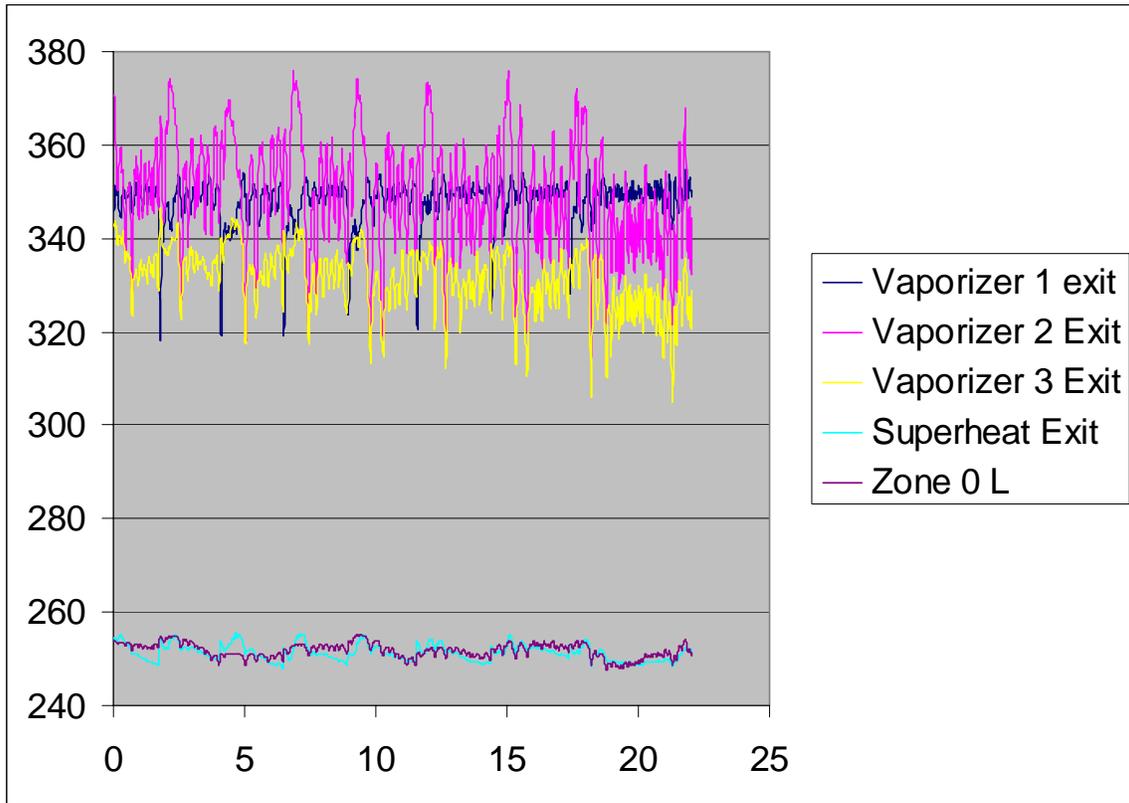


Figure 18: Temperature Profile of Reactor B with High Pressure using new Set Points

Fuel Cell System Integration

The fuel cell system shown in Figure 8 is ready for integration with the purification unit as soon as the hydrogen purity can be confirmed to be 99.95% pure hydrogen. The fuel cell will only require a pure hydrogen input. The current method shown in Figure 10 and Figure 11 which controls the current draw is large and is more complicated than necessary. In the mean time we are working on building a variable resistance load bank. We will add resistance to the system to increase the load demand, instead of controlling the current draw.

CONCLUSION

The results show that the powder catalyst can increase the methanol conversion by almost 10 % over crushed catalyst, and 20% over pelletized catalyst at 4.0 LHSV-M. Figure 13 doesn't show the dramatic increase in conversion over crushed or pelletized catalyst, but approximately shows a 15% increase over powdered catalyst for the case without eight bluff body packages. The conversion rate can be 94% at 3.75 LHSV-M. The pelletized catalyst case without bluff bodies had a 58% conversion at 4.0 LHSV-M. The powdered catalyst with eight bluff body packets created a pressure drop up to 50 psi. Therefore, the LHSV-M (2.5, 3.0, 3.5, 4.0 LHSV-M) runs need to be re-corrected based on the mass of premix used instead of the flow rate shown on the micro pump. A high methanol conversion rate is possible with powder catalyst and eight bluff body packets while creating a large pressure drop. Further research is planned to analyze the bluff body geometry and catalyst dimension's flow influence in the packed bed such as the pressure drop and determine if the overall improvement in performance overcomes the pressure drop.

At an O₂/MeOH ratio equal to 0.27 without inert material, radiation losses from catalyst surface and heat generation by fuel combustion is balanced so the oxygen to methanol ratio would have greater autothermal reformation efficiency than other O₂/MeOH ratios. If the O₂/MeOH ratio is increased, fuel consumption by combustion by the oxidation reaction increases and likewise heat generation via fuel oxidation increases. The results show that catalyst surface temperature without inert material is close to the catalyst surface temperature with inert material at O₂/MeOH ratios equal to 0.27. Consequently, a 0.27 O₂/MeOH ratio would be the optimal operating condition in the case without inert material. On the other hand, a 0.22 O₂/MeOH ratio could be the optimized operating condition with inert material. Gas analysis is needed to confirm the effect of the inert material. The lower O₂/MeOH ratio would reduce the fuel required to exothermic reaction, and increase the overall reaction efficiency.

Fuel lean startup shows higher temperatures during transient warm-up time when compared with fuel rich start up. The transient time of lean fuel start up was shorter than that of fuel rich startup. The results mean that fuel lean startup would be preferred over fuel rich startup in that deposited components on the surface of catalyst, such as carbon, can be burnt off during a fuel lean startup process. Removing the deposits off the surface of the catalyst could improve catalyst activity, and reduce catalyst degradation. The end result is that the degradation caused by deposits on the catalyst more typical of coal derived methanol can be potentially removed during a fuel lean startup procedure, or at least minimized.

It was confirmed in the ninth quarterly report (October-December 2005) that autothermal reforming of coal-derived methanol is more proper than steam reforming of coal-derived methanol due to the higher operating temperature attained in autothermal reformation. Some of problematic chemical compounds found in coal-derived methanol can react with oxygen and can be also volatilized rather than deposit on the surface of catalyst. Consequently, no degradation was observed during a 30 hour autothermal reforming degradation test. A new catalyst degradation test will be implemented for autothermal reformation degradation. It will consist of 60 startup and shut down processes during a 100 hour degradation test. The test has been

initiated at 0.27 O₂/MeOH and lean fuel startup process. These results will be compared with the results of steam reforming.

The reformat purification unit has been built, and testing of the system has begun. One of the challenges of the new system was figuring out how to pressurize the system so the micro gear pump wouldn't get over loaded. The other challenge was determining the methanol flow rate without a scale. An alternative way to calculate the LHSV-M can be done by measuring the mass and the density of condensate for a given run time when methanol conversion can be confirmed. The accuracy of this method can be affected by the condenser's working ability. By comparing the calculated LHSV-M values using this method and the previous method, the off set error is within 0.1 LHSV-M. The third challenge was determining the new set points for the pressurized system. Using the set points of the steam reformation at ambient pressures created the temperature drops shown in Figure 17. By raising the temperature set points and increasing the heat flux into the system in the following test run, the fuel temperature before entering into the catalyst bed can be stabilized above 250°C as shown in Figure 18. More effort will be taken to find the best temperature set point for running the pressurized system. The pure hydrogen sample coming out from the reactor will be analyzed using the gas chromatograph (GC) system in the laboratory before using in the PEM fuel cell in the coming experiment schedule as the clean up system reaches its stable and optimum function.

The NEXA PEM fuel cell is in the Hydrogen Production and Utilization Lab and is ready for operation. The fuel cell does not require any control and as a result it is fairly easy to integrate. All it requires is a 24 Volt key on, a pure hydrogen source, and a place to dump the generated power. Currently the system is setup to control the current draw. We plan on building a smaller system that would control the amount of resistance or load through a series of switches.

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