

HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

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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 ninth 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 October 1, 2005 – December 31, 2005.

This quarter saw progress in four areas. These areas are:

1. reformatte purification,
2. heat transfer enhancement,
3. autothermal reforming coal-derived methanol degradation test
4. and model development for fuel cell system integration.

The project is on schedule and is now shifting towards the design of an integrated PEM fuel cell system capable of using the coal-derived product. This system includes a membrane clean up unit and a commercially available PEM fuel cell.

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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 ninth 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 October 1, 2005 – December 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 schedule.

This quarter saw progress in four main areas. These areas are:

1. reformat purification,
2. heat transfer enhancement,
3. autothermal reforming coal-derived methanol degradation test
4. and model development for fuel cell system integration.

Progress has been made on the reformat purification system. The purified hydrogen stream will be used to fuel a PEM fuel cell. The Hydrogen Production and Utilization Lab will be 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. Previous quarter's results show that using different dimension disk-ring bluff body resulted in different steam reforming enhancement. Also a swirl tape passive flow disturber was tested and showed no significant difference compared to the base line, or the results without any flow disturbers. In a recent experiment, different bluff body geometries were tested to determine the effect in bluff body enhancement. Also, smaller dimension catalyst powder was also tested and compared with the crushed catalyst in another experiment set. 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.

Autothermal reforming of coal-derived methanol has taken place with a high-grade catalyst. Initial findings show that reactor performance was similar to fuel cell grade methanol. The high temperature oscillations experienced during the autothermal reformation reported in the second annual report has been solved. From the initial tests, autothermal reformation continues to show promise for extended use.

Fuel cell system modeling will occur and will be validated and calibrated with experimental data. This calibration is necessary because the reformer obviously does not follow equilibrium concentration because of the heterogeneous chemical reaction. There are also many unknown parameters which can determine reformer performance such as reactor geometry and catalyst degradation mentioned previously. Therefore, modeling of fuel cell system will be validated based on experimental data.

Two of the funded graduate researchers have passed the PhD qualifying exam. In one research project, an investigation utilizing bluff bodies as an artifice to create a passive flow disturbance inside a reforming reactor is proposed as a potential enhancement scheme. Parameters including flow velocity, bluff body geometry and dimension, and catalyst size will be varied to study related effects on the reforming reactions. It is expected that by using this reactor set up, hydrogen production via steam or autothermal reformation can be increased. The proposal with data from previous research on coal based methanol can be found in the appendix.

The goal of the second researcher is to investigate and compare steam reformation and autothermal reformation when considering use of coal-derived methanol for hydrogen fuel cell systems. This will be done with both theory based models and with actual experiments with the available laboratory facilities. Specifically the integration of the reformer system will be considered, the overall fuel cell system will be modeled, and the degradation of the system with typical impurities in the fuel stream will be quantified. In this proposal, a variety of critical factors will be identified and explored in order to increase the overall efficiency of a methanol-fueled fuel cell system. The proposal with data from previous research on coal-based methanol can be found in the appendix.

EXPERIMENTAL

The following section describes the experimental methods used and developed during the reporting period for the following areas: reformat purification, heat transfer enhancement, autothermal reforming coal-derived methanol degradation test and model development for fuel cell system integration.

Reformat Purification

The objectives of this project are to establish and prove a hydrogen production pathway from coal-derived methanol 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.

The existing infrastructure will be modified to accommodate the reformat purification system. 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 1. 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: 1

From experimental results, the reformat by percent volume is typically 75% H₂, 1% CO and 24% CO₂ dry. The maximum reformat flow rate is 32 SLPM for a premix flow rate of 20 mL/min. Since the reformat gas is only 75% hydrogen, a gas purification step will need to be included in the methanol reformation infrastructure in the Hydrogen Production and Utilization Lab. Large scale hydrogen purification systems are currently in operation for industrial applications, but we found difficulty in finding a small and inexpensive method to purify hydrogen. The lab has looked into pressure swing absorption, palladium membranes and hydrogen purifiers. Most of the solutions were

large and expensive and not designed to handle mixed gases, or input less than 99% hydrogen.

Hydrogen purifiers were investigated but found to not be ideal for purifying the reformat gas. Most hydrogen purifiers such as the ones shown in Figure 2 are intended to purify pure hydrogen gas into ultra pure hydrogen gas. The input hydrogen purification required is usually greater than 99.5%, with an output purity of up to 99.9999999%, or 9, 9's hydrogen purity. Some of the devices would not be able to handle the reformat impurities and could become clogged or permanently damaged. From communication with sales representatives, they recommended hydrogen separators versus a purifier. The hydrogen separator usually has a membrane that is selectively permeable to hydrogen. The remaining larger molecules are purged off as exhaust gasses.



Figure: 2

The second hydrogen purifier investigated was the HP-100 shown in Figure 3. The hydrogen purifier was manufactured by Johnson Matthey and could achieve hydrogen flow rates up to 42 SLPM at an output purity of 99.9999999%. The unit was quoted at \$13,220 and could handle a “dirtier” hydrogen gas composition. Later the lab was informed that the hydrogen purity in the reformat was below the minimum required hydrogen purity input to the machine. The life of the machine was uncertain due to the lower hydrogen concentration in the reformat and the resulting potential damage to the machine.

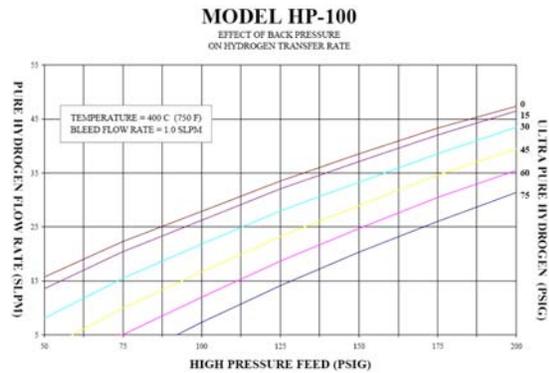


Figure: 3

Pressure swing absorption is used for large scale hydrogen purification and is used on reformat gases with high levels of impurities. The pressure swing absorption unit would be ideal for the current setup in the lab except for the large size and cost. An example of the unit is shown in Figure 4. A price quote for the smallest unit from Air Products was \$75,000 and the price did not include the base the unit was to be mounted on.



Figure: 4

REB Research & Consulting was founded in 1987 by Robert Buxbaum to consult on hydrogen separations and membrane reactors. Dr. Buxbaum continues to consult and to build membrane separators as well as hydrogen purifiers. The membrane separators require a 200 psi operating pressure and temperatures above 200 C. The membrane developed by Dr. Buxbaum is 100% selective to hydrogen. The membrane separators provide a smaller hydrogen output flow rate, as well as a lower cost. The units are roughly a foot in length. Table 1 shows the increase in price related to hydrogen flow rate.

Table: 1

H2 Flow Rate (SLPM)	Cost (\$)
1	3910
2	5330
3	7075

Heat Transfer Enhancement

The disk-shape swirls were machined from 316 stainless square steel sheets. Disk used in bluff body configuration 1 with diameter of 1.25 inch was machined in the following shape (Figure 5).

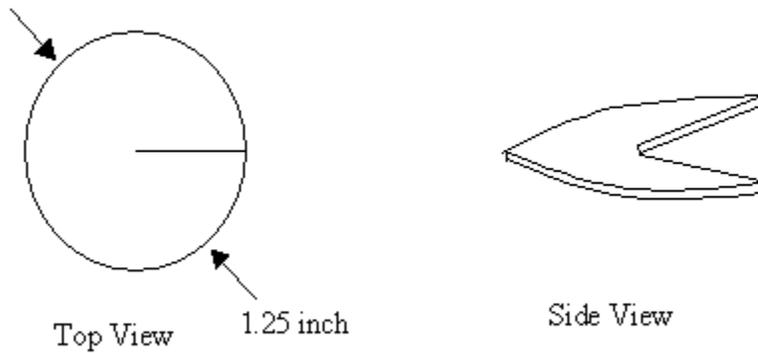


Figure: 5

Eight disk-shape swirls were evenly piled up inside reactor B and packed with crushed catalyst. The other conditions were the same as the previous experiment in the second annual report. A disk-shape swirl bluff body can create a longer flow path length compared to other bluff body geometries investigated. Since the disk-shape swirl does not drive the fluid from hot (near wall) back to the cold region as disk-ring combination does, it is not expected to raise the centerline temperature as much as disk-ring bluff body. By testing disk-shape swirl, it can analyze whether the flow path length or temperature has more influence in enhancement. Because 1.0 LHSV-M for crushed catalyst always located after the break point (always with 99% fuel conversion for every experiment set), 1.5 and/or 2.0 LHSV-M were chosen for a low flow rate in different experiment.

Autothermal Reforming Coal-derived Methanol Degradation Test

Autothermal reforming of coal-derived methanol has taken place with a high-grade catalyst. The monolithic types of catalyst (1.5”X1.5”) has been used in this experiment. This test has been performed for 31 hours. O₂/C ration and S:C ratio has been set up 0.30 and 1.5 respectively.

The high temperature oscillations experienced during the autothermal reformation reported in the second annual report has been solved. The high temperature fluctuations were caused by small variations in methanol water premix vaporization rate. The autothermal reformation reaction has a high dependence on the O₂/C carbon ratio. The control program had a fixed oxygen flow rate, while the actual methanol vapor flow rate would oscillate. The result was a high temperature spike followed by a low temperature spike. The variation in premix was caused by the heating element located at the liquid entrance would turn on and off at maximum power as instructed. This problem was fixed using a variable AC control to reduce the voltage to the heating element. This would allow the heating element to be constantly turned on, but at a reduced power. The end result is a constant stream of methanol, and a constant O₂/C ratio. The reaction was much more stable, and the decrease in fuel conversion previously noticed was fixed as well. This shows how high temperature oscillations can reduce fuel conversion.

Model Development for Fuel Cell Systems Integration

Overall fuel cell system descriptions

The general schematic of the fuel cell system adapted for steam reformation and autothermal reformation can be shown in Figure 5 and 7 respectively.

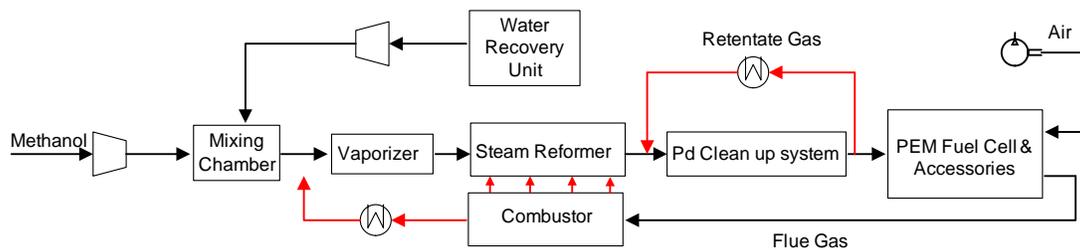


Figure 5: General Schematic of Steam Reformer Fuel Cell System

As shown in Figure 5, the steam reforming fuel cell system requires a combustor to supply heat into the steam reformer. Vaporizer should be adapted with steam reformer because 60% of overall steam reforming power consumption is consumed for vaporizing methanol/water premix as indicated in Table 2. Water can be reutilized by a water separation unit connected with the PEM fuel cell and combustor retentate gas. Before the vaporizer, methanol and water should be mixed together to prevent coking.

Table 2: The percentage of power consumption for methanol and water vaporization at different liquid hourly space velocity (LHSV)

LHSV(1/hr)	1	2	3	4
Percentage of Power consumption of Vaporizer (%)	64	64	69	72

After the endothermic reaction, reformat is routed into palladium (Pd) membrane hydrogen separation unit. Steam reforming reformat temperature will be around 200~230°C depending on Liquid Hourly Space Velocity (LHSV) as well as steam/carbon ratio. Reformat should be heated and pressurized before clean up system in order to increase hydrogen permeability through palladium membrane as shown indicated in Figure 6. For safety and energy consumption reasons, liquid (methanol and water mixture) compression is preferred. High operating temperature of clean up system can be supplemented by heat integration with retentate gases including small amounts of hydrogen with internal heater. Retentate gas can be rerouted into combustor of the steam reformer. If water or unconverted methanol exists in the reformat, either a condenser or higher operating temperature (>400°C) should be integrated or adapted in order to reduce the absorption of water and hydrocarbons onto the palladium membrane.

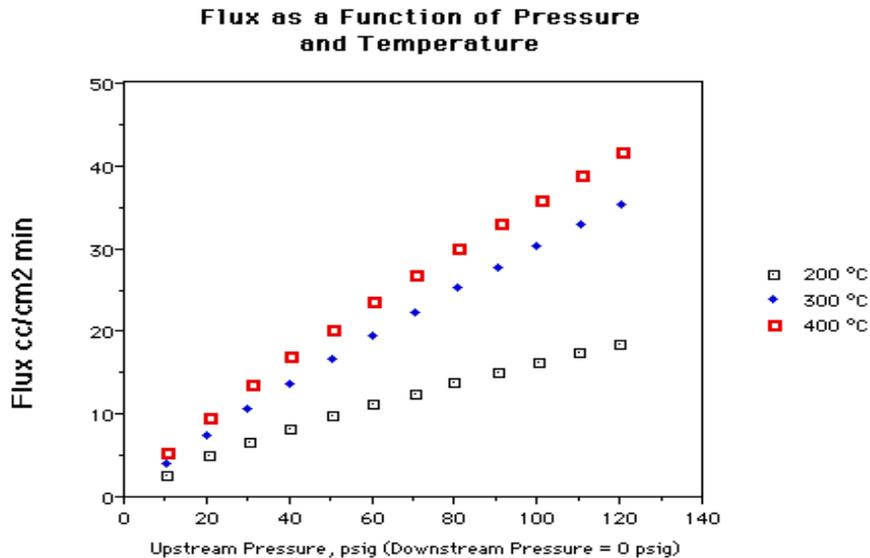


Figure 6: Hydrogen Permeation at different temperature and upstream pressure (Reb research)

Hydrogen utilization of proton exchange membrane fuel cell might be around 91% so that almost 9% of unutilized hydrogen which is referred to as flue gas comes out of the anode. Flue gas can be used in either the cathode or combustor. The excess air after cathode can be directed into the combustor so that it can reduce the compression power if required. Through the energy balance in PEM fuel cell, available thermal energy in the fuel cell system can be estimated as shown in Equation 1.

$$Q_{cooling-air} = Q_{Theoretical} - (Q_{anode} + Q_{cathode} + Q_{loss,radiation})$$

Equation 1

Compared to steam reforming fuel cell system, autothermal reformer fuel cell system can be described as shown in Figure 7. Basically, the autothermal reforming fuel cell system can be more efficient than a steam reforming system due to self-sufficient heat generation by combustion. This can give a variety of prospects to autothermal reforming fuel cell system even with a cold start up fuel cell system.

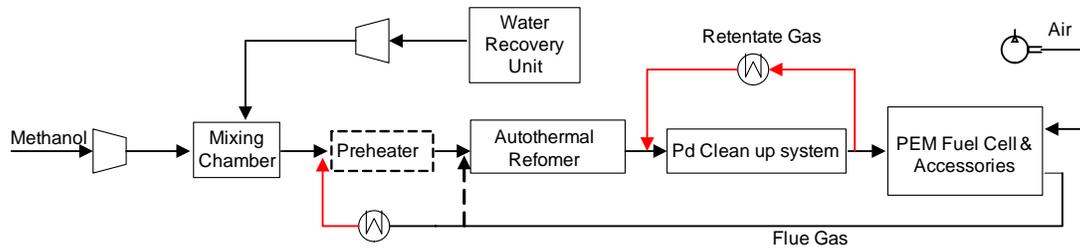


Figure 7: General Schematic of Autothermal Reforming Fuel Cell System

As already mentioned previously, vaporizing premix is the barrier for both steam and autothermal reformation. As shown in Figure 8, temperature can be increased from room temperature to 300C° within 40 seconds (Schuessler et al. 2001). Liquid fuel spray injection can not only reduce the start up time of reformer but also increase dynamic response.

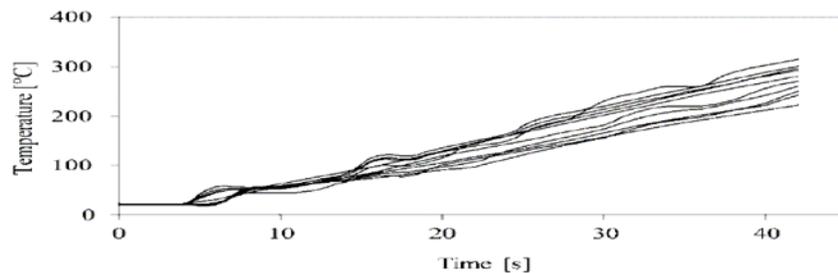


Figure 8: Temperature in the catalyst during start up from room temperature with liquid methanol (Schuessler et al. 2001)

As previously explained, hydrogen from flue gas can be utilized in the autothermal reformer which might be helpful for light-off below 200°C because hydrogen mass diffusion velocity is fast. Moreover, hydrogen addition into the reactor can decrease the O/C ratio so that hydrogen production increases because of small portions of methanol is combusted and the nitrogen dilution effect is reduced. Higher reformate temperatures with an autothermal reformer requires less thermal energy to heat up to the operating temperature of the Pd clean up system. Air requirements can be solved by reutilizing pressurized air from the cathode. Consequently, more opportunities of increasing efficiency by heat integration are given to autothermal reforming fuel cell system as compared with steam reforming of methanol fueled-fuel cell systems.

Modeling fuel cell systems

PEM fuel cell system modeling includes a compressor, autothermal reformer and steam reformer, palladium alloy membrane clean up system, heat exchanger and PEM fuel cell. All components are based on thermodynamic analysis. Wide range of operating conditions which are pressure (0~250 PSI), temperature (100~1000 C°), steam carbon ratio (0~4.0) and oxygen carbon ratio (0~1.5) are used for the reformer model. Product concentration is based on equilibrium. Hydrogen permeability is chosen from either REB Research & Consulting data or empirical equations. The reformer efficiency is based on lower heating value of fuel, lower heating value of hydrogen and heat of reaction as explained previously. In addition, vaporization of fuel is also included for the overall reformer efficiency. Heat exchange efficiencies of the steam reformer are based on experimental results. Other heat exchanger efficiencies are assumed at 80%. All systems are thermally integrated to use waste heat from the fuel cell as well as clean up system. Based on this model, we can estimate the standard flow rate of hydrogen after the clean-up system. Furthermore, approximate active surface area as well as thickness of palladium alloy membrane can be calculated by using this model. Ultimately, high pressure and temperature for isobaric fuel cell systems can be adapted from thermodynamic calculation through modeling results because clean up system and fuel cell need to be pressurized to increase of the efficiency.

Palladium Alloy Membrane Clean Up System

Due to competitive adsorption hydrogen with reformat (i.e. carbon monoxide, carbon dioxide, unconverted hydrocarbons and water) through palladium membrane; optimized operating conditions should be required. The effect of mass transfer resistance and competitive adsorption due to impurities can be a significant factor for clean up system [Ward and Dao, 1999, Hou and Hughes, 2002, Vandyshev and Murav'ev et al., 2001]. Build-up of impurities can make a barrier so that hydrogen permeability through palladium is decreased [Hou and Hughes, 2002]. Furthermore, some amounts of impurities can be adsorbed and desorbed through palladium alloy membrane. Thus, high purity of hydrogen might not be achieved in those circumstances. Therefore, relative high gas velocities (>100cm/s) and high operating temperature (>673K) were consequently suggested to minimize the inhibition of above barriers [Hou and Hughes, 2002].

Hydrogen separation from impurities can be accomplished by pressure driven processes (Loffler and Taylor, et al., 2003). Assuming that the rate-controlling step is diffusion of hydrogen, the hydrogen flux can be described by the integration of Fick's Law,

$$N_{H_2} = -k \frac{(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{l}$$

Equation 2

where k is palladium membrane permeability, l is membrane thickness and P is hydrogen partial pressure at different sides. As shown in Equation 2, increasing

differential pressure through the membrane, increasing membrane surface area and decreasing membrane thickness can enhance the hydrogen flux from retentate to permeate side. However, increasing surface area and decreasing thickness can lead to improperly increase size and decrease the hydrogen purity. Hydrogen permeation through palladium might be calculated based on either empirical equation in the literature

$$k = 2.2 \times 10^{-7} \exp(-1600/T)$$

Equation 3

Operating Temperature should be greater than 400°C to prevent palladium membrane degradation from hydrocarbon [Hou and Hughes, 2002]. Figure 9 shows the hydrocarbon concentration change caused by degradation after the condenser. The catalyst does absorb some of the hydrocarbons early in the tests. As the catalyst degradation is continuing the excess hydrocarbons pass through or partially react in the catalyst bed.

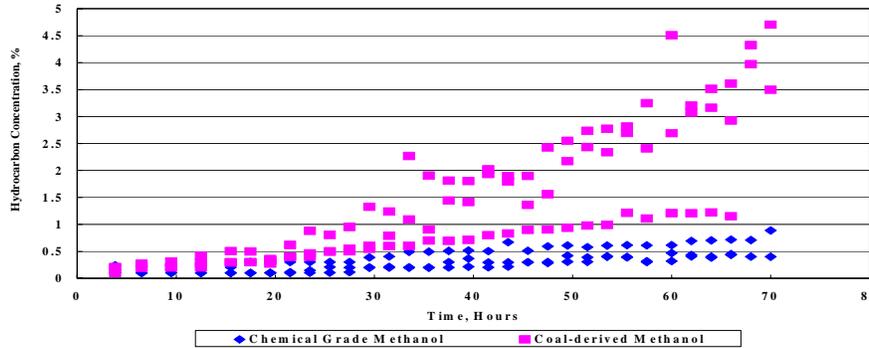


Figure 9: Hydrocarbon concentration for both chemical grade and coal-derived methanol

Proton Exchange Membrane Fuel Cell Modeling

A fuel cell operating voltage can be expressed as shown in Equation 4.

$$V_{cell} = E_{Nernst} - \Delta V_{ohm} - \Delta V_{act} - \Delta V_{transfer}$$

Equation 4

The ΔV term indicates the irreversibility losses which are ohmic losses, activation losses both cathode and anode, mass transfer losses. Ohmic losses are mainly caused by the resistance of electrons and ions flow across the electrodes and electrolyte and various interconnections. Activation losses are caused by the slowness of the chemical reaction on the surface of electrodes. Transfer losses (concentration losses) indicate mass transfer resistance between reactants and electrode surface [Larminie and Dicks, 2003].

Nernst Equation can be expressed as shown in Equation 5.

$$E = E^o + \frac{RT}{2F} \ln\left[\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}}\right]$$

Equation 5

Pressure gain caused by the reduction of cathode activation losses can be expressed as Equation 6 [Larminie and Dicks, 2003].

$$\Delta V = \frac{RT}{4F} \ln(\Delta P)$$

Equation 6

RESULTS AND DISCUSSION

Reformate Purification

After evaluating all the options, the Hydrogen Production and Utilization Lab has chosen the 1.0 SLPM membrane unit from REB Research. The membrane from REB Research will be able to provide pure hydrogen to the fuel cell at 1 SLPM. The output hydrogen flow rate of 1 SLPM is limited by the membrane and ultimately cost. The membrane reactor operates between 200 and 450 C with a maximum pressure of 300 psi at 350 C. The membrane is made of a specially developed material with 100% selectivity to hydrogen. The four tube reactor is 5/8" in diameter and 9" tall. The membrane reactor contains four membrane tubes 0.079" diameter by 7" tall.

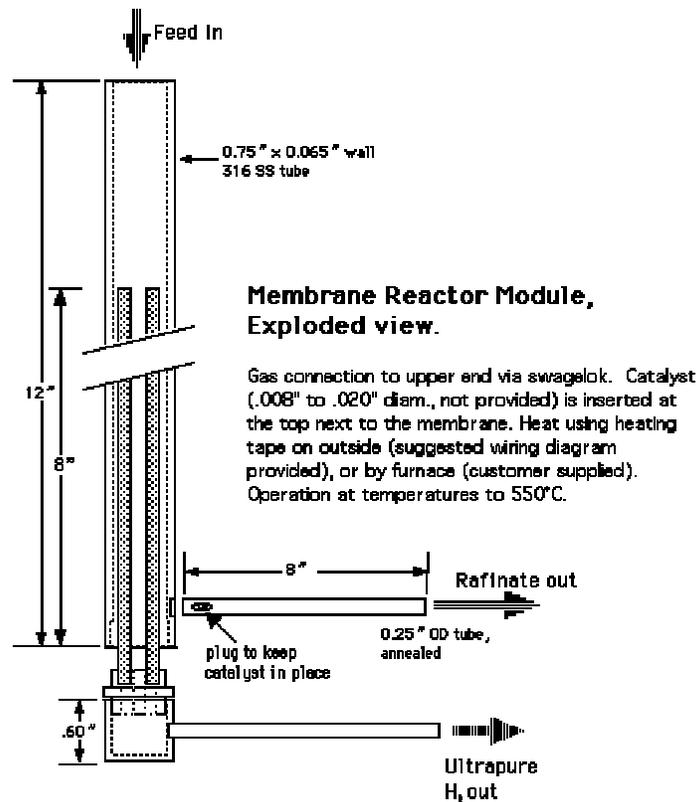


Figure: 10

The membrane reactor as shown in Figure 10 will be externally heated using the heating element shown in Figure 11. The reformate gases should be hot enough for the membrane reactor when they leave the reactor, but will cool down before the gases reach the membrane separator. The heating element will allow the reformed gases to be reheated to the appropriate temperature. The heat tape was chosen because the diameter was smaller than the smallest heat band. The heat tape will provide uniform heating, but

will not be able to provide localized heating to colder regions of the membrane reactor in the way heat bands would allow.

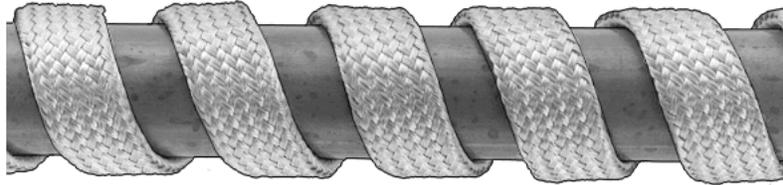


Figure: 11

The main challenge with the membrane purification system is the required pressure of 200 psi at the membrane. Since the reformat gas is required to be at 200 psi, the medium can either be pressurized as a gas, or as a liquid before the methanol water mixture is vaporized. The current infrastructure operates at low pressure, but can tolerate higher pressure. Compressors that can handle corrosive materials and pressurize a gas from 0 to 200 psi are not very common and are expensive. The alternative is to pressurize the methanol premix before the vaporizer train.

The gear pump can operate at a maximum pressure of 250 psi, but can only handle a 50 psi pressure difference. The premix will be pressurized in a stainless steel tank shown in Figure 12 using high pressure CO₂ to pressurize the vessel. The premix will be sealed in the container and be pressurized before the liquid is vaporized and reformed. Using this method, the reformat will enter the membrane separator at the desired 200 psi.



Figure: 12

The diagram in Figure 13 shows how the hydrogen purification system will be added to the current infrastructure. When the reformer operates at high pressure the chemistry will change, and the set points which work well for low pressure reforming may not work as for high pressure reforming.

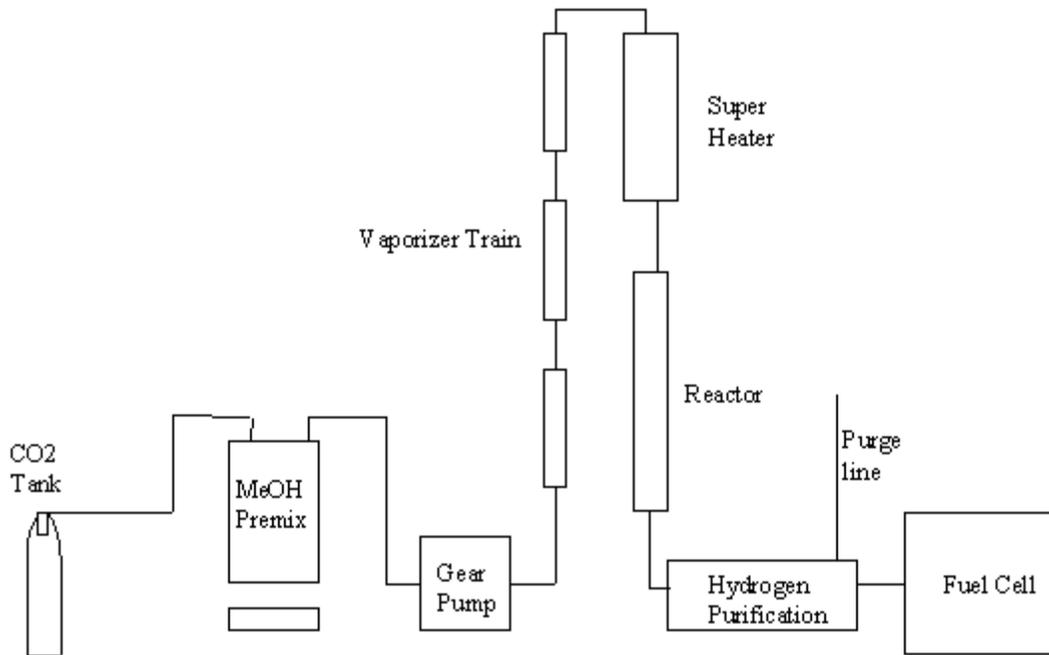


Figure: 13

Heat Transfer Enhancement

All disk-shape and ring-shape bluff bodies were tested, except the disk-shape swirl. The schematics of the bluff bodies are shown in Figure 14. Three shapes of bluff bodies were tested individually. Each experiment used four pieces of identical bluff body with crushed catalyst in reactor B. The fuel conversion versus space velocity for different shaped bluff bodies were compared and shown in Table 4. The 0C and 4C represent zero and four packs of disk-ring shaped bluff bodies. 4CLD, 4CMD and 4CMR represent four pieces of LD, MD and MR bluff bodies. And 8C d-s is eight pieces of disk-shape swirls. The swirl tape was tested during last quarter and presented here for comparison. The centerline temperature of the packed bed with 2.0 LHSV-M is shown in Figure 15.

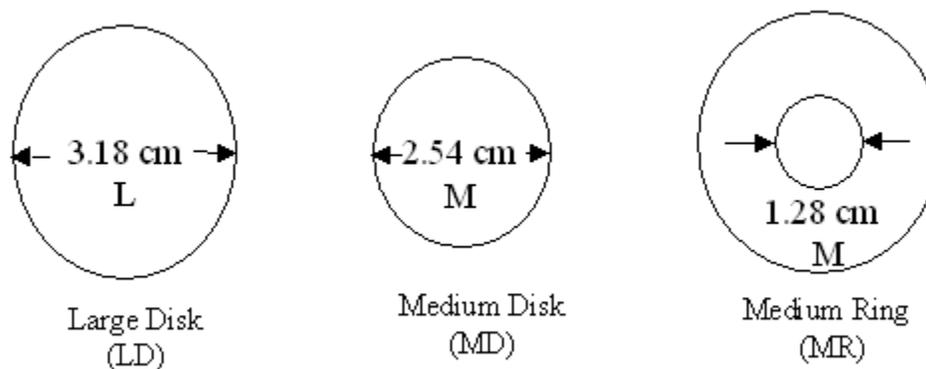


Figure 14

Table 3: Fuel conversion

LHSV\CONFIG	0C	4C	4C LD	4C MD	4C MR	8C d-s	Swirl Tape
1.0	99.56	99.83	NA	Na	NA	NA	99.78
1.5	NA	NA	NA	NA	NA	99.44	NA
2.0	91.57	97.02	98.77	96.33	87.48	97.70	92.57
2.5	NA	NA	95.23	91.34	81.36	NA	NA
3.0	79.71	88.63	90.29	86.83	76.57	87.31	80.71
4.0	71.02	80.66	78.60	75.86	66.62	74.26	70.75

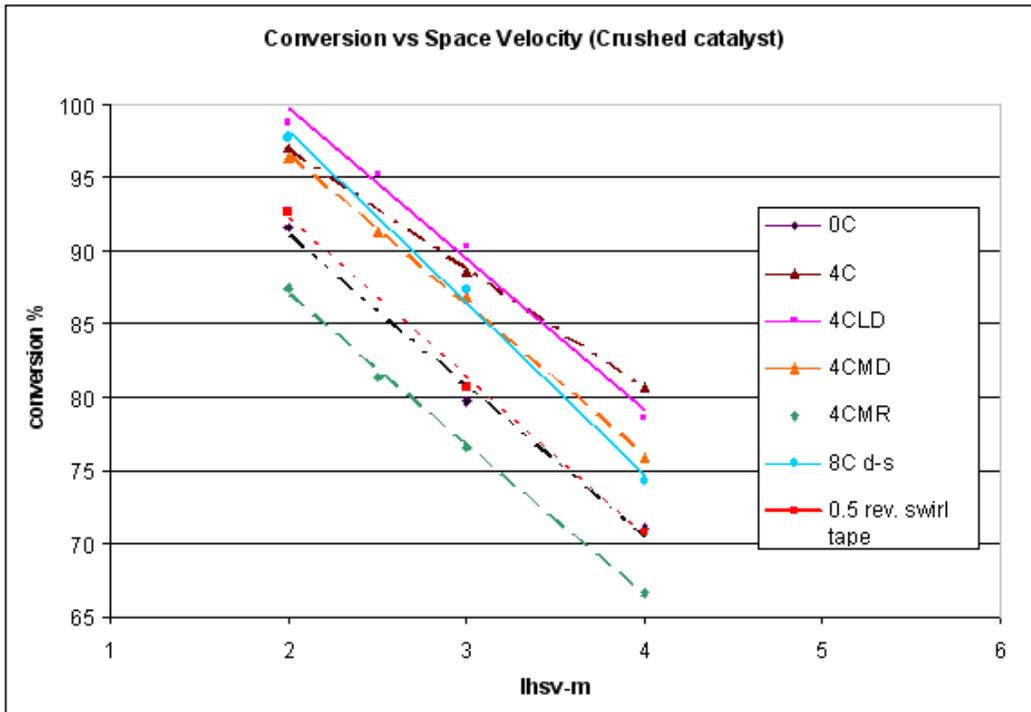


Figure 15: Fuel conversion comparison of different shape bluff bodies.

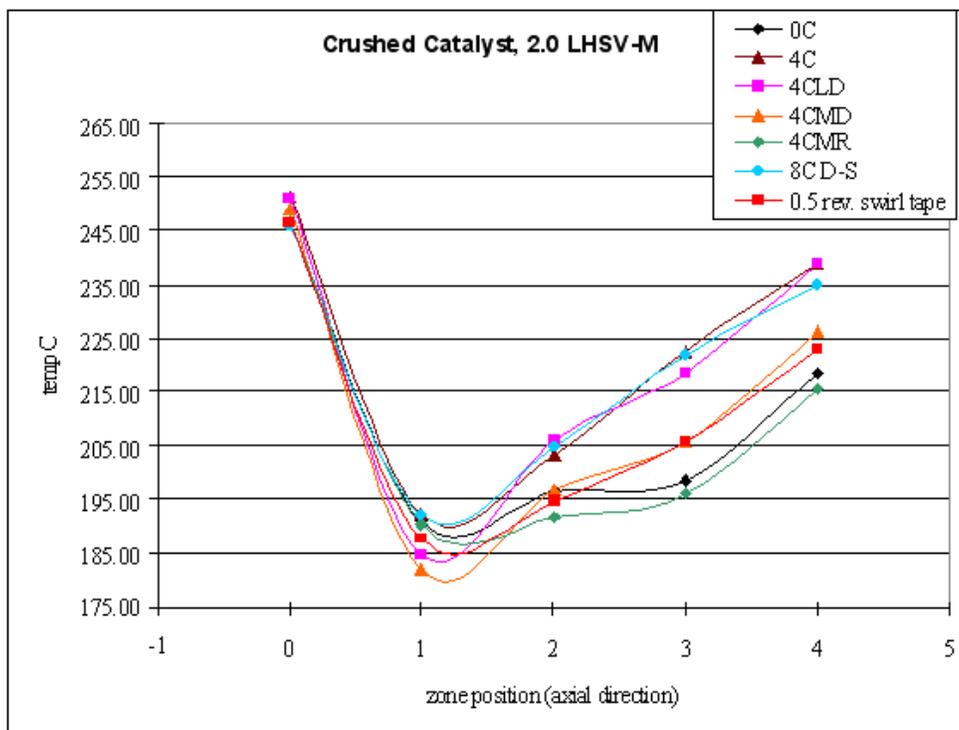


Figure 16: Centerline temperature of different bluff body shape within the packed bed with 2.0 LHSV-M.

Figure 15 indicates that 4CLD had the best fuel conversion among different shapes. In Figure 16, even though 4 CMD did not have a high centerline temperature like 8C D-S, its fuel conversion performance was still comparable to 8C D-S. The fuel conversion for disk-ring (4C) was higher than disk-shape swirl (8C D-S) at higher space velocities (3.0 and 4.0 LHSV-M). However, the disk-shape swirl performed slightly better than disk-ring bluff body running at low space velocity (2.0 LHSV-M). The centerline temperature profiles for both disk-ring and disk-shape swirl are similar. It indicates that for a same thermal environment, the flow path length may determine the fuel conversion.

Catalyst dimension effect:

The powder when crushing the catalyst was collected. This catalyst powder was used to compare with pelletized and crushed catalyst as a smaller dimension catalyst with eight packs of BB1 (small ring and large disk, in previous report) bluff body. Since the powder particle is 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. Fuel conversion versus space velocity for different catalyst particle sizes is shown in Figure 17. The fuel conversion increase was up to 22.5% running at 4.0 LHSV-M. For a fixed 99% fuel conversion comparing to 0C base line, the results show that the space velocity (or hydrogen generating capacity) can be increased from 1.0 to 2.7 LHSV-M. This increase is 2.7 times the original value. Examining the profile in Figure 18, the powder catalyst further increased the centerline temperature about 20°C more than the crushed one. It is important to note that the temperature at main reaction region

(position 1) was able to increase for catalyst powder compared to not increasing much in experiments done before.

Even though the fuel conversion and heat transfer showed a great increase by using powder size catalyst with bluff body, it was found that the pressure drop built up rapidly during the experiment.

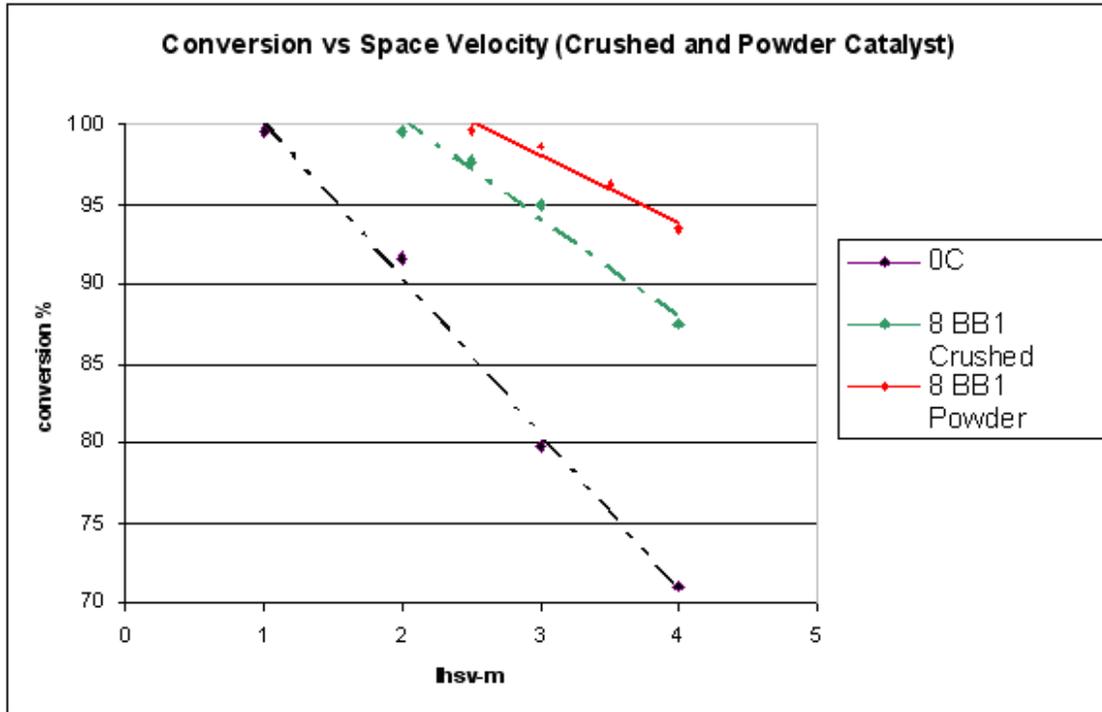


Figure 17: Fuel conversion comparison for different catalyst dimension

Table 4: Fuel Conversions

Flow Rate\Cat. Size	0C	8 BB1 Crushed	8BB1 Powder
1.0	99.56	NA	NA
1.5	NA	NA	NA
2.0	91.57	99.59	NA
2.5	NA	97.70	99.61
3.0	79.71	94.97	98.67
3.5	NA	NA	96.19
4.0	71.02	87.45	93.49

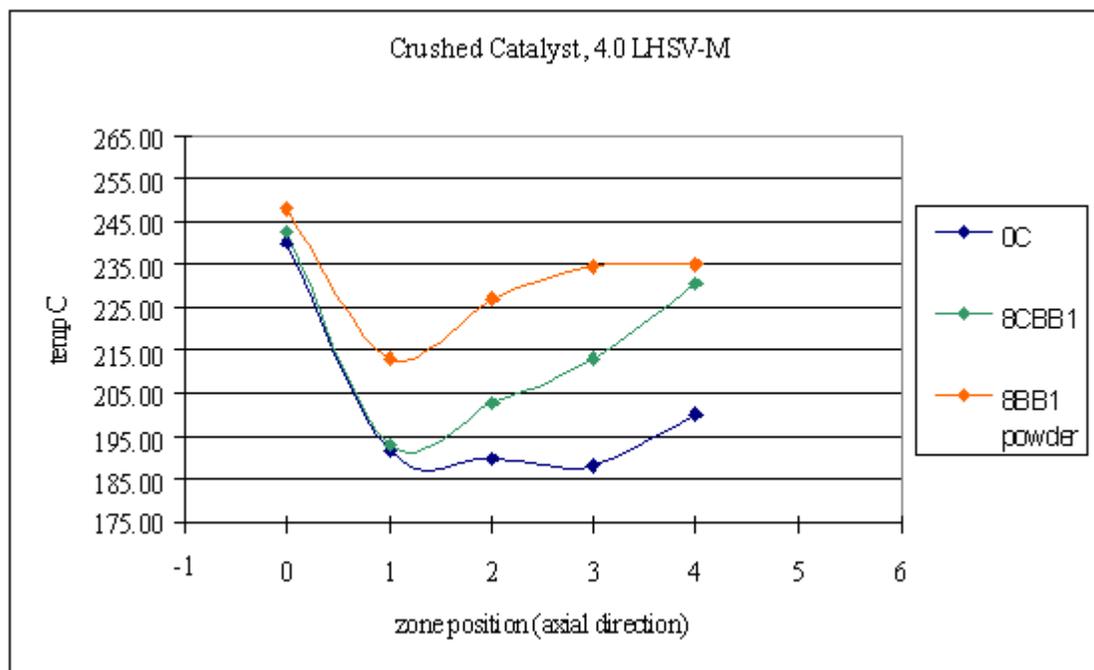


Figure 18: Centerline temperature of different catalyst dimension

Autothermal Reforming Coal-derived Methanol Degradation Test

In the second annual report, temperature fluctuation caused by methanol oxidation on top surface of catalyst was observed during autothermal reformation. This occurred by inappropriate control schematic of the first vaporizer. This problem has been fixed and new degradation tests for coal-derived methanol have been performed. The monolithic types of high grade catalyst (1.5”X1.5”) has been used in this experiment. The high grade catalyst is the same catalyst used in the research on methanol autothermal reformation done by Dorr, J.L. for *Oxygen-to-Carbon Ratio and Reaction Progression*. The current degradation test was performed for 31 hours. The O₂/C and S:C ratios has been set to 0.30 and 1.5 respectively.

Table 5: Autothermal Reforming Coal-derived Methanol Degradation Test for 31 hours

Time	Condensate	Density	Premix used	Conversion(%)
2.116667	298.4	0.9967	625.5	100
3.616667	293.9	0.9967	611.3	100
5.116667	301.4	0.9967	626.3	100
6.616667	304.7	0.997	631.6	100
8.116667	301.7	0.997	627.2	100
12.61667	498.6	0.9966	984.7	100
13.78333	190.9	0.9967	393.3	100
15.28333	301.9	0.9972	638.2	100
16.78333	305	0.9972	630.3	100
18.28333	300.5	0.9971	636.9	100
19.78333	301.9	0.9971	630.5	100
21.28333	295.6	0.9969	632.2	100
22.78333	303.2	0.997	630.5	100
24.28333	309.4	0.9969	648.5	100
25.78333	302.6	0.9968	629.1	100
27.28333	304.4	0.9967	632.2	100
28.78333	304.2	0.9968	631.2	100
30.28333	303.5	0.9968	630.8	100
31.11667	166.7	0.9968	341.8	100

As shown in Table 5, the percent conversion of hydrogen gas from methanol fuel and the reformat condensate density has not changed significantly during the 31 hour degradation test using coal-derived methanol. Autothermal reforming of coal-derived methanol occurs at temperatures over 600 C°. As expected, impurities which made steam reforming catalyst degrade in the previous experiments can be either volatized or reacted for high temperatures (~600 C). Consequently, as compared with steam reforming coal-derived methanol (~250C°), coal-derived methanol would be more proper for hydrogen production via autothermal reformation rather than hydrogen production via steam reformation.

Model Development for Fuel Cell Systems Integration

Fuel cell system modeling will occur and will be validated and calibrated with experimental data. This calibration is necessary because the reformer obviously does not follow equilibrium concentration because of the heterogeneous chemical reaction. There

are also many unknown parameters which can determine reformer performance such as reactor geometry and catalyst degradation mentioned previously. Therefore, modeling of fuel cell system will be validated based on experimental data.

CONCLUSION

Research is now shifting towards the design of an integrated PEM fuel cell system capable of using the coal-derived product. This system includes a membrane clean up unit and a commercially available PEM fuel cell. The membrane clean up unit has added complexities to the current infrastructure at the Hydrogen Production and Utilization lab, as well as allows researchers at the lab to strengthen their investigations. If conversion performance can increase under a prescribed condition, and the condition is valid for various temperatures and pressures, the argument for coal-derived hydrogen becomes much more persuasive. The third year of research allows energy to be transferred from coal derived methanol to hydrogen and finally to electricity via a hydrogen fuel cell.

Eight disk-shape swirls were evenly placed inside reactor B and packed with crushed catalyst. The other conditions were the same as in the previous experiments. A disk-shape swirl bluff body can create a longer flow path length compared to other bluff body geometries investigated. Since the disk-shape swirl does not drive the fluid from a hot region (near wall) back to the cold region as disk-ring combination does, it is not expected to raise the centerline temperature as much as disk-ring bluff body. The 4CLD had the best fuel conversion among different shapes. Even though 4 CMD did not have a high centerline temperature like 8C D-S, its fuel conversion performance was still comparable to 8C D-S. The fuel conversion for disk-ring (4C) was much higher than disk-shape swirl (8C D-S) at higher space velocities (3.0 and 4.0 LHSV-M). However, the disk-shape swirl performed slightly better than disk-ring bluff body running at low space velocity (2.0 LHSV-M). The centerline temperature profiles for both disk-ring and disk-shape swirl are similar. It indicates that for a same thermal environment, the flow path length may determine the fuel conversion with the methanol.

The high temperature oscillations experienced during the autothermal reformation reported in the second annual report has been solved. This problem was fixed using a variable AC control to reduce the voltage to the heating element. This would allow the heating element to be constantly turned on, but at a reduced power. The end result is a constant stream of methanol, and a constant O₂/C ratio. The reaction was also much more stable. Autothermal reforming of coal-derived methanol has taken place with a high-grade catalyst. The monolithic ATR catalyst (1.5"X1.5") has been used in this experiment. This test has been performed for 31 hours. The O₂/C and S:C ratios were set at 0.30 and 1.5 respectively. The percent conversion of methanol fuel and the reformat condensate density has not changed significantly during the 31 hour degradation test using coal-derived methanol. Autothermal reforming of coal-derived methanol occurs at temperature over 600 C°. As expected, impurities which made steam reforming catalyst degrade in the previous experiments can be either volatilized or reacted for such a high temperature (~600 C). Consequently, as compared with steam reforming coal-derived methanol (~250C°), coal-derived methanol would be more proper for hydrogen production via autothermal reformation rather than steam reformation. The results are also beneficial for those looking to use coal-derived methanol for fuel cell applications, because no noticeable degradation occurred for the coal-derived methanol. Autothermal reformation continues to show promise for extended use.

Fuel cell system modeling will occur and will be validated and calibrated with experimental data. This calibration is necessary because the reformer does not follow equilibrium concentration because of the heterogeneous chemical reaction. There are also many unknown parameters which can determine reformer performance such as reactor geometry and catalyst degradation mentioned previously. Therefore, modeling of fuel cell system will be validated based on experimental data.

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APPENDIX

Chang-Hsien Liao Research Proposal

The Effect of Passive Disturbers on Heat and Mass Transfer in the Hydrogen Production Process

Research Proposal

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1. Background

Hydrogen fuel cells have attracted attention because of their potential for high-energy efficiency and eco-friendly emissions. For transportation applications, they are also considered by many to be the future replacement of the internal combustion engine. Two types of fuel cell systems for transportation applications, direct hydrogen powered fuel cell vehicles (FCV) and liquid hydrocarbon fueled FCV, have been widely studied and investigated by industry and academia.

For a liquid hydrocarbon fueled FCV, an on-board fuel processing system is needed to transform the liquid fuel into a hydrogen-rich stream for use in a Polymer Electrolyte Membrane (PEM) or Phosphoric Acid Fuel Cell (PAFC). Steam reformation, partial oxidation, and autothermal reformation are three hydrogen production methods studied for on-board fuel processing systems. Each processing pathway has its advantages and disadvantages [1,2]. In the case of an on-board fuel processing system, lower on-board energy efficiency results due to the extra entropy increase in the conversion process. On-board reformers also complicate a FCV design due to the extra weight and under-hood volume needed for the fuel processing system. These systems also require long start-up and shutdown times due to the warm-up and cool-down period for the fuel processing system [3]. Therefore, any possible strategy to raise the efficiency of the fuel processing system is worth investigating.

In this Ph.D. research project, an investigation utilizing bluff bodies as an artifice to create a passive flow disturbance inside a reforming reactor is proposed as a potential enhancement scheme. Parameters including flow velocity, bluff body geometry and dimension, and catalyst size will be varied to study related effects on the reforming reactions. It is expected that by using this reactor set up, hydrogen production via steam or autothermal reformation can be increased.

2. Literature Review

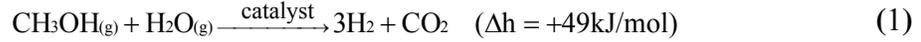
Pellet packed beds and monolith packed beds are typical catalyst structures used in steam and autothermal reformation. An ideal reforming system should have characteristics of high reforming capacity, short transient response time, and long catalyst lifetime. These characteristics are deeply affected by the flow rate of reactants, heat transfer rate, mass transport, chemical kinetics, and the catalyst degradation rate inside the catalytic reactor. In transportation applications, the above characteristics are especially critical.

2.1 Pellet packed beds in steam reformation

Over 90% of industrial hydrogen is produced using a steam reforming process over a pellet packed bed reactor fed with natural gas. However, pellet packed bed reactors have undesirable characteristics such as hot spots existing inside the catalyst bed, large concentration gradients and large pressure drops. It is believed that these are the results of heat and mass transfer limitations.

2.1.1 Heat Transfer Limitation

Due to the endothermic nature of the reaction, a catalytic steam reformer requires that heat energy be transferred from an external heat source to the reaction site. Equation (1) presents the ideal methanol steam reforming reaction.



There are three modes of heat transfer: radiation, conduction, and convection. As the relatively low local temperature difference, radiation is usually negligible. In a packed-bed cylindrical reformer, as shown in Fig. 1, heat conduction from the external heat source is limited by point-to-point contact between the catalyst pellets. Although conduction can be significant at the catalyst bed-housing wall, the small contact area limits the heat conduction within the catalyst bed. Therefore, heat is mainly transferred via bulk fluid convection.

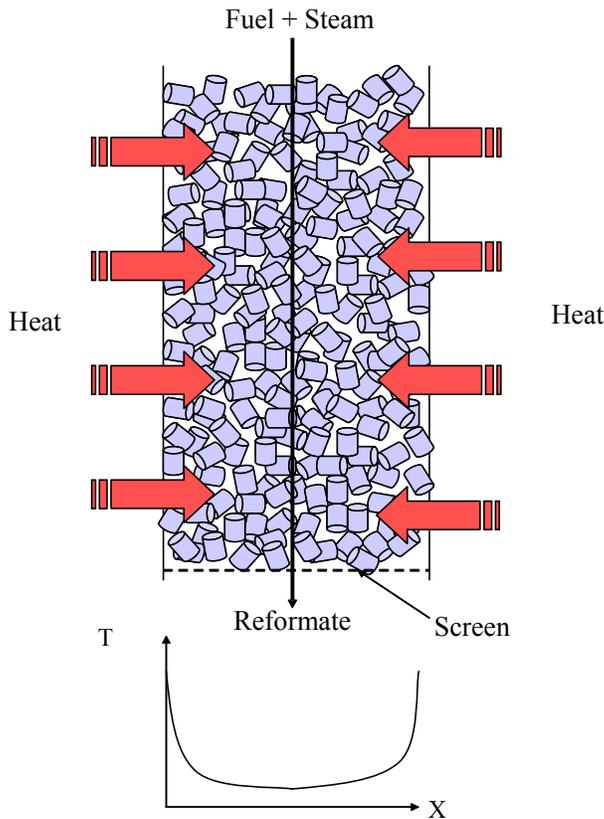


Figure 1: Schematic of heat conducting into a cylindrical catalyst bed and a typical temperature profile in radial direction.

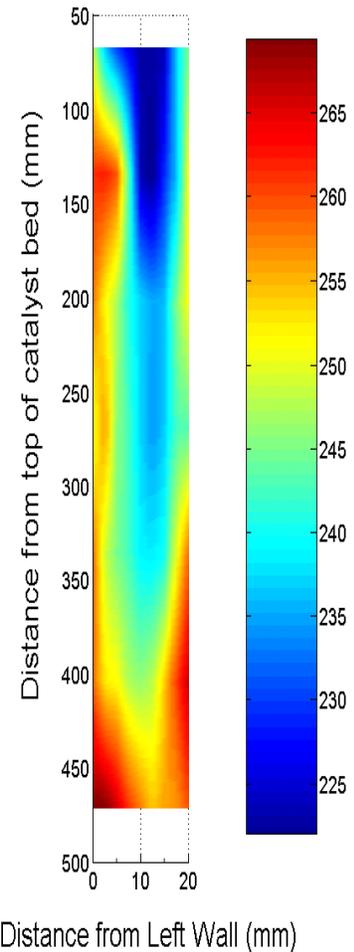


Figure 2: Temperature profile cross catalyst bed radial direction [11].

Inside a steam reforming packed bed, the irregular packing configuration and endothermic nature make the reactor experience severe temperature gradients [4]. Some numerical models to simulate the fluid state inside cylindrical packed beds have been carried out [5-10]. Continuity, energy conservation and momentum equation are governing equations for these models. To simplify the numerical model, some of the studies make assumptions including: plug flow, isothermal environment, negligible diffusion resistance of catalyst particle, no pressure drop, and axial dispersion; ideal gas behavior, and constant wall temperature. However, the more assumptions made, the more un-realistic the model is. In a large-scale cylindrical packed bed reactor, the temperature gradient in the radial direction between the heat source and the centerline of the packed bed is considerably large. A simplified temperature profile across the radial direction is shown in Fig.1. An experimental temperature profile in a 20 mm diameter reactor (Fig 2) [11] shows that the profile line has a sharp curve near the wall. This large thermal gradient inside the catalyst bed results in a non-ideal condition for steam reformation thus lowering the fuel conversion. It also increases the risk of catalyst degradation due to the uneven temperature distribution. Therefore, the poor convective heat transfer inside the catalyst bed always limits a steam reformer's performance.

2.1.2 Mass Transfer Limitation

Aside from heat transfer limitations, mass transfer also affects overall reformer performance [4,12,10]. Some research studying the mass transfer coefficient in packed beds has been presented [13,14]. Figure 3 represents the overall steps within the diffusion process.

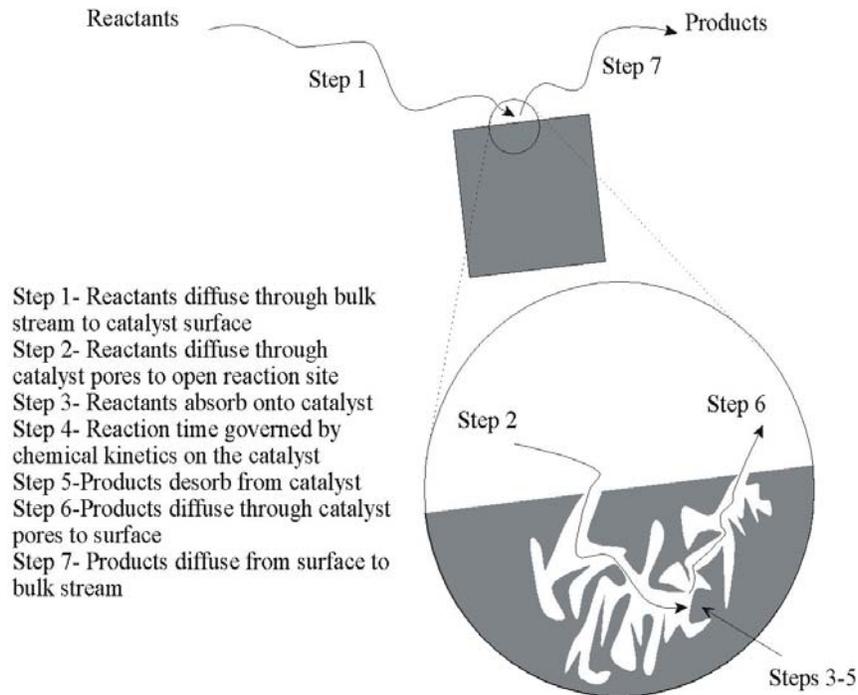


Figure 3: Steps required within the catalytic steam-reformation process [4].

Depending on the diffusion paths, these steps can be classified into three categories including external diffusion (step1 and step 7), internal diffusion (step 2 and step 6) and surface reaction (step 3 through step 5).

Literature research [15] indicates that the overall reaction rate can be limited by these three categories depending on factors of velocity, particle size and temperature. Table 1 summarizes the dependence of different limitations on these three factors.

Table 1: Diffusion rate dependence on factors. [15]

Type of Limitation	Variation of Reaction Rate with:		
	Velocity	Particle Size	Temperature
External Diffusion	$U^{1/2}$	$(d_p)^{-3/2}$	~ Linear
Internal Diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface Reaction	Independent	Independent	Exponential

In a catalytic reaction, as depicted above, the slowest step determines the overall rate of reaction. When external diffusion determines the overall reaction rate, the molecules diffusion rate is slower outside catalyst particle than inside catalyst particle and surface reaction rate. In this circumstance, parameters like reactant flow rate or catalyst size may affect the overall reaction rate. In the situation internal diffusion is slower than the external diffusion and surface reaction, changing the catalyst size may affect the overall reaction. In above two cases, mass transfer is an important mechanism. For a slow surface reaction step relative to the two diffusion mechanisms, reactant concentration and temperature could affect the overall reaction rate.

The surface reaction rate is governed by the chemical kinetics as shown in Eq. (2).

$$\frac{d[\text{CH}_3\text{OH}]}{dt} = -k_r \cdot [\text{H}_2\text{O}] \cdot [\text{CH}_3\text{OH}] \quad (2)$$

$[\text{CH}_3\text{OH}]$, $[\text{H}_2\text{O}]$ and k_r are the concentration of methanol, concentration of water and the reaction rate constant, respectively. Based on the Arrhenius mechanism, the reaction rate constant can be expressed as an exponential function of the temperature, T.

$$k_r(T) = A \exp(-E_a / R_u T) \quad (3)$$

The coefficient A is a constant designated as a pre-exponential factor with units of $[\text{mol}/(\text{sec} \cdot \text{kg} \cdot \text{bar})]$. E_a is the activation energy, and R_u is the universal gas constant.

From Table 1, one can see that temperature has a strong effect on the two diffusion limitations and the surface reaction (exponential dependence). Therefore, elevating temperature can effectively reduce diffusion limitations. In addition to temperature, particle size also has an inverse relationship with both external and internal diffusion. Reducing the particle size by crushing the catalyst pellet may reduce the diffusion time from the bulk stream to open catalyst sites. It may also increase more active area to reactants without having to increase the reactor size or catalyst loading. In reformer study, space velocity is usually used which combining the fluid velocity and catalyst loading (reactor volume) in one parameter. The definition of space velocity is shown in Eq. (4).

$$\text{Space Velocity} = \frac{\text{Volumetric Flow Rate}}{\text{Reactor Volume}} \quad (4)$$

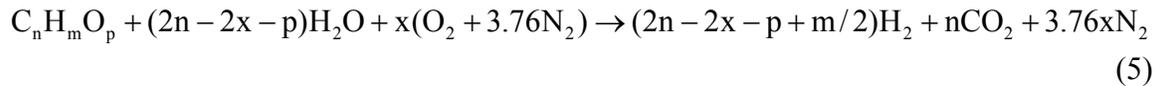
Table 1 indicates that reducing the space velocity decreases the external diffusion rate. It is also undesirable in reformer design since that would decrease the reforming capacity for a specified reformer volume or require a larger reforming processor. Past studies have shown that the space velocity plays an important role in reformation systems [16-18]. However, it has been shown that space velocity is not sufficient to characterize reformer system performance [19]. A recent study has also demonstrated that the reactor

geometry (the aspect ratio of a cylindrical type reactor or flat plate reactor) also has large effects on fuel conversion in steam reformation [20].

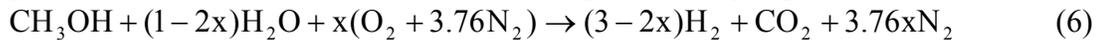
As deduced from the above discussion, elevating the overall temperature minimizes the limiting influences in a pellet packed bed reformation process. Due to a severe temperature gradient always existing within the catalyst bed, the reactor cannot be brought up to proper temperature uniformly because catalyst can be overheated near the heat source. Several methods have been investigated for heat transfer enhancement of an internal flow within a pipe. These methods include placing coil springs, swirl tape, longitudinal fins and helical ribs inside the tube [21]. Some studies have shown heat transfer enhancement inside a pellet catalyst bed in an endothermic reformation reaction [4,22,9]. This research project proposes another method to enhance the reforming process.

2.2 Monolith Catalyst in an Autothermal Reformation

Another attractive pathway to hydrogen production is autothermal reformation. Differing from the endothermic nature of steam reformation, autothermal reformation can generate heat from a partial oxidation reaction by feeding oxidant (usually air) into the catalyst bed to provide the reaction energy for the proceeding steam reformation reaction inside the catalyst bed. A general autothermal reformation of hydrocarbon fuel is shown in Eq.5.



Using methanol as the fuel, the ideal reaction is represented by Eq.6.



A typical catalyst used for autothermal reformation is a monolith structure. Heat and mass transfer also influence the reaction rate in monolith structures. Parameters including the washcoat thickness of the monolith, inlet temperature, cross geometry of a channel, void fraction, porosity and the catalyst loading can influence the reaction rate [23, 24]. Some studies have presented the investigation using metal as support material in a monolith structure, which gives a better thermal conductivity for heat transfer inside the structure [24-26]. However, no studies have quantified mixing limitations of reactant species for autothermal reformation. Because partial oxidation occurs in an autothermal reforming process, oxygen (usually air) is required. Past studies have shown that the steam to carbon ratio (S/C), oxygen to carbon ratio (x: O₂/C), and the inlet temperature play important roles in the autothermal reforming process. [27-29]. The theoretical chemical kinetics also indicates that hydrogen yield can be increased by decreasing the oxygen to carbon ratio [27, 30, 32]. However, when the oxygen feed rate is low, mixing of the fuel and oxidant before entering the catalyst bed may influence the performance of the reactor. This proposed research attempts to improve mixing for a catalytic autothermal reformer.

3. Research Objectives & Theoretical Approach

To increase the hydrogen yield in a steam reforming system, raising the overall packed bed temperature to its optimizing level as well as enhancing the heat transfer inside the packed bed becomes critical. The temperature increase also increases external and internal diffusion [15]. For an autothermal reformer, decreasing the O₂/C ratio will theoretically increase hydrogen [27], but poor mixing of fuel and oxidant needs to be addressed. This study proposes placing passive flow disturber in flow pathway to enhance the limiting mechanisms. The result of this approach is four possible mechanisms to enhance the whole reforming system:

- (1) Enhancing heat transfer via (a) conduction and (b) convection.
- (2) Flow disturbance (i.e. redirected channeling)
- (3) Changing the thermal entrance length and increased the effective path length
- (4) Increasing the mixing of Oxidant and Fuel for monolith catalyst in autothermal reformation.

3.1 Enhancing Heat Transfer via Conduction and Convection

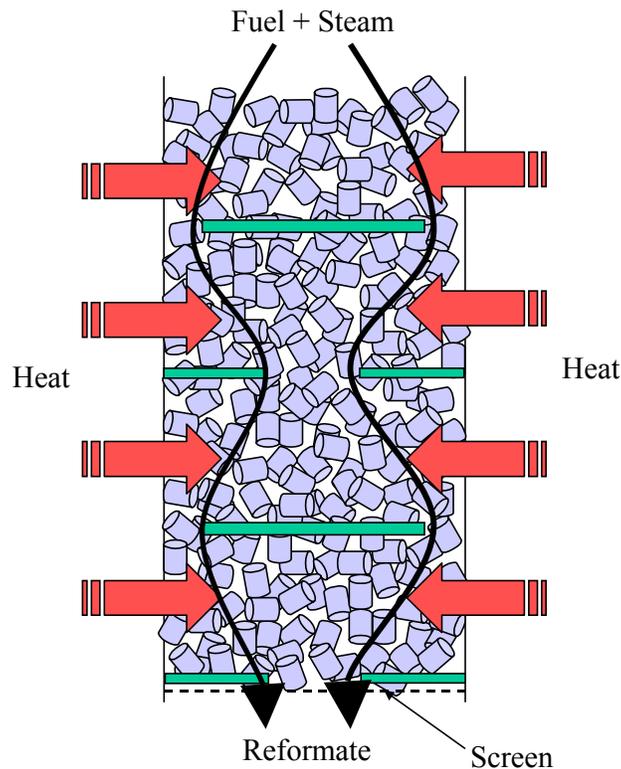


Figure 4: Schematic of catalyst bed introduced with two packages of bluff bodies.

Figure 4 shows a schematic of a pellet packed bed introduced with passive flow disturber consisted of bluff bodies. One bluff body package is composed of a thin disk and a thin ring. The main heat transfer mode inside a pellet packed bed is convection, which can be expressed as Eq. (7).

$$Q = h \cdot A \cdot \Delta T \quad (7)$$

In Fig.4, the two bluff body rings act as two fins. In addition to increase heat conduction, these fins also increase the convection area A in Eq. (7). By increasing the number of rings, the heat transfer is expected to increase. Empirical studies indicated that the Nusselt number of a packed bed has a positive exponent correlation with Reynolds number [7,31] as shown in Eq. (8).

$$Nu_D = \frac{h \cdot D}{k} \propto Re_D^x \quad (8)$$

X is a positive value and Reynolds number is proportional to the stream velocity. Assuming constant D and k , the convection coefficient, h , is a velocity-based function. Increasing the local velocity can effectively increase the local convection coefficient. As shown in Fig. 5, the minimum streamline in a normal reactor (a) is shorter than the minimum streamline in a bluff body reactor (b). Under a fixed space velocity condition, the local speed in a bluff body reactor is larger than the local speed in a normal reactor. Therefore, introducing bluff bodies may raise the local velocity, thus increases the convection coefficient h in Eq. (7),

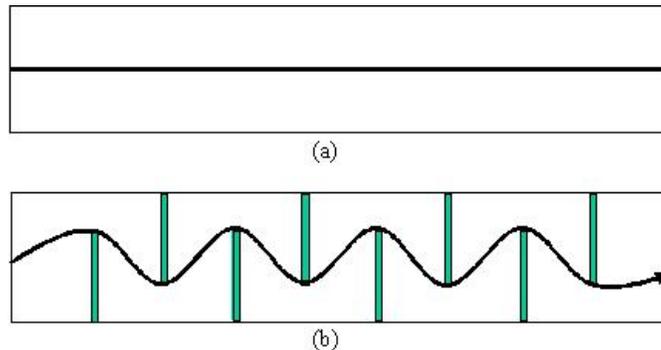


Figure 5: Scheme of streamlines inside: (a) normal reactor; and (b) reactor with bluff bodies.

3.2 Flow Disturbance

For a reactor packed with pelletized catalyst, when reacting species flow through the reactor they do not flow uniformly through the catalyst bed. Rather, the fluid flows through specific channels inside the reactor, which offer less resistance resulting in a channeling effect inside the catalyst bed as shown in Fig. 6.

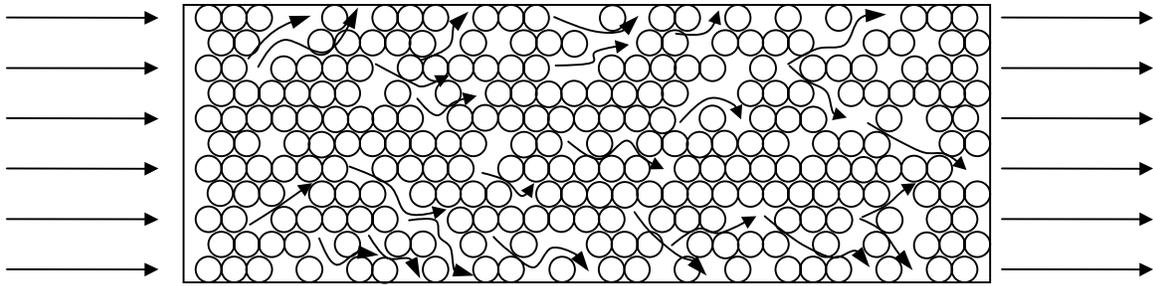


Figure 6: Channeling effect inside catalyst bed.

Consequently, some molecules spend less time flowing through these pathways than others flowing through ones with higher resistance. For a pellet packed bed with no reaction occurring inside, more molecules flow down near the wall than the centerline because more void space exists between pellet and the flat wall surface. When the reforming reaction occurs inside a catalyst bed, the reformate flows away from the hot reaction site. Since the temperature near the outer radial region is higher than that near the centerline, the reaction rate is larger than that near the centerline. From Eq.(1), one can see how the reacting species expand. As the total number of moles at the reformate side (4) is greater than that at the reactant side (2), one hypothesis states that the pressure pushes the species flow toward the relatively colder central direction as shown in Fig. 7. This phenomenon may increase the down-stream velocity near the centerline and increases the channeling effect.

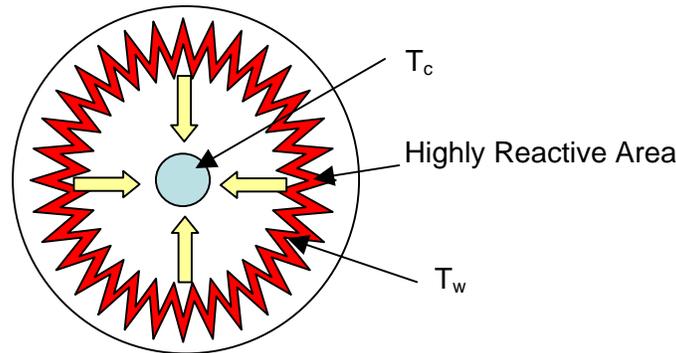


Figure 7: Schematic of reaction in pipe cross section. $T_w > T_c$

Introducing bluff body packages inside the packed bed forces all the fluid to flow by the outer hot region near the wall and draws it back to the cold region at centerline, as shown in Fig. 8. This passive flow disturbance is expected to bring the cold centerline fluid to the hot region. In other words, it enlarges the ΔT term in Eq. (7), thus increasing heat transfer near the wall. It also spreads out the flow more uniformly inside the packed bed thus decreasing the channeling effect and potentially provides better mixing of the reactants to improve mass transfer in the catalyst bed.

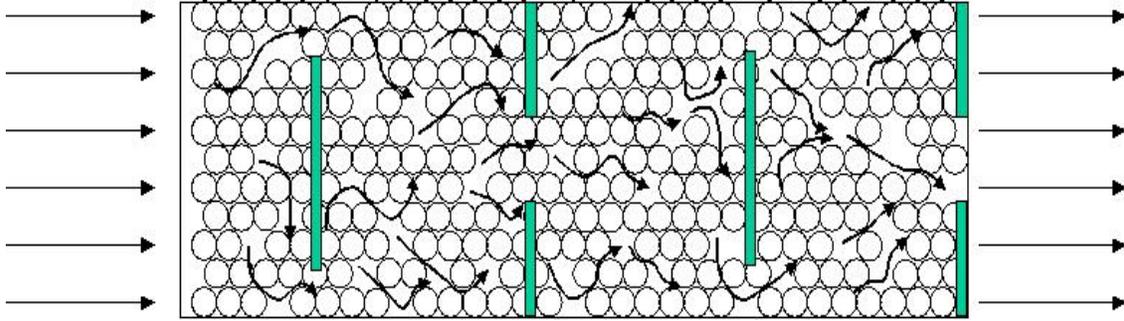


Figure 8: Decreasing channeling effect by introducing bluff bodies

3.3 Changing the Thermal Entrance Length (L_{te})

An axial mean temperature profile of an internal flow inside a constant wall temperature pipe is shown in Fig. 9 [16]. In a real situation, a reforming reactor pipe is filled with porous catalyst. At the same time an endothermic reaction also takes place within it. Aside from these deviations, the surface temperature may not stay constant due to the control limitation. Therefore, a reactor's actual thermal mechanism is much more complicated. Even though the thermal mechanism is more complex, it is expected to have the same general phenomenon as the thermal entrance length as Fig. 9.

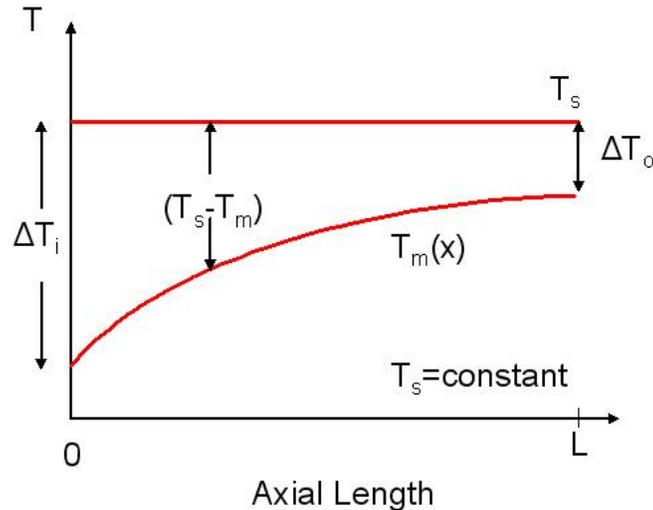


Figure 9: Mean temperature profile (T_m) along axial direction for a constant wall temperature (T_s) inside a pipe [21].

It is known that the heat convection at the thermal entrance region is larger than that at downstream due to greater temperature difference [21]. For a given pipe length L , a reactor with bluff bodies has a longer effective fluid pathway as compared to a normal reactor. This longer effective pathway is expected to help create a more fully developed thermal state thus elevating the mean temperature of the fluid for higher conversion of fuel to hydrogen.

Aside from the heat transfer enhancement, a longer effective path length created by the bluff body may also enhance mass transfer and consequently the fuel conversion in a

pellet packed bed. As described above, a longer path length can increase the local velocity.

3.3.1 Mass transfer: a single catalyst particle.

At the boundary surface of a catalyst particle, the molar flux of species A, (W_A), of a 1st order reaction equals the rate of reaction on the surface ($-r''_{As}$) in steady state and can be written as Eq.(9) [15, p704]

$$W_A = -r''_{As} = \frac{k_c k_r C_A}{k_c + k_r} = k_{eff} C_A \quad (9)$$

C_A : Concentration of species A

k_c : mass transfer coefficient (m/s), analogous to heat transfer coefficient “h”

k_r : reaction rate constant (m/s)

k_{eff} : effective transport coefficient

k_c is a function of temperature, pressure, velocity of fluid (V) and particle size (d_p). k_r is independent of V but may depend on d_p for a porous catalyst. Figure 10 shows the reaction rate of a single particle as a function of particle size and local velocity flow through the particle. From the figure, increasing the local velocity of the fluid as well as decreasing the particle diameter is expected to increase the molar flux to the surface of the catalyst (external diffusion) for a diffusion limited reactions.

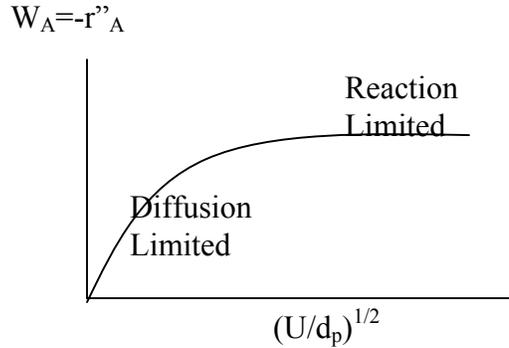


Figure 10: Regions of mass transfer-limited and reaction-limited reactions for a single particle. [15]

3.3.2 Mass transfer: through packed bed

For the case when mass transfer (diffusion) is the limiting reaction, the reactant conversion (X) depends on the mass transfer coefficient (k_c), velocity (U), and the reactor length (L) in steady state as shown in Eq.(10) [15]

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L \quad (10)$$

X : reactant conversion, $X = \frac{C_{A0} - C_{AL}}{C_{A0}} < 1$

a_c : external surface area of catalyst per volume of catalytic bed, (m^2/m^3)

$a_c = 6(1-\phi)/d_p$, is inverse proportional to particle diameter.

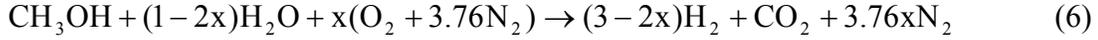
ϕ : porosity of the bed.

Equation 10 indicates that for a fixed superficial velocity U , increasing the reactor length L (or the effective path length) can raise the conversion (X).

The above theory indicates the benefit of increasing the length, local velocity and small particle diameter on the reaction rate of a pellet packed bed.

3.4 Increasing the mixing of oxidant and fuel for monolith packed bed in autothermal reformation.

Autothermal reformation is a combination of exothermic partial oxidation and endothermic steam reformation. Air is fed into the catalyst as oxidant for partial oxidation to generate heat for the steam reformation. As shown in Eq.(6);



depending on how much air (x) input to the reactor, the reaction can reach a thermal-neutral point. Equation (11) shows the heat of reaction for ideal methanol autothermal reformation, which is a function of O₂/C (x). O₂/C determines whether the reaction is exothermic, thermal-neutral, or endothermic.

$$\Delta H_r = \Delta H_{f,\text{CO}_2} - (1 - 2x)\Delta H_{f,\text{H}_2\text{O}(l)} - \Delta H_{f,\text{fuel}(l)} \quad (11)$$

Steam to carbon ratio (S/C) of 1-2x in Eq.6 is the minimum amount of water required by the ideal reaction. To prevent coke formation in the reaction, practical values for S/C are higher than 1-2x. Figure 11 is a plot evaluating the heat of reaction as a function of x ranging from 0 (steam reformation) to 1.5 (complete combustion) with the minimum amount of water for 1-2x.

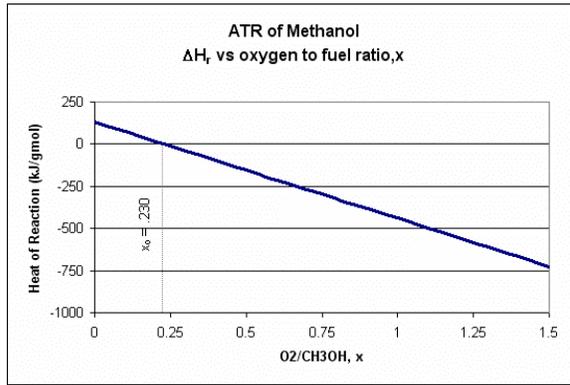


Figure 11: Heat of reaction as function of O₂/C [28]

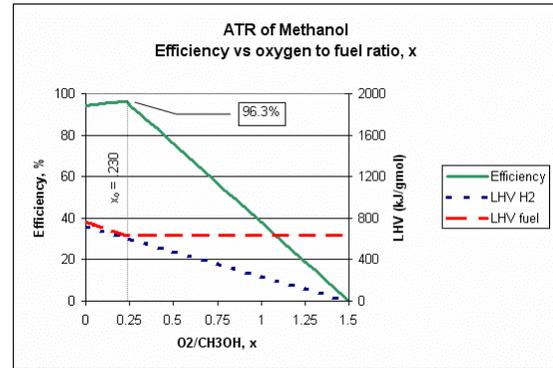


Figure 12: Efficiency vs. O₂/C [28]

The plot shows that $x_0 = 0.230$ is the thermal-neutral point. By defining the efficiency as Eq.(12):

$$\eta = \frac{\text{LHV } H_{2\text{output}}}{\text{LHV fuel}_{\text{input}}} \quad (12)$$

Figure 12 shows that the highest efficiency for ATR (96.3%) occurs at the thermal-neutral point. It is important to note that this efficiency value does not include experimental effects like reactant mixing, excess water input, catalyst effects, heat loss from the reactor and variation in reactant products from the theoretical products of reaction. A previous study showed that an experimental value of O₂/C=0.30 gave the highest efficiency [28]. But based on the theoretical calculation it is desirable to operate at a lower O₂/C of 0.230. This proposed research will investigate the mixing issue which may influence the performance of ATR at low O₂/C.

A schematic of passive flow disturbers (bluff bodies) placed before the monolith catalyst is shown in Fig. 13. By placing the obstacles in the fluid pathway, eddies will be created near the edges of the disks and rings. These eddies and a longer flow path help increase the fluid turbulence thus achieves a better mixing state for the species before entering the monolith packed bed.

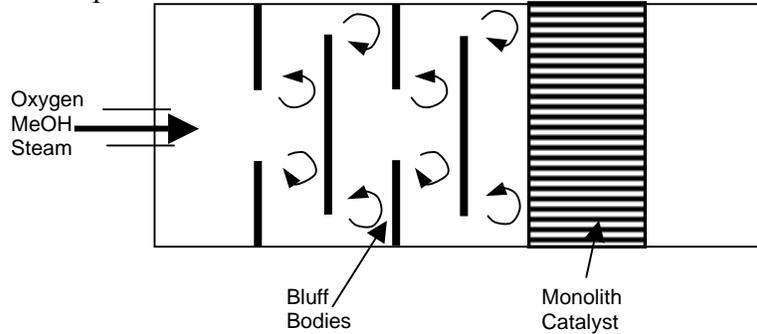


Figure 13: Schematic of bluff bodies placed before monolith catalyst.

4. Preliminary Results

4.1. Pelletized packed bed (Steam reformation)

Some preliminary results using a disk-ring bluff body set as passive flow disturbers are shown below. For a pellet packed bed steam reforming system, Figures 14 and 15 show the plots of fuel conversion percentage as a function of liquid hourly space velocity of methanol (LHSV-M). The results show that both the catalyst size (pelletized or crushed) and the number of bluff body package performing a remarkable difference in fuel conversion.

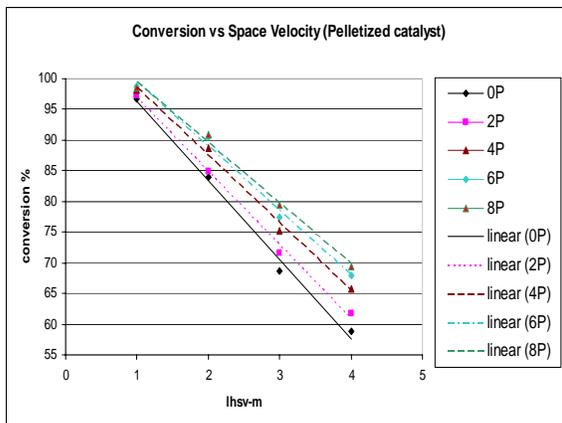


Figure 14: Methanol conversion percent as a function of space velocity (lhsv-m) with pelletized catalyst.

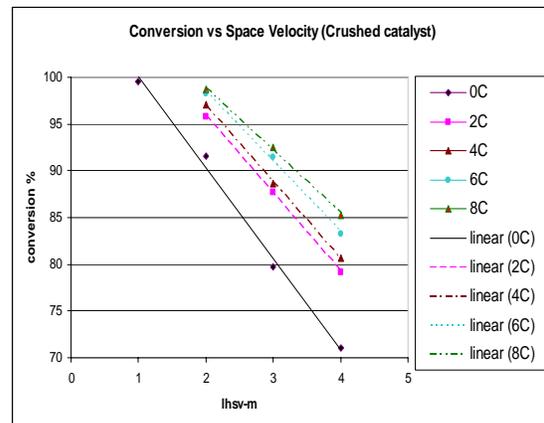


Figure 15: Methanol conversion percent as a function of space velocity (lhsv-m) with crushed catalyst.

As previously mentioned, because the bluff body packages create a longer effective pathway inside the packed bed, better temperature and mass transfer enhancements were achieved resulting in an increase of fuel conversion. When decreasing the catalyst size to

a smaller diameter (crushed catalyst), the dimension effect seemed to increase enhancement due to bluff bodies. For a given conversion of 95%, the improvement by eight packages of bluff body set increased the space velocity from 1.5 lhsv-m to 2.5 lhsv-m. This represents a 67% increase in hydrogen generating capacity (31.8 g/hr to 53.1 g/hr based on ideal reaction of Eq.1) or similarly a reduction in reactor volume over the non-bluff body case.

To examine the heat transfer enhancement inside the pellet packed bed, the centerline temperature profiles along the axial direction are shown in Figures 16 and 17. The plots show that placing bluff body packages in the flow pathway raised the temperature significantly. The centerline temperatures are generally higher when using greater numbers of bluff body packages.

The shown temperature profiles demonstrate that introducing bluff bodies effectively enhanced the heat transfer in the packed bed. Due to the temperature increase at the centerline, the overall reactor temperature approached to its optimizing operating temperature for reaction. Consequently the fuel conversion was improved.

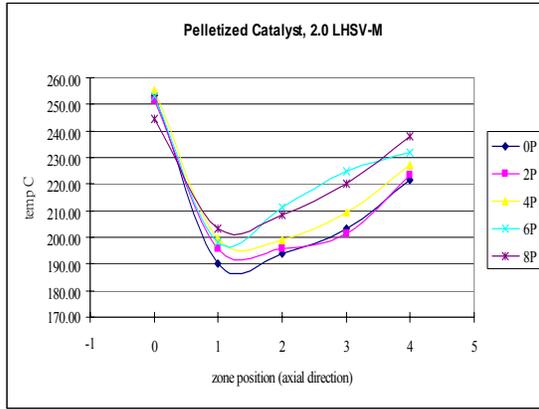


Figure 16: Temperature profile along the axial direction inside the pelletized catalyst bed.

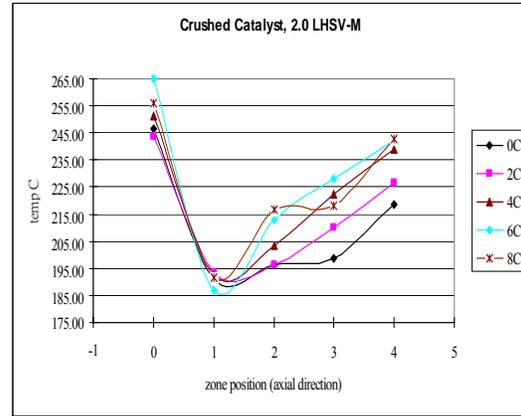


Figure 17: Temperature profile along the axial direction inside a crushed catalyst bed.

4.2. Monolith packed bed (Autothermal reformation)

Figures 18, 19, and 20 show how the bluff bodies improve the mixing over a monolith catalyst for methanol autothermal reformation. The fuel conversion is plotted as a function of oxygen to carbon ratio (O₂/C) in the figure. The dashed blue line represented the experiment using passive flow disturbers (with three bluff body packages) above the catalyst and the solid red line was without disturbers.

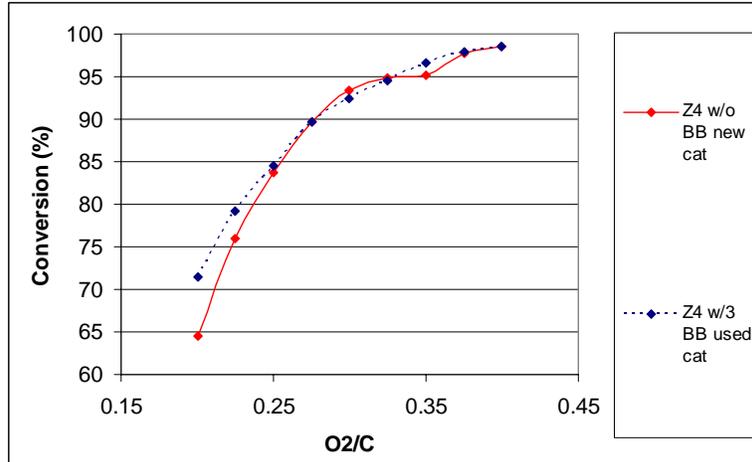


Figure 18: Conversion against the O₂/C ratio using three bluff body compare to one without disturber.

The results show that at lower oxygen to carbon ratios, the bluff body increases fuel conversion relative to the reactor without bluff bodies. When running at low O₂/C, insufficient oxygen feed enlarged the poor mixing problem and resulted in a lower fuel conversion for the configuration without disturbers. After increasing O₂/C ratio, enough oxygen feed overcame the insufficient mixing for both experiment conditions; therefore the fuel conversions presented no difference at a higher O₂/C. Figures 19 and 20 shows the centerline temperature along the axial direction of the reactor at high and low O₂/C ratio. Position 3 and Position 4 are thermal couple locations right above and below the monolith catalyst respectively. These temperature profiles explain how the bluff bodies help the mixing mechanism for fuel and oxidant before entering the monolith packed bed.

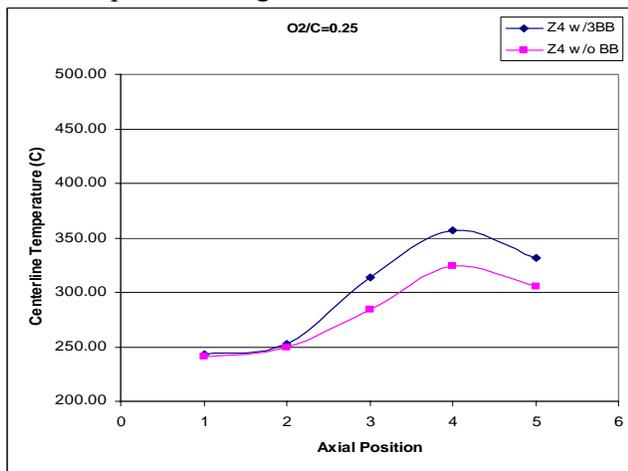


Figure 19: Centerline Temp for O₂/C=0.25

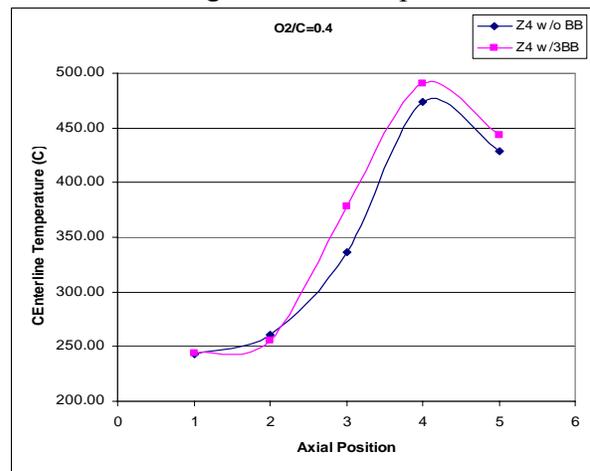


Figure 20: Centerline Temp for O₂/C=0.4

5. Research Contribution

In industry, large-scale tubular fixed-bed reactors are widely used. A pellet packed-bed reactor has the advantages of low capital cost, easy design, construction, maintenance and replacing catalyst. However, an isothermal condition and uniform concentrations of species inside a catalyst bed are issues not easy to overcome. As well, for a monolith packed bed like an autothermal reforming reactor, mixing of the reactant species before entering the catalyst can also influence the reaction rate and the overall system performance. From the conversion plots and temperature profiles shown above, this proposed research project shows potential to improve a packed bed reactor performance. At the same time, it is also necessary to investigate the physical mechanisms behind this enhancement method. A detailed study of this research is expected to yield the following:

1. further development of the fundamental principles and theories behind the passive flow disturber enhancement method;
2. optimization of the catalytic reactor's performance with minimal investment. For an on-site reforming system, the benefit is to increase the hydrogen yield thus increasing the efficiency; for an on-board fuel processor, this enhancement is expected to reduce the reformer volume as well as increasing the reformer capacity thus improving the fuel cell vehicle design;
3. a general theory-based model to capture the effect of the limiting mechanisms in reactor design. This model should be able to capture the effects of general systems and thus be widely applicable to other fields in addition to the hydrogen production arena;
4. experimental data proving out the theories involving the limiting mechanisms in steam and autothermal reformation. Specifically the data generated will prove that by changing the stream flow characteristics, enhancing heat and mass transfer with passive flow disturbance, catalytic reactor performance can be significantly enhanced.

6. Future Work

1. Other catalyst sizes will be tested with pelletized packed bed steam reformation to quantify the effects of catalyst size on reaction rate.
2. Different bluff body geometries and dimensions affecting the flow paths will be investigated.
3. Pressure drop cross the catalyst bed will be quantified. Because more pressure drop was observed by using passive disturbers, yet it is still unknown how much drawback will result. It is necessary to investigate this effect on overall reactor performance.
4. A reformer model based on thermodynamics, chemical kinetics and the limiting mechanisms will be developed. Pressure, heat exchange efficiency, pellet size, and disturber's geometry as well as dimension will be considered as input parameters of the model. By developing this model, it is expected to yield an advanced understanding of how the flow disturbance inside the reactor affects the performance of the system.
5. Thus far, the proposed methodology only presents the enhancement ability in forms of fuel conversion and reactor temperature profiles. To specifically demonstrate the enhancement, quantifying the convective heat transfer coefficient change and the

overall system efficiency will be carried out based on the experimental results. By analyzing these values, more specific heat transfer enhancement can be quantified. The results will be compared to the model.

6. Passive flow disturber's effect on catalyst degradation will also be quantified.

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The Effect of Passive Disturbers on Heat and Mass Transfer in the Hydrogen Production Process

Research Proposal

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Abstract

This proposed study investigates two different reforming methods; autothermal and steam reforming of methanol for fuel cell systems. Generally, the efficiency of overall fuel cell system can be improved by utilizing thermal waste energy from integrated fuel cell system components. This waste energy typically originates from retentate gas from membrane hydrogen separation units and/or flue gas from anode of the fuel cell. Theoretically, steam reforming fuel cell systems have higher thermal efficiencies than autothermal reforming fuel cell systems due to the resultant high concentration of hydrogen. Therefore, steam reforming is generally recognized as the more suitable fuel processor for fuel cell applications. However, steam reforming can be adversely affected by mass and heat transfer limitations and catalyst degradation. Heat exchanger efficiency of steam reformers has been found in experimental units to be less than 50%. As compared to a steam reformer, an autothermal reformer has internal heat generation which allows for lessened radial temperature gradients and higher resultant heat exchange. Impure methanol streams as found in practice have minute quantities of higher order hydrocarbons which can result in significant catalyst degradations. Due to increased temperature an autothermal method can reform the small quantities of higher order hydrocarbons and thus increase the effective catalyst lifetime. It is presently unknown if these theoretical and practical benefits of autothermal reformation can balance the entropy increase associated with higher temperature reformation.

It is the goal of this proposed dissertation topic to investigate both steam reformation and autothermal reformation when considering use of methanol for hydrogen fuel cell systems. This will be done with both theory based models and with actual experiments with the available laboratory facilities. Specifically the integration of the reformer system will be considered, the overall fuel cell system will be modeled, and the degradation of the system with typical impurities in the fuel stream will be quantified. In this proposal, a variety of critical factors will be identified and explored in order to increase the overall efficiency of a methanol-fueled fuel cell system.

I. Motivation

CuO/ ZnO catalyst steam reforming of coal-derived methanol and chemical grade methanol study has been performed in Hydrogen Production and Utilization laboratory. A fuel analysis shows that coal-derived methanol has slightly more petroleum hydrocarbons than chemical grade methanol typically used for fuel cell applications. With fresh catalyst the reformation characteristics are very similar for a variety of space velocities. The degradation rate with coal-derived methanol is slightly faster than with chemical grade methanol for this specific steam reformer. Due to heat transfer limitations, a lower centerline temperature as compared with wall temperature usually forms. This can cause catalyst fouling by liquid phase impurities. Moreover, reactor geometry effects in the steam reformer are more significant than the effects of fuel impurities in terms of catalyst degradation. However, autothermal reforming has been shown to have less temperature

gradient in the radial direction as compared to the steam reformer because of internal heat generation by heterogeneous combustion on the platinum catalyst surface. Moreover, reactor geometry effects of the autothermal reformer could be neglected in case of which air/fuel premix are well mixed and air/fuel is evenly distributed onto the catalyst surface. The higher operating temperature of the autothermal reformer could possibly reduce the effects of fouling caused by the impurities. However, an autothermal reformer can have the possibility of sintering of catalyst due to hot zone mostly caused by heterogeneous combustion. When reformers are integrated with proton exchange membrane fuel cell, some amounts of flue gas from fuel cell can be differently utilized into autothermal reformer as well as burner of steam reformer. This could lead to an increase of hydrogen concentration in case of autothermal reformer because less amount of methanol with oxygen can be consumed by catalyst oxidation reaction and nitrogen dilution effects can be reduced. Based on above contradictory factors between steam reformer and autothermal reformer, autothermal reformer could be the better solution for fuel cell applications.

II. Comparison between Autothermal Reformer and Steam Reformer

1. Reformer Efficiency

Generally, reformer efficiency is based on the ratio of lower/higher heating value of hydrogen and lower/higher heating value of fuel to produce that amount of hydrogen [Amphlett and Mann, et al., 1998, Docter and Lamn, 1999, Ahmed and Krumpelt, 2001, Kamarudin et al., 2004, Feitelberg, and Rohr et al, 2005]. Differently defined reformer efficiencies have been used in the literatures. One method adds the amount of carbon monoxide to the amount of produced hydrogen because carbon monoxide converts into hydrogen via the water gas shift reaction (WGS) [Docker and Lamn, 1999, Heinzl and Vogel, et al. 2002]. However, the efficiency of WGS and SR should be considered separately because different operating conditions between SR and WGS are associated with different heating values of reactants and products. Hence, carbon monoxide concentration can not add up with hydrogen concentration in the definition of reformer efficiency. Furthermore, SR efficiency can be 120% based on complete conversion when the enthalpy of reaction is disregarded [Feitelberg, and Rohr et al, 2005]. Hence, general reformer efficiency can be defined as shown in Equation 1

$$\eta = \frac{Q_{LHV, H_2}}{Q_{LHV, Fuel} + \Delta H_{rxn}}$$

Equation 1

A critical discrepancy between ATR and SR is the enthalpy of the heat of reaction. Generally, steam reformers require external heating to supply thermal energy into the reactor for the endothermic reaction ($\Delta H_{rxn} > 0$). However, autothermal reformers internally generate thermal energy by fuel combustion with oxygen. By controlling O/C ratios, the autothermal reformer can be operated at either thermal neutral ($\Delta H_{rxn} = 0$) or slightly exothermic reaction ($\Delta H_{rxn} < 0$) setting. Two different efficiencies of reforming methods can be defined separately, as shown in Equation 2 and Equation 3 respectively.

$$\eta_{SR} = \frac{Q_{LHV,H_2}}{Q_{LHV,Fuel} + \Delta H_{rxn}}$$

Equation 2

$$\eta_{ATR} = \frac{Q_{LHV,H_2}}{Q_{LHV,Fuel}}$$

Equation 3

A burner should be implemented to supply sufficient heat into the steam reforming reactor for endothermic reaction. However, the thermal integration efficiency between the burner and steam reformer can not be 100%. As a result, ΔH_{rxn} should be substituted with $\Delta H_{combustion} / \eta_{HEX}$. If the efficiency of heat exchanger is 50% derived from experimental data as well as mentioned by Kolios et al. 2004, the output of thermal energy from the burner would be two times of heat demanded for the endothermic reaction. Heat exchange efficiency was calculated based on experimental data as shown in Figure 2.

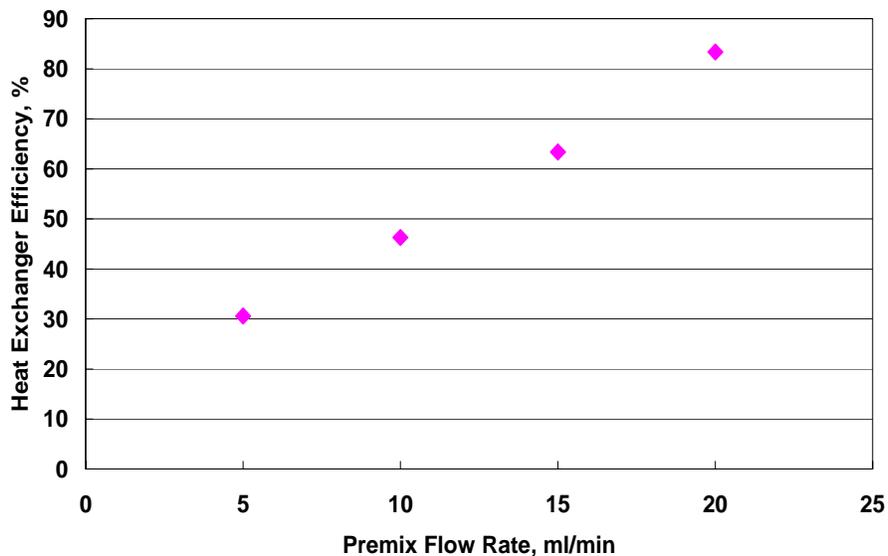


Figure 2: Heat Exchange Efficiency (%) based on different premix flow rate (ml/min)

2. Monolithic washcoated catalyst(Autothermal reformer) versus Pelletized Catalysts(Steam Reformer)

A variety shape of catalyst which are pelletized (crushed), monolithic, plate and corrugated form can be adapted for hydrogen production via reforming hydrocarbons. Specially, pelletized and monolithic washcoated catalysts have been used in Hydrogen Production and Utilization Laboratory. In comparison between pelletized and monolithic catalyst, degradation, activity and heat and mass transfer under different reactor circumstances should be discussed. First of all, pelletized catalyst shows the advantage against catalyst degradation compared with monolithic washcoated catalysts in case of poisoning because it is hard to access poisons into the subsequent region compared with

monolith type of catalyst due to tortuous path of chemical reaction region [Richard Carranza, 2004]. The disadvantage of pelletized catalyst has higher pressure drop, and heat and mass transfer resistance compared with catalytic monolith with washcoat. In case of monolithic washcoated catalyst loaded in autothermal reformer, much more evenly distributed temperature profile compared with pelletized catalysts loaded in steam reformer can be sustained in case of monolith catalysts so that it could lead to reduce fouling of catalyst caused by higher hydrocarbon. Due to parallel structure of monolithic catalyst, impurities could slip through with the products without severe deactivation of catalysts [Richard Carranza, 2004]. However, impurities can be contained in the products so that different operation condition of hydrogen separation unit might take into account to prevent palladium membrane degradation from higher hydrocarbons.

2.1 Mass transfer limitation of steam reformation in case of pelletized catalyst

Mass transfer or diffusion also is known as a significant limiting step on the reforming process. As seen in Figure 3, where mass transfer is coupled with the chemical reaction, the phenomenon begins with the reactants diffusing through the bulk stream to catalytic surface. Then the reactants (Steam hydrocarbon mixture) diffuse through the catalyst pores to open reaction site and then absorb onto the reactive site. After absorbing, the chemical reaction occurs on the catalyst. The product gases desorb from the catalyst and then diffuse from the catalyst pore into the bulk stream. To improve the rate of mass transfer from the bulk of the fluid to the catalyst surface, decreasing distance of diffusion to minimize pore diffusion resistance can be accomplished by providing more active site and increasing the amount of loading catalyst. However, this is not proper case for vehicle application due to increasing size.

Decreasing the length of internal diffusion can also be accomplished by crushing the catalyst.

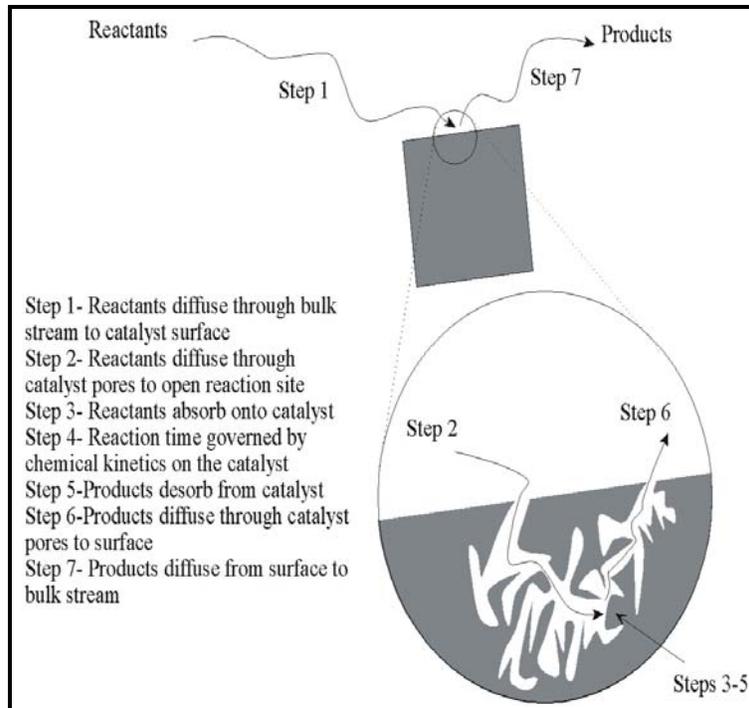


Figure 3: Steps required within the catalytic steam reformation process

2.2 External Mass transfer limitations of monolithic washcoated catalyst

The heterogeneous combustion is catalytic combustion occurring at lower than the auto-ignition temperature of the fuel/oxidizer mixture and can significantly reduce NO_x due to much lower temperature as compared to homogenous combustion [Pfefferle, L. D. and W. C. Pfefferle, (1987) Maas and Warnatz (1993), Roy et al, 1999, Appel et al, 2004]. Catalytic combustion can not take place at a steady state rate greater than reactants mass transfer rate to washcoat or products mass transfer rate away from the washcoat [Pfefferle, L. D. and W. C. Pfefferle, 1987]. In other words, diffusion limitation on the washcoat surface is the critical factor to determine light-off [Ramanathan et al, 2003]. In the absence of heat radiation, heat transfer rate can be expressed in terms of temperature difference between catalyst surface and bulk gas fluid as shown in Figure 4. An Arrhenius type reaction rate can be drawn in terms of heat rate and temperature so that flow rate has only minor effects on light-off temperature [Pfefferle, L. D. and W. C. Pfefferle, 1987]. Kinetically limited catalyst temperature is indicated as subscript 1 and mass transfer limited catalyst temperature is indicated as subscript 3. Catalyst temperature should be high enough to ignite by preheating and maintain ignition during steady state [Pfefferle, L. D. and W. C. Pfefferle, 1987]. As gas temperature increases, catalyst temperature reaches the ignition temperature. Above this gas temperature (T_{gas}), the catalyst temperature jumps into the mass transfer limited region so that catalyst temperature (T_1) is called as catalyst light-off temperature. As gas inlet temperature decreases slightly and maintains above light-off temperature, catalyst temperature decreases with the slight change of reaction rate due to the mass transfer limitation [Pfefferle, L. D. and W. C. Pfefferle, 1987]. At catalyst temperatures lower than T^* ,

catalyst temperature drops into reaction limited zone and reaction rate is not sufficient to maintain the light-off so that T_3 is referred to as catalyst extinction temperature.

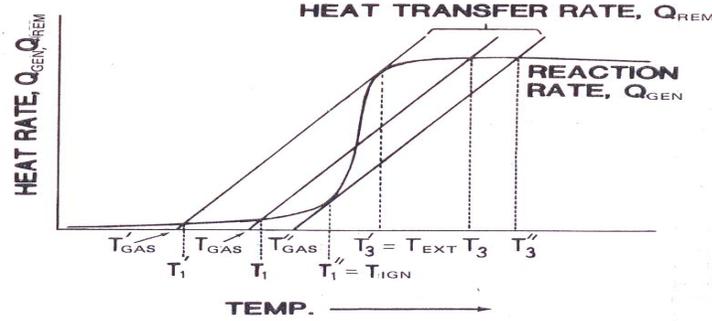


Figure 4: catalytic rate versus heat transfer rate [Pfefferle, L. D. and W. C. Pfefferle, 1987]

If gas temperature stays in the reaction limited region, light-off cannot take place because catalyst temperature is nearly equal to bulk gas fluid temperature as shown in Figure 3. In the bulk gas diffusion in mass transfer limited catalytic combustion, reactant diffusion onto the washcoated surface is equal to burning rate of oxidation as shown in Equation 4 [Castaldi et al., 2000].

$$C = 1 - \exp(-k_c A / Q)$$

Equation 4

where C is the conversion of reactants, A is the monolithic surface area, k_c is the mass transfer coefficient, Q is the volumetric flow rate. Volumetric expansion of boundary layer leads to increase much higher downstream temperature than inlet as temperature so that it causes a large increase gas velocity in the channel [L.D. Pfefferle and W.C. Pfefferle, 1987]. If the gas flow rate is beyond certain points, reactant conversion by light-off decrease as shown in Equation 4. This might lead to change from mass transfer limited control to kinetically limited control [Rosner, 1964] so that light-off turns into extinction for the unreacted species reaching the downstream catalyst [L.D. Pfefferle and W.C. Pfefferle, 1987]. Autothermal reforming of methanol is the combined processes of catalytic oxidation and steam reforming. Generated heat is consumed by methanol and water conversion into a hydrogen-rich gas. It might lead to decreased surface temperature caused by endothermic reaction so that mass transfer limited reaction might change to kinetically limited process which leads to localized extinction. Gas chromatography certifies that oxygen is included in the hydrogen-rich gas and a temperature gradient in the axial direction is manifest confirming this theory.

Since the active surface of monolithic catalyst is located in a washcoat, Thiele modulus can explain the diffusion effects through the pores [Wanker and H. Raupenstrauch, et al. (2000)]. Washcoated monolith Thiele modulus for catalytic oxidation can be expressed as shown in Equation 5

$$\phi = \delta_c \sqrt{(k_v (T_{f,in}) / D_e)}$$

Equation 5

in terms of washcoat thickness (δ_c), first order reaction rate constant per unit washcoat volume (k_v), inlet fluid temperature ($T_{f,in}$) and effective diffusivity of reactant in the washcoat (D_e) [Ramanathan et al, 2003]. As you can see, increase temperature can raise Thiele modulus value, which means mass transfer limited is critical for catalytic oxidation.

Flue gas can be utilized in the autothermal reformer which can be helpful for light-off below 200°C as well as speed up the light-off process. Small amounts of hydrogen added can increase the heterogeneous combustion temperature higher than adiabatic combustion temperature, contributed by the Soret effect which is explained by mass diffusion caused by thermal gradients [L.D. Pfefferle and W.C. Pfefferle, 1987]. Moreover, hydrogen addition into reactor can lower O/C to achieve autothermal operation so that hydrogen production increases because of small portions of methanol is combusted and the nitrogen dilution effect diminishes.

2.3 Heat transfer characteristics of autothermal reformer loaded with monolithic catalyst

The heat transfer occurring in the monolithic catalyst can be categorized by conduction in the wall through radial/axial direction, convection between gas and wall and radiation losses. Radiation losses can be negligible due to the nested arrangement of monolithic catalyst [L.D. Pfefferle and W.C. Pfefferle, (1987)]. Conduction and convection between the catalyst and the wall can be minimized by insulation. Therefore, the majority of heat transfer takes place between the gas and the catalyst. However, the hot spots with the monolithic catalyst might cause the sintering of catalysts [Lassi, U., R. Polvinen, et al. (2004)]. As shown in Figure 5, a hot spot is located at the top of the catalyst, and temperature decreases as axial direction increase.

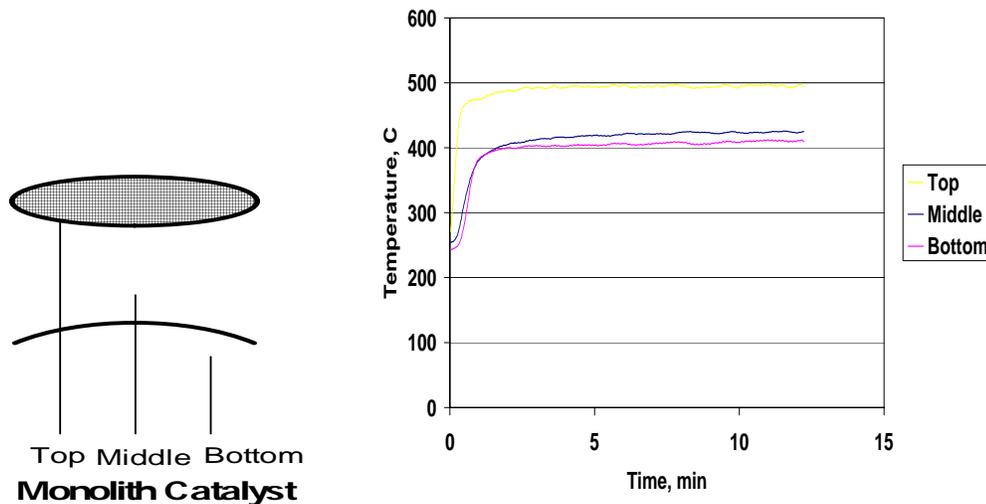


Figure 5: Temperature inside the urban catalyst at different locations ($O_2/C=0.2$)

2.4 Heat Transfer characteristics of steam reformer packed with pelletized catalysts

Due to endothermic reaction, heat is supplied into the reformer by radiation, conduction and convection. Heat transfer into the reactor usually occurs by means of

conduction through the reactor walls. Radiation can be neglected due to small local temperature differences. On account of point-to-point contact between catalyst particles, conduction is relatively smaller than convection within the reactor. Therefore, heat conduction is negligible so that convection results in governing heat transfer through the fluid inside the reactor. Another significant problem is the condensation of gas onto the solid catalyst caused by heat transfer limitation.

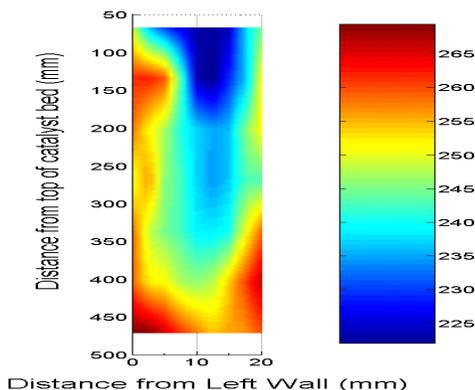


Figure 6: Typical Reactor Temperature Profile in Reactor A (Deg C)

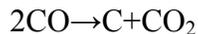
Note that the geometry is not to scale (David Vernon, 2005)

This temperature profile creates higher hydrogen concentration near the wall than near the center with better transport properties brought by higher temperature (Murray, A. P et al. 1985) as shown in Figure 6 (measured by David Vernon). Naturally, this convective heat transfer limitation near the centerline (cold spot) can lead to unreacted feed gas decreasing the overall conversion. Furthermore, unreacted feed gas can deactivate the catalyst by means of fouling which is physical hydrocarbon accumulation blocking pore of catalyst. Literally, increasing surface area in both the gas/catalyst pellet interface and wall/gas/catalyst pellet can enhance convective heat transfer. However, this usually means increasing size of fuel processor which is inadequate for transportation.

3. Theoretical Backgrounds of Catalyst Degradation

The degradation of Cu/ZnO/Al₂O₃ catalyst results in a decrease in both total surface area and total rate of production of reformat gas. Furthermore, as hydrogen selectivity decreases due to deactivation, the rate of production of CO relative to the rate of hydrogen production increases (Thurgood et al., 2003). In general, poisoning, sintering and coking or fouling is thought as the main mechanisms of catalyst deactivation. Vapor compound formation caused by different phase reactions (i.e. vapor-solid reaction) might be possible for catalyst degradation (Forzatti et al., 1999, Bartholomew, 2001, Jiang et al., 1993, Twigg and Spencer, 2003). To begin with, poisoning occurs with chemisorptions of impurities on reaction site (Bartholomew, 2001, Forzatti, 1999). Likewise, copper-based catalysts which have been used in this study are highly reactive with other compounds by chemical adsorption and reaction. Secondly, fouling or coking can occur by physical deposition of species (i.e. carbonaceous residue) onto the catalytic surface and in catalyst pores (Bartholomew, 2001, Forzatti, 1999). Usually, carbon is created by the Boudouard Reaction (Equation 10) whereas coke or

fouling can also be produced by decomposition (cracking) or condensation of hydrocarbons (Forzatti, 1999).



Equation 6

The Boudouard reaction as shown in Equation 6 would indicate that CO_2/CO ratio is relatively high in the steam reforming reaction. As already mentioned, coking problems can be prevented by use of excess steam (1.3~1.5 steam carbon ratio) in the copper-based catalyst (Cheng et al., 1999). However, fouling can be caused by hydrocarbons in the methanol under low-temperature steam reforming process due to condensation of these compounds on the surface. Those condensate hydrocarbons can coat onto the surface as well as leave deposits to block the pores of catalyst. To prevent coking or fouling, higher temperature and excess steam are required. Sintering is the main mechanism of catalyst degradation in the case of copper catalysts. This is due to the low melting point and occurs by means of thermally induced loss of catalytic surface area (Bartholomew, 2001). This occurs due to crystallite growth, also resulting in loss of support area due to support collapse and loss of catalytic surface (Bartholomew, 2001). Excess heat by means of the external heat sources can occur in the steam reformer. Sintering strongly depends on temperature thus the temperature should be maintained below the sintering limit.

3.1 Steam reformer catalyst degradation

Steam reformation has shown the drawback of catalyst degradation with impurities due to heat transfer limitations. Even worse, the effects of reactor geometry are more significant than the effects of fuel impurities as shown in Figure 7. The degradation rate of coal-derived methanol was greater than that of chemical grade methanol for both reactor B and reactor C, in terms of fuel (Different reactor schematics are found in the Appendix). However, reactor geometry apparently has a much greater effect on degradation and overall conversion than the 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 effect on catalyst aging than fuel impurities in the case of steam reforming.

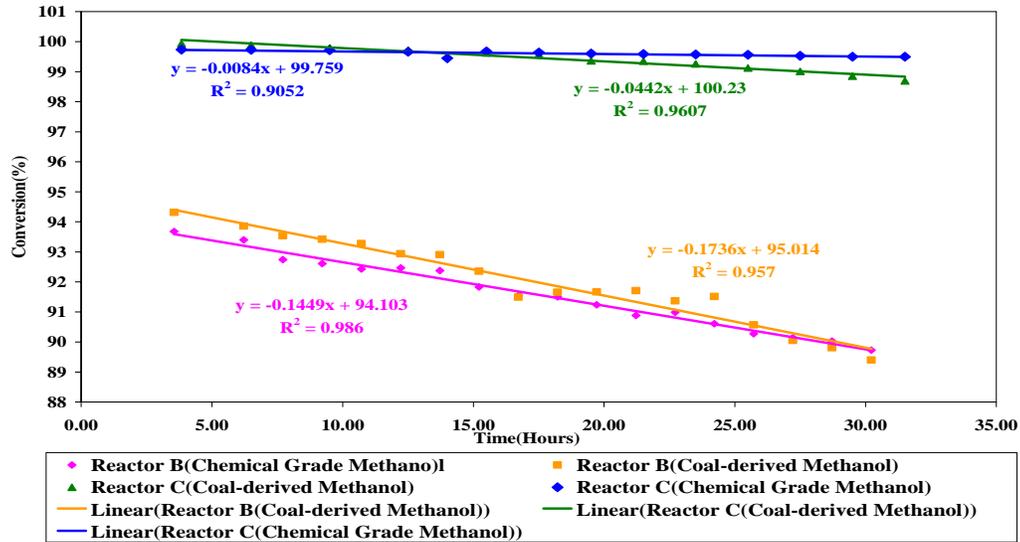


Figure 7: Steam reforming chemical grade and coal-derived methanol of catalyst degradation test in different reactor geometry

Figure 8 represents the zone 1 centerline temperature change occurring with degradation of the catalyst with Chemical Grade (CGM) and Coal Based (CBM) methanol. This temperature increase can account for the degradation of catalysts occurred by loss of activity of endothermic reaction in the center of reactor.

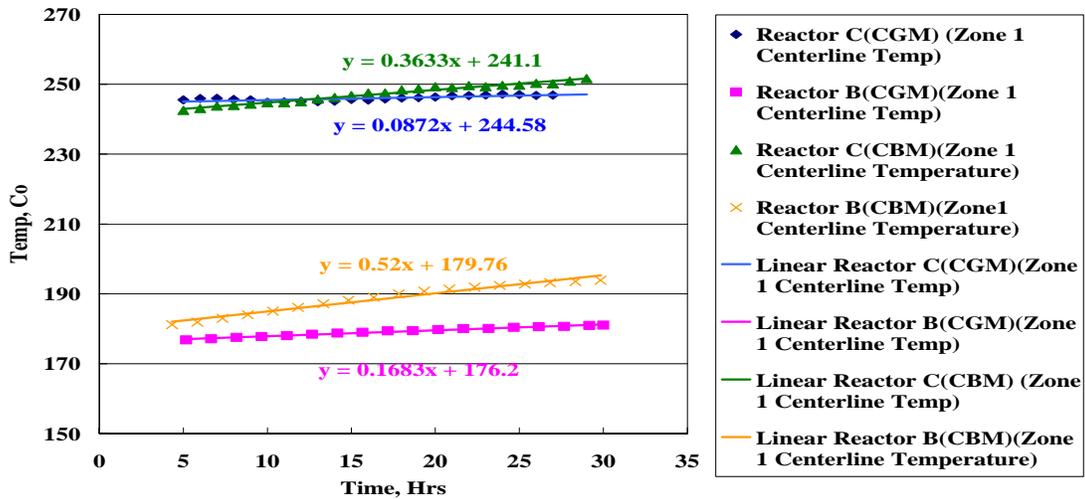


Figure 8: Zone 1 centerline temperature change for 30 hours degradation test for reactor B and C

As show in Figure 9, a cold spot (indicated as black region) is moving down and getting narrower due to loss of activity. This result brings out the importance of heat transfer for catalysts life cycle.

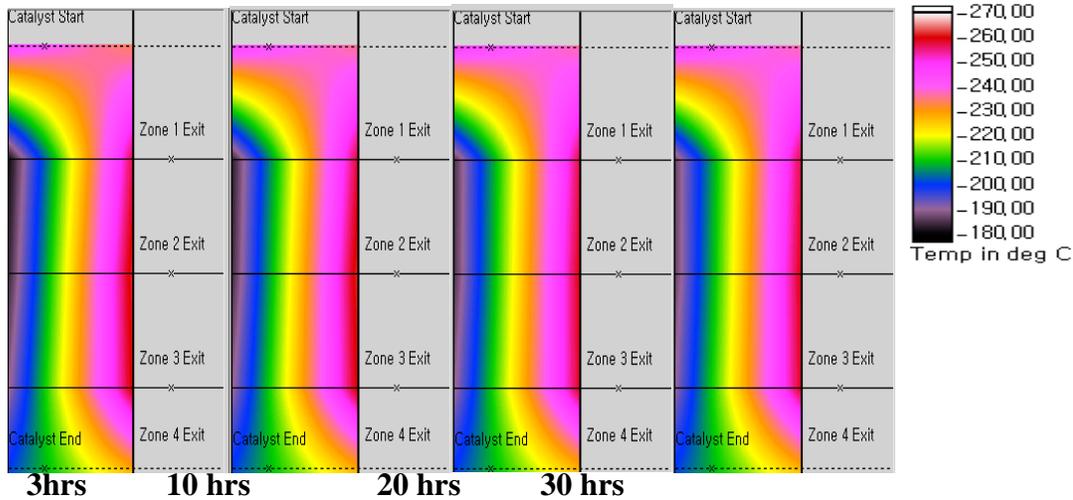


Figure 9: Temperature profile change in reactor B for 30 hours

Loss of activity of catalyst can be compensated by the increase of reactor temperature so that reaction rate can be equal to initial reaction rate according to modified Arrhenius equation as shown in Equation 7 [Michael S. Spencer and Martyn V. Twig(2005)].

$$\Delta T = T_1 \left\{ \left[1 + \frac{RT_1 \ln(0.5)}{E_A} \right]^{-1} - 1 \right\}$$

Equation 7

However, it can lead to catalyst sintering caused by excess heat supply into the reformer.

3.2 Autothermal Reformer Degradation

Autothermal reformer operating temperature is much higher than CuO/ZnO pelletized catalyst. The hot spot in case of ATR loaded with monolith type catalyst might cause the degradation of the catalyst by sintering the substrate [Lassi and. Polvinen, et al. (2004)]. On the other hand, the hotter temperatures can reduce catalyst poisoning because some of poisons (volatiles) will react rather than condense as with the steam reformer. Fouling problems can reduce if reactants are distributed evenly onto the catalyst surface and fuel water and air are well-mixed so that all hydrocarbons volatilize. Figure 10 shows the importance of fuel mixing effects with air. The conversion of methanol using a catalyst located lower in the bed (zone 4) was higher than when it was placed higher in the bed (Zone 1) as shown in Figure 10. This indicates that mixing effects of fuel with oxygen should be considered for ATR experiments.

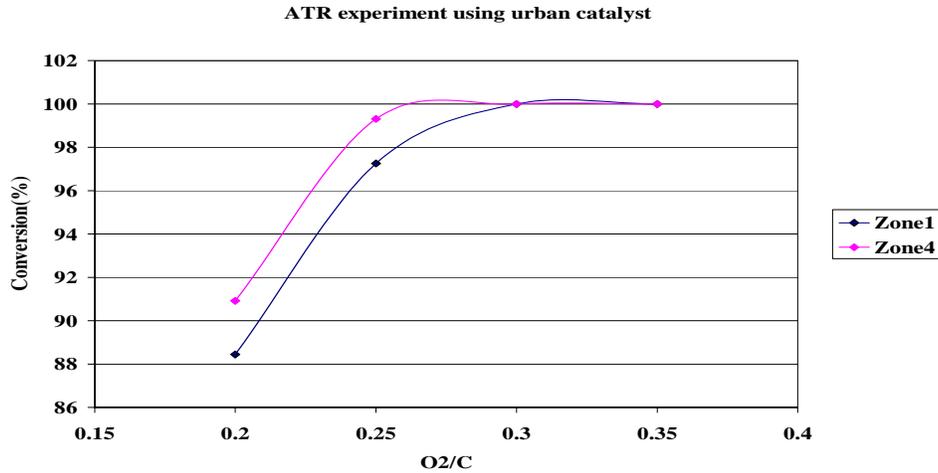


Figure 10: Methanol conversion associated with different O₂/C ratio

Autothermal reformer degradation test has been performed using monolithic catalytic converter for vehicle applications, composed of Palladium Rhodium. As shown in Figure 11, conversion difference between coal-based and chemical grade methanol might come from either the difference in reduction catalyst or different unstable operations. The conversion of chemical grade methanol did not change for 30 hours. However, the conversion of coal-derived methanol was slightly decreased. To verify the autothermal reformer degradation test, a 2nd round of autothermal degradation tests for both methanol fuels has been planned.

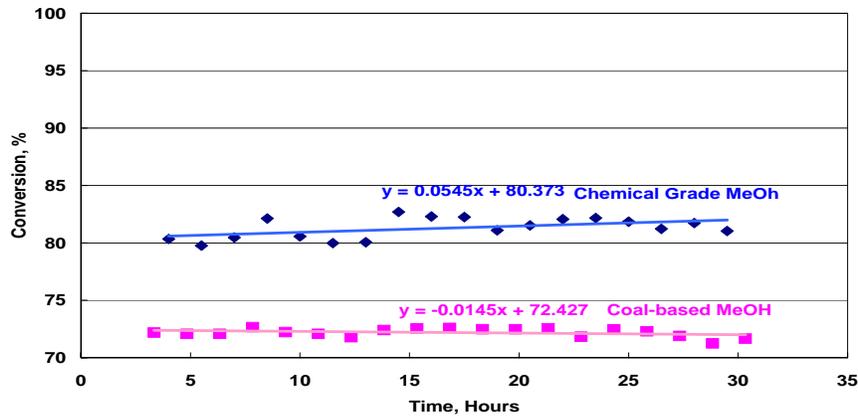


Figure 11: Autothermal Reformer Degradation

IV. Fuel Cell System Modeling

Fuel cell system modeling will occur and will be validated and calibrated with experimental data. This calibration is necessary because the reformer obviously does not follow equilibrium concentration because of the heterogeneous chemical reaction. There are also many unknown parameters which can determine reformer performance such as reactor geometry and catalyst degradation mentioned previously. Therefore, modeling of fuel cell system will be validated based on experimental data.

1. Overall fuel cell system descriptions

General schematic of fuel cell systems adapted two different reformers can be described in Figure and Figure respectively.

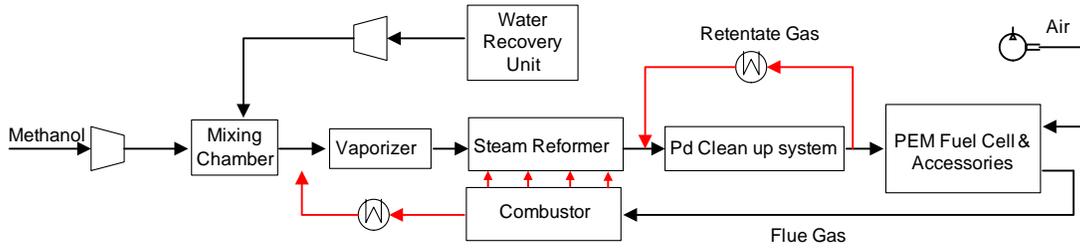


Figure 12: General Schematic of Steam Reformer Fuel Cell System

As shown in Figure , steam reforming fuel cell system requires a combustor to supply heat into the steam reformer. Vaporizer should be adapted with steam reformer because 60% of overall steam reforming power consumption is consumed for vaporizing methanol/water premix as indicated in Table 1. Water can be reutilized by a water separation unit connected with the PEM fuel cell and combustor retentate gas. Before the vaporizer, methanol and water should be mixed together to prevent coking.

Table 1: The percentage of power consumption for methanol and water vaporization at different liquid hourly space velocity (LHSV)

LHSV(1/hr)	1	2	3	4
Percentage of Power consumption of Vaporizer (%)	64	64	69	72

After the endothermic reaction, reformat is routed into palladium (Pd) membrane hydrogen separation unit. Steam reforming reformat temperature will be around 200~230°C depending on Liquid Hourly Space Velocity (LHSV) as well as steam/carbon ratio. Reformat should be heated and pressurized before clean up system in order to increase hydrogen permeability through palladium membrane as shown indicated in Figure 12. For safety and energy consumption reasons, liquid (methanol and water mixture) compression is preferred. High operating temperature of clean up system can be supplemented by heat integration with retentate gases including small amounts of hydrogen with internal heater. Retentate gas can be rerouted into combustor of the steam reformer. If there is water or unconverted methanol in the reformat, either a condenser or higher operating temperature (>400°C) should be integrated or adapted in order to reduce the absorption of water and hydrocarbons onto the palladium membrane.

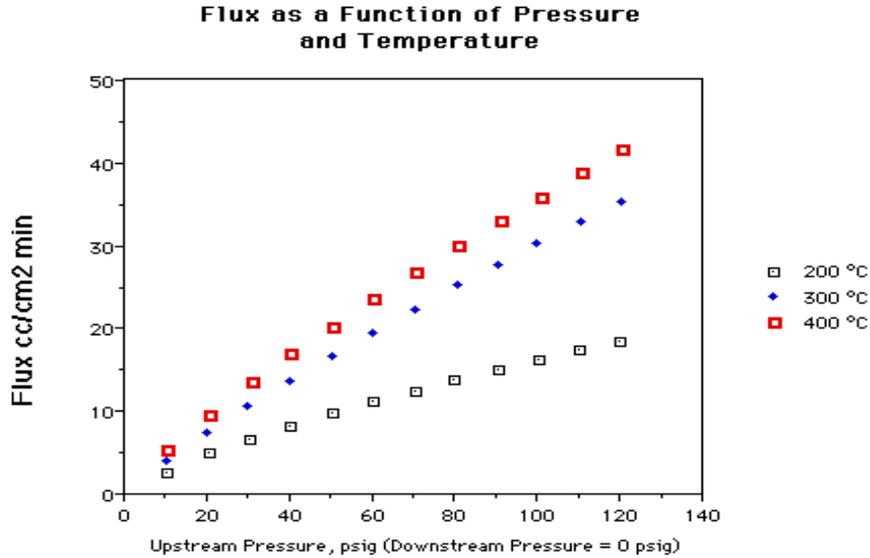


Figure 13: Hydrogen Permeation at different temperature and upstream pressure (Reb research)

Hydrogen utilization of proton exchange membrane fuel cell might be around 91% so that almost 9% of unutilized hydrogen which is referred to as flue gas comes out of the anode. Flue gas can be used in either the cathode or combustor. The excess air after cathode can be directed into the combustor so that it can reduce the compression power if required. Through the energy balance in PEM fuel cell, available thermal energy in the fuel cell system can be estimated as shown in Equation 12.

$$Q_{cooling-air} = Q_{Theoretical} - (Q_{anode} + Q_{cathode} + Q_{loss,radiation})$$

Equation 8

Compared to steam reforming fuel cell system, autothermal reformer fuel cell system can be described as shown in Figure . Basically, autothermal reforming fuel cell system can be more efficient than a steam reforming system due to self-sufficient heat generation by combustion. This can give a variety of prospects to autothermal reforming fuel cell system even with a cold start up fuel cell system.

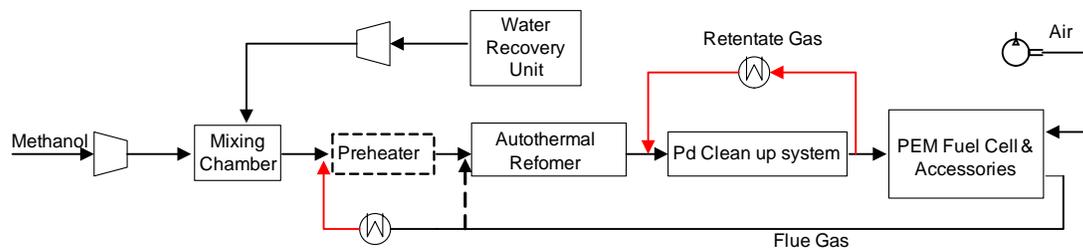


Figure 14: General Schematic of Autothermal Reforming Fuel Cell System

As already mentioned previously, vaporizing premix is the barrier for both steam and autothermal reformation. As shown in Figure , temperature can be increased from room temperature to 300C⁰ within 40 seconds (Schuessler et al. 2001). Liquid fuel spray injection can not only reduce the start up time of reformer but also increase dynamic response.

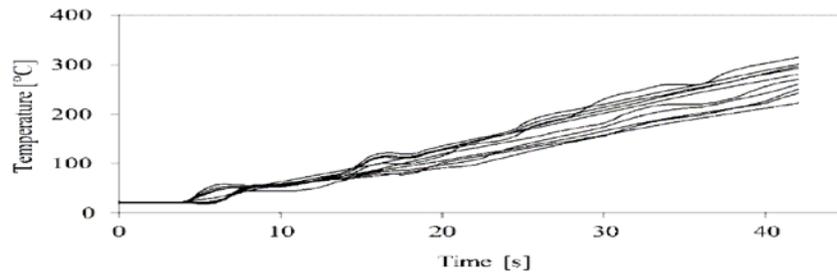


Figure 15: Temperature in the catalyst during start up from room temperature with liquid methanol (Schuessler et al. 2001)

As previously explained, hydrogen from flue gas can be utilized in the autothermal reformer which might be helpful for light-off below 200°C because hydrogen mass diffusion velocity is fast. Moreover, hydrogen addition into reactor can decrease O/C so that hydrogen production increases because of small portions of methanol is combusted and nitrogen dilution effect is reduced. Higher reformate temperatures with an autothermal reformer requires less thermal energy to heat up to the operating temperature of the Pd clean up system. Air requirements can be solved by reutilizing pressurized air from the cathode. Consequently, more opportunities of increasing efficiency by heat integration are given to autothermal reforming fuel cell system as compared with steam reforming of methanol fueled-fuel cell systems.

2. Modeling fuel cell systems

PEM fuel cell system modeling includes compressor, autothermal reformer and steam reformer, palladium alloy membrane clean up system, heat exchanger and PEM fuel cell. All components are based on thermodynamic analysis. Wide range of operating conditions which are pressure (0~250 PSI), temperature (100~1000 C°), steam carbon ratio (0~4.0) and oxygen carbon ratio (0~1.5) are used for the reformer model. Product concentration is based on equilibrium. Hydrogen permeability is chosen from either REB Research & Consulting data or empirical equations. The efficiency of reformer is based on lower heating value of fuel, lower heating value of hydrogen and heat of reaction as explained previously. In addition, vaporization of fuel is also included for the overall reformer efficiency. Heat exchange efficiencies of the steam reformer are based on experimental results. Other heat exchanger efficiencies are assumed at 80%. All systems are thermally integrated to use waste heat from the fuel cell as well as clean up system. Based on this model, we can estimate the standard flow rate of hydrogen after the clean-up system. Furthermore, approximate active surface area as well as thickness of palladium alloy membrane can be calculated by using this model. Ultimately, high pressure and temperature for isobaric fuel cell systems can be adapted from thermodynamic calculation through modeling results because clean up system and fuel cell need to be pressurized to increase of the efficiency.

3. Palladium Alloy Membrane Clean Up System

Due to competitive adsorption hydrogen with reformate (i.e. carbon monoxide, carbon dioxide, unconverted hydrocarbons and water) through palladium membrane; optimized operating conditions should be required. The effect of mass transfer resistance and competitive adsorption due to impurities can be a significant factor for clean up

system [Ward and Dao, 1999, Hou and Hughes, 2002, Vandyshev and Murav'ev et al., 2001]. Build-up of impurities can make a barrier so that hydrogen permeability through palladium is decreased [Hou and Hughes, 2002]. Furthermore, some amounts of impurities can be adsorbed and desorbed through palladium alloy membrane. Thus, high purity of hydrogen might not be achieved in those circumstances. Therefore, relative high gas velocities (>100cm/s) and high operating temperature (>673K) were consequently suggested to minimize the inhibition of above barriers [Hou and Hughes, 2002].

Hydrogen separation from impurities can be accomplished by pressure driven processes (Loffler and Taylor, et al., 2003). Assuming that the rate-controlling step is diffusion of hydrogen, the hydrogen flux can be described by the integration of Fick's Law,

$$N_{H_2} = -k \frac{(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{l}$$

Equation 9

where k is palladium membrane permeability, l is membrane thickness and P is hydrogen partial pressure at different sides. As shown in Equation, increasing differential pressure through the membrane, increasing membrane surface area and decreasing membrane thickness can enhance the hydrogen flux from retentate to permeate side. However, increasing surface area and decreasing thickness can lead to improperly increase size and decrease the hydrogen purity. Hydrogen permeation through palladium might be calculated based on either empirical equation in the literature

$$k = 2.2 \times 10^{-7} \exp(-1600/T)$$

Equation 10

Operating Temperature should be greater than 400°C to prevent palladium membrane degradation from hydrocarbon [Hou and Hughes, 2002]. Figure shows the hydrocarbon concentration change caused by degradation after the condenser. The catalyst does absorb some of the hydrocarbons early in the tests. As the catalyst degradation is continuing the excess hydrocarbons pass through or partially react in the catalyst bed.

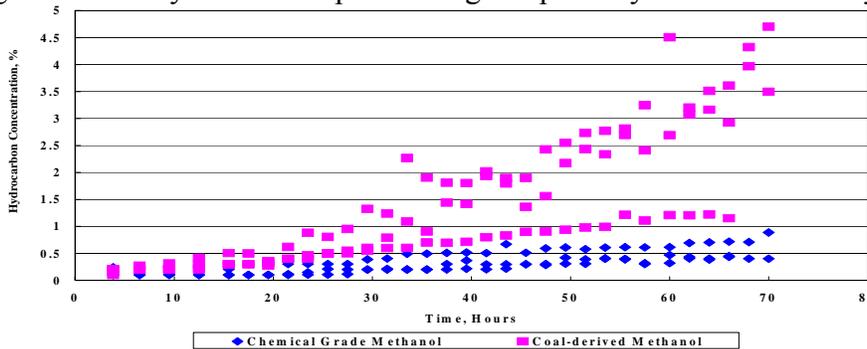


Figure 16: Hydrocarbon concentration for both chemical grade and coal-derived methanol

4. Proton Exchange Membrane Fuel Cell Modeling

A fuel cell operating voltage can be expressed as shown in Equation

$$V_{cell} = E_{Nernst} - \Delta V_{ohm} - \Delta V_{act} - \Delta V_{transfer}$$

Equation 11

ΔV indicates the irreversibility losses which are ohmic losses, activation losses both cathode and anode, mass transfer losses. Ohmic losses are mainly caused by the resistance of electrons and ions flow across the electrodes and electrolyte and various interconnections. Activation losses are caused by the slowness of the chemical reaction on the surface of electrodes. Transfer losses (concentration losses) indicate mass transfer resistance between reactants and electrode surface [Larminie and Dicks, 2003].

Nernst Equation can be expressed as shown in Equation

$$E = E^o + \frac{RT}{2F} \ln\left[\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}}\right]$$

Equation 12

Pressure gain caused by the reduction of cathode activation losses can be expressed as Equation [Larminie and Dicks, 2003].

$$\Delta V = \frac{RT}{4F} \ln(\Delta P)$$

Equation 13

V. Contribution

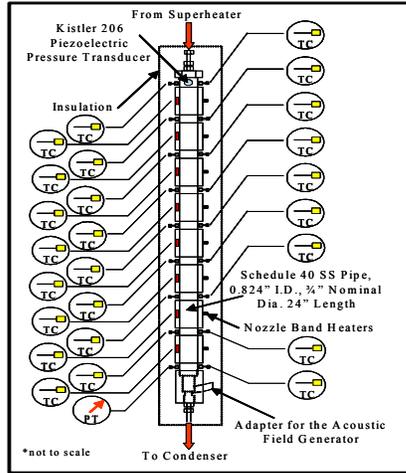
This proposal can evaluate the differences between steam and autothermal reformer based on experiments and a model. There are some papers with regard to the evaluation of reforming fuel cell system performance. In the past, steam reforming is typically chosen over autothermal reforming with methanol because of the higher concentration of hydrogen. However, steam reforming methanol can have poor heat exchange efficiency, higher degradation rates caused by impurities and severe reactor geometry effects.

The efficiency of autothermal reforming methanol has been considered lower than steam reforming methanol in the literature due to lower hydrogen concentration caused by nitrogen dilution. However, no one has attempted to evaluate the efficiencies between autothermal and steam reformers from an experimental basis as approached in this proposed method. Neglecting practical constraints such as catalyst degradation and theoretical mistakes (assuming high heat transfer) may have made steam reforming more attractive in the past. However based on the previously described potential advantages of autothermal reforming it is now prudent to reevaluate the possibility of using ATR for methanol FC systems.

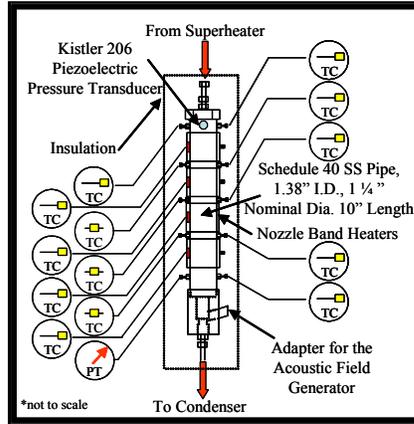
Consequently, through this proposed work, the overall efficiencies and lifecycles for both autothermal and steam reformer can show us which reformer will be better for real fuel cell application through experiments and modeling based on empirical equations.

Appendix: Reactor Schematics

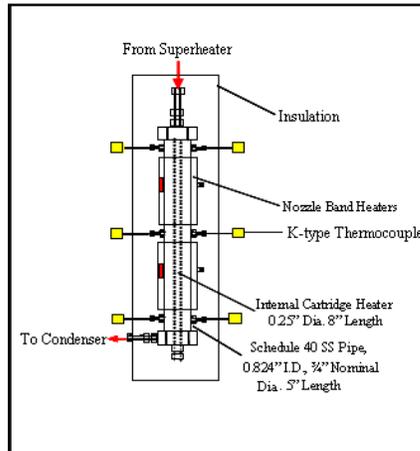
Steam Reformer



Reactor A

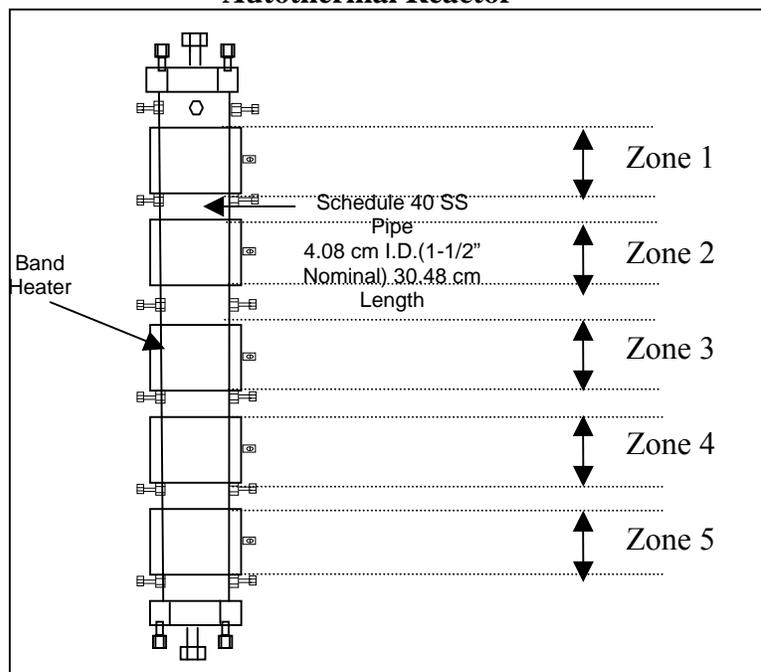


Reactor B



Reactor C

Autothermal Reactor



Reference

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