

HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

41850R01.pdf

Quarterly Technical Progress Report

Reporting Period Start Date: October 1, 2003

Reporting Period End Date: December 31, 2003

Principal Author: Paul A. Erickson

Report Issue Date: April 2004

DOE Award Number: DE-FC26-03NT41850

Submitting Organization:

The Regents of the University of California, Davis
One Shields Avenue
Davis, California 95616

DISCLAIMER

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

ABSTRACT

Hydrogen can be produced from many feed stocks 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 first such report that will be 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, - December 31, 2003. This quarter saw progress in three areas. These areas are:

1. Evaluations of coal based methanol and the fuel cell grade baseline fuel,
2. Design and set up of the autothermal reactor, as well as
3. Set up and data collection of baseline performance using the steam reformer.

All of the projects are proceeding on schedule. During this quarter one conference paper was written that will be presented at the ASME Power 2004 conference in March 2004, which outlines the research direction and basis for looking at the coal to hydrogen pathway.

TABLE OF CONTENTS

DISCLAIMER	2
ABSTRACT.....	3
TABLE OF CONTENTS.....	4
EXECUTIVE SUMMARY	5
EXPERIMENTAL.....	7
RESULTS AND DISCUSSION	16
CONCLUSION.....	16
REFERENCES	16

EXECUTIVE SUMMARY

This progress report is the first such report that will be 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, - Dec 31, 2003. This quarter saw progress in three areas. These areas are:

1. Evaluations of coal-based methanol and the fuel cell grade baseline fuel,
2. Design and set up of the autothermal reactor, as well as
3. Set up and data collection of baseline performance using the steam reformer.

All of the projects are proceeding on schedule. During this quarter one conference paper was written that will be presented at the ASME Power 2004 conference in March 2004, which outlines the research direction and basis for looking at the coal to hydrogen pathway.

External and internal evaluations to compare the coal based methanol to the fuel cell grade methanol have been initiated. A laboratory has been selected to perform the external blind analysis. The analysis will cover the amounts of methanol, ethanol, water, "mineral oil" as petroleum hydrocarbons, total chlorides, and total sulfur. Preparations have been made to send the required samples of both the coal based methanol and the baseline to the laboratory. Tests of the fuels using an internal evaluation were also performed. Several differences between the coal-derived methanol and the baseline fuel cell grade methanol were qualitatively described with one or more methods. Further work is taking place to not only identify and quantify the compounds in the two methanol samples but to also determine the best and most accurate method of quantifying these differences for the project.

Several pieces of equipment for the steam reformer (SR) and autothermal reformer (ATR) were purchased including a specially manufactured ATR catalyst that allows various placement and separation of the catalyst bed. This catalyst is a monolithic ATR catalyst on a Ceria substrate. ATR reactor design and set up continues and is expected to be completed within six months. Additionally an ATR model is also being developed. This model allows sizing of the individual components required to construct the associated hardware.

Data collection with baseline fuel (fuel cell grade) monitoring reactor performance was accomplished with the existing steam reformer set ups. The flow rate was varied to allow multiple space velocities. Preliminary studies present the large effect that geometry and corresponding flow fields can have on the hydrogen production process and add fundamental knowledge that will aid the construction and development of hydrogen production reactors. The data presented establishes the baseline performance with fuel cell grade methanol and explains the experimental facilities that will be used in reforming coal-derived methanol. Further investigations into the proper parameter for capturing the geometry in steam reformers are planned as are methods of enhancing the heat transfer characteristics as outlined in the original proposal.

Much progress has been made on the project this quarter. Initial investigations have been started in the evaluation of the composition of coal-derived methanol and the baseline fuel cell grade methanol. Autothermal reactor design has been initiated and continues with several integral pieces of equipment purchased. The first baseline study with the steam reformers and fuel cell grade methanol has been completed. Several projects are scheduled for the next quarter including analysis of the external evaluations, further ATR reactor design and preliminary evaluation of Coal-Based Methanol in the steam reformers.

EXPERIMENTAL

Evaluations of Methanol

External and internal evaluations to compare the coal based methanol to the fuel cell grade methanol have been initiated. Severn Trent Laboratories – Mobile (STL-Mobile) has been selected to perform the external blind analysis. The analysis will cover the amounts of methanol, ethanol, water, “mineral oil” as petroleum hydrocarbons, total chlorides, and total sulfur. Preparations have been made to send the required samples of both the coal based methanol and the baseline to STL-Mobile. Tests regarding the internal evaluation were also performed. Liquid chromatography mass spectography (LC-MS), Nuclear Magnetic Resonance (NMR), gravimetric, and gas chromatography mass spectography (GC-MS) were performed on various samples to determine the most accurate methods of determining sample constituents. Several differences between the coal derived methanol and the baseline fuel cell grade methanol were qualitatively described with one or more methods. Figures 1 and 2 are samples of the differences found by LC-MS. Peaks indicate different compounds present in each of the methanol samples. Further work is taking place to not only identify and quantify the compounds in the two methanol samples but to also determine the best and most accurate method of quantifying these differences for the project.

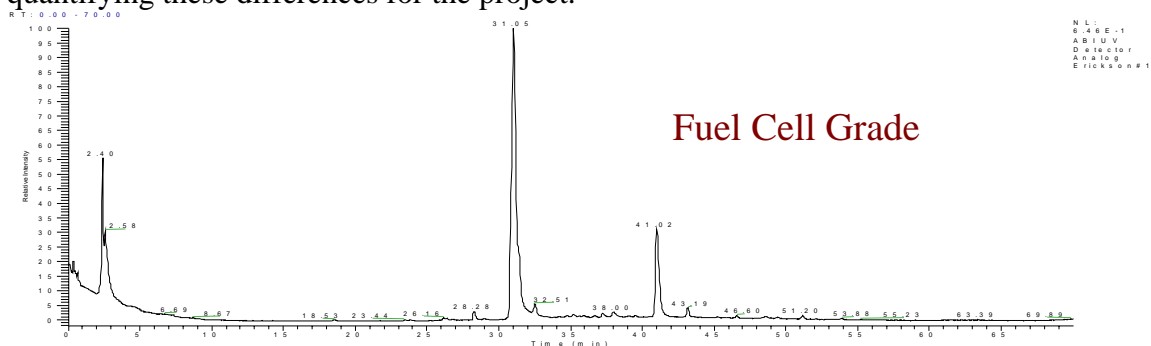


Figure 1: LC-MS time trace of UV detector for Fuel Cell grade Methanol

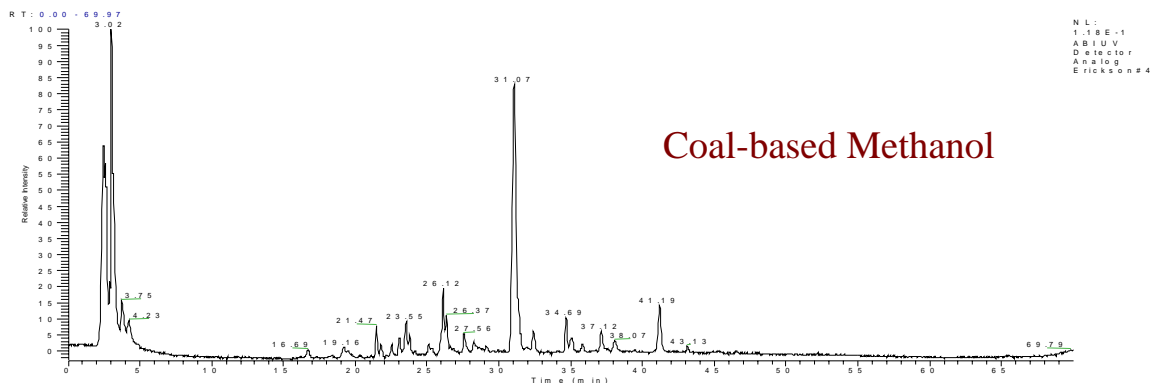


Figure 2: LC-MS time trace of UV detector for Coal-Based Methanol

ATR Reactor Design and Construction

This is an on-going project for this quarter. Several pieces of equipment for the steam reformer (SR) and autothermal reformer (ATR) were purchased including a specially manufactured ATR catalyst that allows various placement and separation of the catalyst bed. This catalyst is shown in Figure 3. This catalyst is a monolithic ATR catalyst on a Ceria substrate purchased from Sud-Chemie. An ATR reactor design and set up continues and is expected to be completed as outlined on the timeline. ATR Preliminary Drawings are shown in Figure 4.

Additionally an ATR model is also being developed in LabVIEW software. This model allows sizing of the individual components required to construct the associated hardware. Further data will be forthcoming on this design in future progress reports.



Figure 3: Autothermal reforming catalyst sections

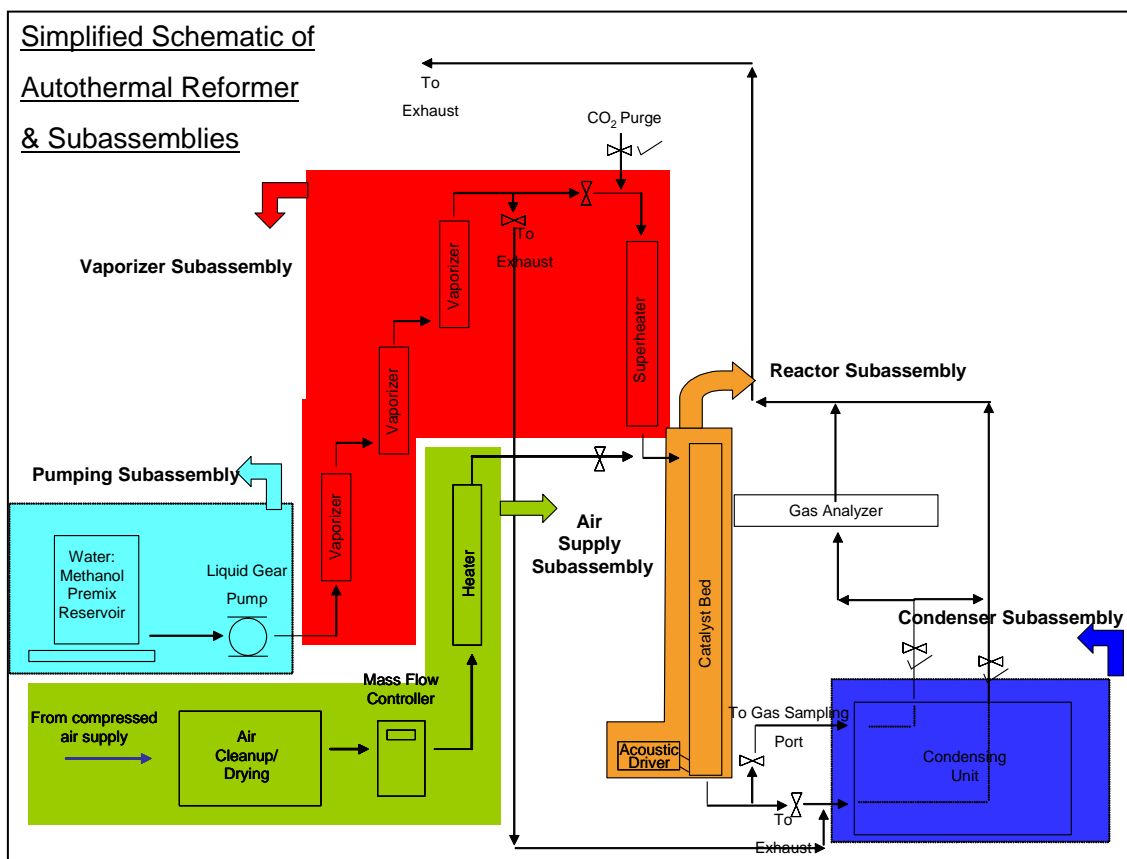


Figure 4: Autothermal reforming schematic and subassemblies

Steam-Reforming Baseline Study

Data collection with baseline fuel (fuel cell grade) monitoring reactor performance was accomplished with the two existing steam reformer set ups. The flow rate was varied to allow multiple space velocities. Preliminary studies present the large effect that geometry and corresponding flow fields can have on the hydrogen production process and add fundamental knowledge that will aid the construction and development of hydrogen production reactors. The data presented here establishes the baseline performance with fuel cell grade methanol and explains the experimental facilities that will be used in reforming coal-derived methanol. Further investigations into the proper parameter for capturing the geometry in steam reformers are planned as are methods of enhancing the heat transfer characteristics as outlined in the original proposal.

Experimental Facility

The experimental facility used in this study includes two methanol-steam reformers incorporating a scale, pump, vaporizers, superheater, catalyst bed housings and a condensing unit, as shown in Figure 5. The methanol-steam reformers are located at the

University of California at Davis in the Hydrogen and Production and Utilization Laboratory.

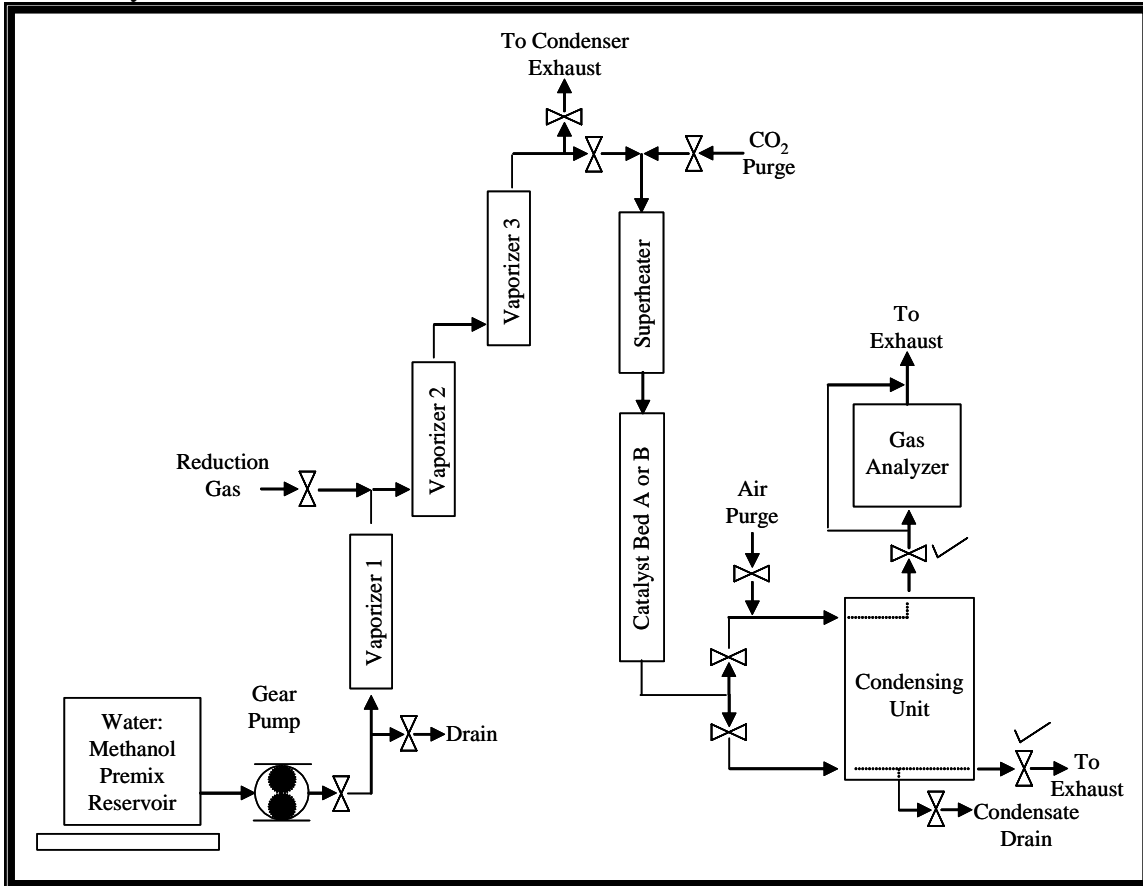


Figure 5: Simplified drawing of the steam reformer.

The process of reformation begins with a reservoir filled with a specific amount of deionized water and methanol, called “premix,” on a mass scale. Stoichiometry of the premix will be discussed in the following section. The premix was then pumped into a three-stage vaporizer, changing the premix from liquid to gas, and bringing it up to a desired temperature. Depending on the experimental procedure, the gaseous species can then be routed into an exhaust, or directed through a superheater by utilizing valves placed in the system. The superheater then holds the species at a constant temperature as it was routed into the catalyst bed housing. For the purpose of this study the catalyst bed housing was designed to be interchangeable with another housing of varying dimensions, but still having the same volume. These catalyst bed housings will be referred to as reactor A and reactor B. After passing through the catalyst bed, the gaseous species was then directed into two tubes via a system of valves. One route was for analysis and the other was for exhausting the reactor products. Both routes lead to the condensing unit where the species, now called “reformat,” reduces in temperature. Liquid water and unreacted methanol are separated from the mixture of dry gases by a condenser and condensate trap. The dry gases are then routed to the gas analyzer. More specific details of the methanol-steam reformer are given below.

Pumping Subassembly

The pumping assembly began with a 4 liter (1 gal.) polyethylene carboy reservoir containing a liquid at room temperature composed of 1.5:1, water:methanol mixture ratio (on a molar basis). This stoichiometric ratio was verified based on the density and temperature of the premix. This was done with a handheld density meter with a resolution of 0.0001 g/cm^3 . The reservoir rested upon a scale with a 0.1 gram resolution. The scale had a 9 pin bidirectional RS-232 port, which allowed the user to electronically record the scale reading during operation. The premix was then drawn out of the carboy by way of a gear pump and driver and enabled the user a resolution of 0.1 ml/min with a premix flow rate range from 2.6 to 85 ml/min. The pump driver was equipped with a frequency output signal, which allowed the user to correspond a frequency (or gear pump RPM) to a flow rate. The user can then electronically record the instantaneous flow rate and control the pump with a voltage signal during operation. Calculations for the mass flow rate could be verified by both the recorded pump flow rate and by recording the change in mass of the scale divided by the time the experiment ran (both were recorded via a computer control program).

Vaporizer Subassembly

Each vaporizer was made of a 20.3 cm (8 in) stainless-steel pipe (nominal $\frac{1}{2}$ " Dia., schedule 40). The energy for vaporization was supplied from 120 V cartridge heaters. The first vaporizer contained a 24.1 cm (9.5 in), 525W cartridge heater, while the last two stages contained 12.7 cm (5 in), 400W cartridge heaters. Each vaporizer was monitored for temperature by two, stainless-steel-sheathed, ungrounded K-type thermocouples. The superheater housing material was a 30.5 cm (12 in) stainless-steel pipe (nominal $\frac{3}{4}$ " Dia., schedule 40). External heating was applied to the superheater using four nozzle band heaters (2.5 cm (1 in) I.D., 5.1 cm (2 in) width), each with a 120 V, 275 W rating. To evenly increase the temperature distribution throughout the superheater, a highly thermal conductive aluminum tape was wrapped around the exterior. Three 0.159 cm (0.0625 in), stainless-steel-sheathed, ungrounded K-type thermocouples were strategically adapted to the superheater to monitor performance.

Catalyst Bed Housing Subassemblies

Reactor A

The housing material for reactor A was a 61 cm (24 in) stainless-steel pipe (nominal $\frac{3}{4}$ in Dia., schedule 40), as shown in Figure 6. External heating was applied to reactor A using 8 nozzle band heaters (2.5 cm (1 in) I.D., 5.1 cm (2 in) width), each with a 120 V, 275 W rating. In a similar fashion as the superheater, a highly thermal conductive aluminum tape was wrapped around the exterior of the pipe to evenly increase the temperature distribution throughout the reactor. An array of seventeen 0.159 cm (0.0625 in) Dia. stainless-steel-sheathed, ungrounded K-type thermocouples was used to monitor the temperature within the reactor.

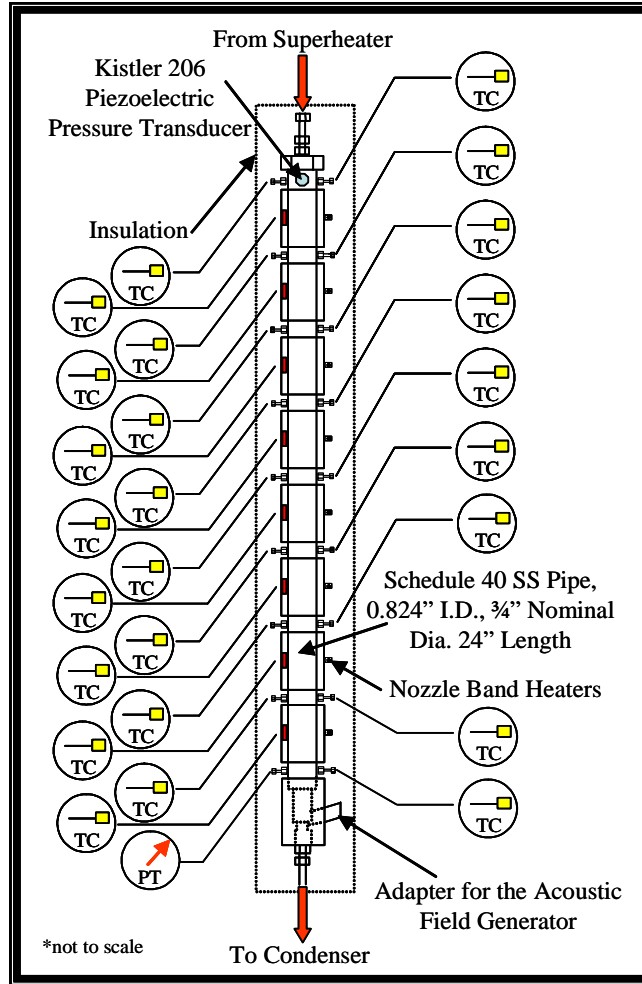


Figure 6: Schematic of reactor A.

To observe the temperature of the heat bands, eight 0.025 cm (0.010 in) Dia., ungrounded K-type thermocouples were placed between the heat bands and the exterior reactor wall. The reactor pressure was monitored using a 0-103.4 kPa (0-15 PSI) pressure gauge and was located at the exit of the reactor (identified as PT in Figure 6).

Reactor B

Reactor B was constructed with a similar design and purpose as reactor A, but with differing dimensions. The housing material for reactor B was a 25.4 cm (10 in) stainless-steel pipe (nominal 1 1/4" Dia., schedule 40) and is represented in Figure 7. To account for the change in outer diameter (1.5 cm (0.61 in)) and length (35.6 cm (14 in)) of the reactor, only four nozzle band heaters with a larger interior diameter (3.8 cm (1.5 in) I.D., 3.8 cm (1.5 in) width) were utilized, each with a 120 V, 350 W rating. Also, fewer thermocouples (nine-0.159 cm (0.0625 in) Dia. and four-0.025 cm (0.010 in) Dia.) were used to monitor the reactor.

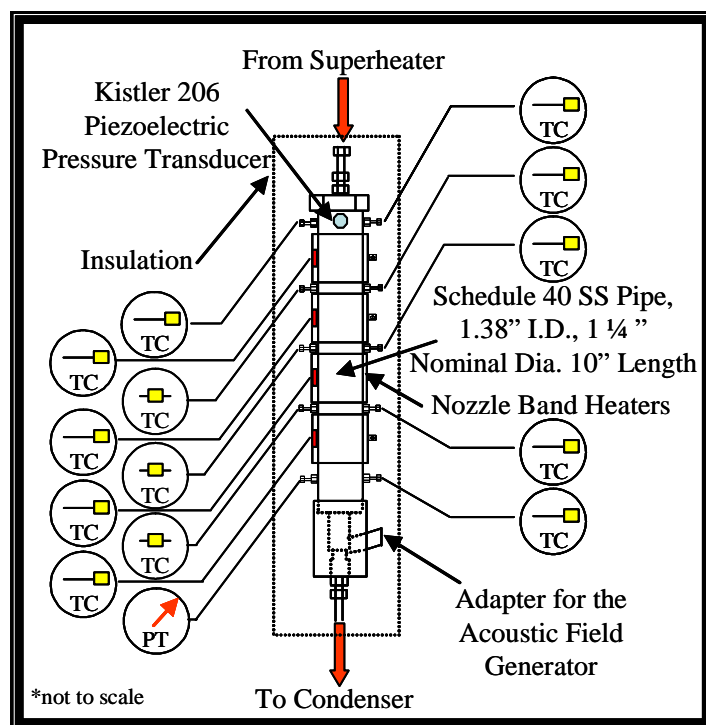


Figure 7: Schematic of reactor B.

The catalyst used in this study was a pelletized commercial-grade copper-zinc catalyst on an alumina substrate. This catalyst (FCRM-2) was manufactured by Sud-Chemie and is recommended for an operating temperature range of 250-280°C (482-536°F). The catalyst was cylindrical in shape and had dimensions consisting of 0.47 cm (0.187 in)-diameter and 0.25 cm (0.100 in)-thickness, as stated by the manufacturer. The catalyst in its original state is referred to in this study as pelletized catalyst. Other tests conducted with this catalyst after being crushed and sieved to vary the dimensions and the exposed surface area. This catalyst had an average length of 0.25 cm (0.098 in) and is referred to as crushed catalyst in this study. Also, Figure 8 displays the designated zones for both reactors and the relative position of the corresponding packed catalyst. The packing factor for the pelletized and crushed catalyst remained constant at 61.7%. The average mass of catalyst used for each run, for both pelletized and crushed, was 253.7g (0.56 lb) with a standard deviation of 4.9g (0.01 lb).

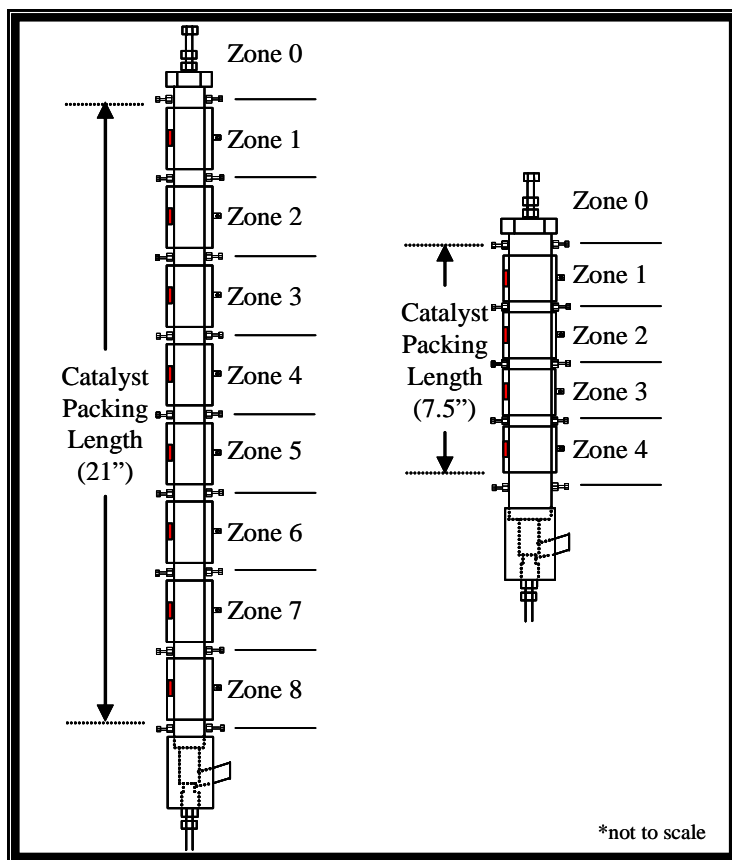


Figure 8: Schematic of zones and catalyst packing lengths for reactors A (left) and B (right).

Condensing Unit Subassembly

The condensing unit utilized water from an ice bath to lower the gas temperature from 250°C (482°F) to 0°C (32°F). The decrease in temperature promotes a phase change, causing water, methanol and other relevant species to condense. To acquire the condensate from the reactant species for fuel conversion analysis, the collection container can be removed from the unit. The dry product gas on the analysis side was then routed to the gas analyzer, while the exhaust gas was directed to the fume hood.

Experimental Methods - Percent Conversion of Methanol

Percent conversion (%C) of methanol to a hydrogen-rich gas is presented in Equation 1. The methanol input and output are on a mass basis.

$$\%C = \left(\frac{CH_3OH_{input} - CH_3OH_{output}}{CH_3OH_{input}} \right) \times 100$$

Equation 1

For each run, the mass of the water:methanol premix consumed was recorded. From this value, the mass of methanol input (CH_3OH_{input}) could be calculated once the initial mass fraction of methanol in the premix was found. The mass fraction of methanol input was

known based on the mass of methanol used to create the premix (1.5:1 water:methanol ratio on a molar basis). This water:methanol ratio was calculated based on the premix density at 24°C (75°F). Percent conversion of methanol was independent of time; however, run time did play a role in how much condensate mass was trapped by the condensing unit subassembly. Too short of a run time would yield a small amount of condensate mass which would be more susceptible to error in collection and analysis. Previous studies suggested a minimum of 35 to 40 grams of condensate was collected for each run to minimize analysis error (Erickson, 2002). Condensate was emptied from the trap and weighed on an Ohaus 1200g (0.1g resolution) scale. To obtain all mass that was left inside the trap, a towel was used to absorb all liquid droplets left behind. Generally for each run, an average of 2.0 grams of condensate was absorbed by the towel. Then, using the previous mass of the towel and mass after collection the residual droplet mass could be collected. To prevent interaction between the condensate and the atmosphere (i.e. evaporation), a density reading was taken within a minute after the condensate mass was collected. The density was recorded using the Anton Parr handheld density meter. The density meter also incorporated a thermocouple allowing the user to correspond temperature with density reading. Once the density was measured at 24°C (75°F), this value was implemented into an empirical calculator that produced the mass fraction of methanol within the condensate. The mass fraction was calculated from the density, as shown in Equation 2, and was verified for this study with empirical data. Using the methanol mass fraction (Y_{CH_3OH}) and the mass on condensate allowed for calculation of CH_3OH_{output} , which subsequently was used for calculating percent conversion with Equation 1.

$$Y_{CH_3OH} = 3859.9 \cdot \rho^2 - 8231.1 \cdot \rho + 4370.0$$

Equation 2

RESULTS AND DISCUSSION

Sample Results from Steam Reformation

Table 1 shows raw data from a preliminary run of the steam reformer using fuel cell grade methanol. The premix density, condensate density, mass of premix used, and the mass of the condensate were reduced using the method described above to determine the percent conversion of methanol.

	Premix Flow Rate (mL/min)	Premix Density (g/cm ³)	Mass of Premix Used (g)	Mass of Condensate (g)	Condensate Density (g/cm ³)	Percent Conversion (%)
Run 1	15	0.9080	208.2	38.6	0.9953	99.56
Run 2	5	0.9080	205.8	38.9	0.9973	99.93
Run 3	15	0.9080	208.4	34.5	0.9965	99.81
Run 4	15	0.9080	207.9	38.0	0.9969	99.86
Run 5	5	0.9080	205.7	37.0	0.9972	99.91
Run 6	5	0.9080	205.8	35.5	0.9973	99.93

CONCLUSION

Much progress has been made on the project funded by the Department of Energy this quarter. Initial investigations have been started in the evaluation of the composition of coal-derived methanol and the baseline fuel cell grade methanol. Autothermal reactor design has been initiated and continues with several integral pieces of equipment purchased. The first baseline study with the steam reformers and fuel cell grade methanol has been completed. Several projects are scheduled for the next quarter including analysis of the external evaluations, further ATR reactor design and preliminary evaluation of Coal-Based Methanol in the steam reformers.

REFERENCES

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