Hydrogen Production for Fuel Cells via Reformation of Coal-Derived Methanol

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Hydrogen Production And Utilization Laboratory

UCDAVIS

With Support from

EASTMAN

METHANEX
A Responsible Care® Company

Project ID # PDP8

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date Oct 03
- Project end date Oct 06
- Percent complete 50%

Budget

- Total project funding 500k
  - DOE share 400k
  - Contractor share 100k
- Funding received in FY04 225k
- Funding received in FY05 125k

Barriers Addressed

- Hydrogen Production

"… develop reforming technologies for gasification and pyrolysis processes."

-DOE technical plan

Partners

- Eastman Chemical
- Methanex (ended support Nov 04)

Motivation

Georgetown 1st Generation Alcohol-Fuelled Fuel Cell Bus at UC Davis

Economic Study by Georgetown University and the University of Florida

Hydrogen Feedstock	Natural Gas	Methanol from Coal (Hydrogen through on-board reforming)	Hydrogen from Coal Gasification
Gasoline Eq ($/gal)	3.44-4.32	1.77	3.18

For full report see http://fuelcellbus.georgetown.edu

Energy Security thru a Diverse Domestic Energy Portfolio

This study also serves as a baseline for bio-derived alcohol feedstocks which come from similar upstream gasification processes.

Overall Objectives

•Quantify the differences between coal-derived and fuel cell grade methanol (completed)
•Demonstrate hydrogen production from steam reforming and autothermal reforming of coal-derived methanol (completed)
•Determine hydrogen quality and conversion degradation for both coal-derived methanol and baseline fuel cell grade methanol (current)
•Determine limiting steps in the reformation process when using Coal-Derived Methanol (current)
•Determine and demonstrate ways to enhance the reforming methods (current)
•Demonstrate and characterize operation of a hydrogen fuel cell fed by coal derived methanol (future)

Technical Approach

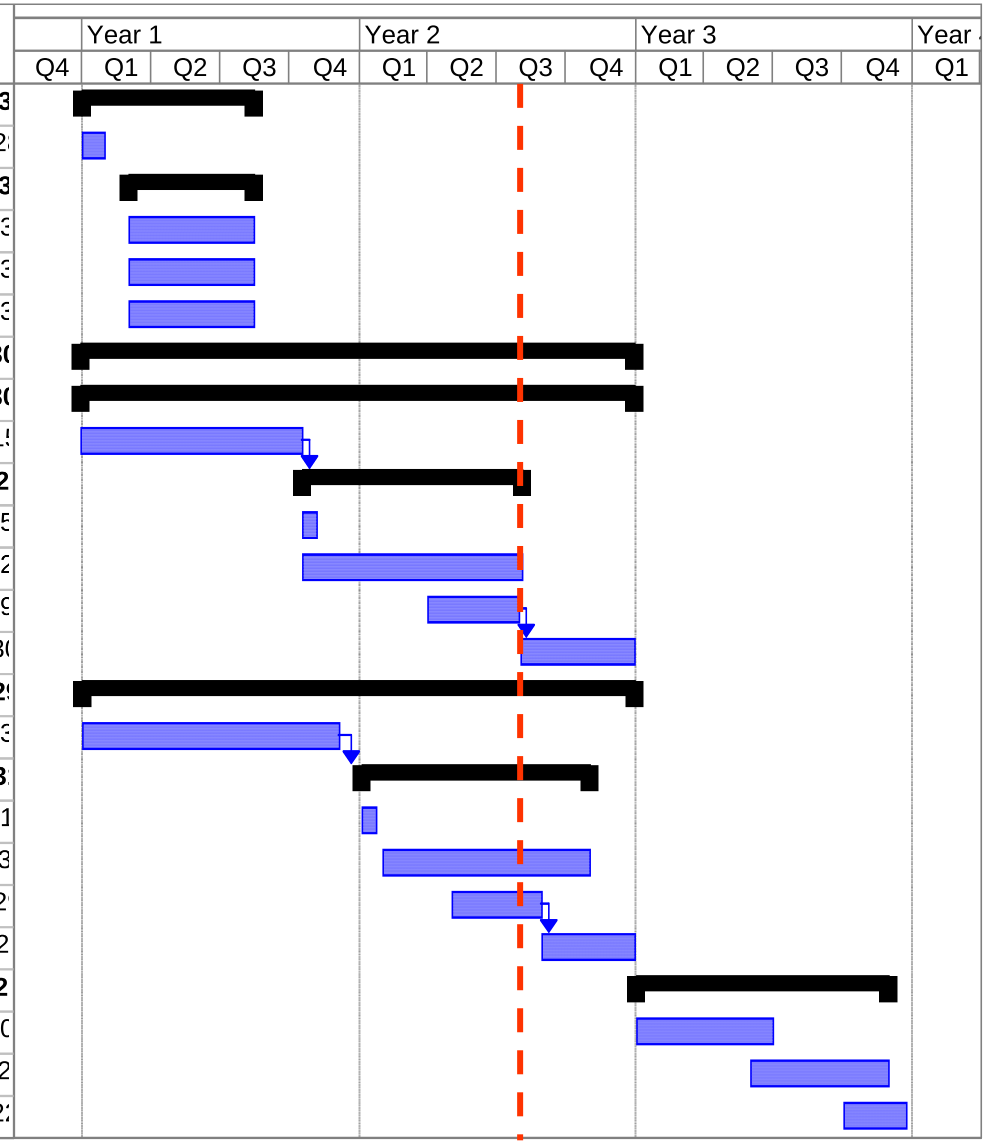
- Demonstrate fuel conversion change over time (degradation) with both coal-derived and baseline fuel
- Identify the limiting steps in the reformation processes
- Identify ways of overcoming the limiting steps in the reformation processes
- Find the relative magnitudes of each process variable on the reformation outputs including fuel type.

Technical Accomplishments/ Progress/Results

- Hydrogen was produced from coal-based methanol through both steam-reformation and autothermal reformation methods.
- An empirical model of steam reformer performance with coal-based methanol (Eastman) as compared to “fuel cell grade” methanol (Methanex) was developed.
- Degradation rates of reactor performance for the steam reforming method and fuels was quantified.
- Passive methods for enhancing steam reformation was investigated.
- An empirical model of the autothermal reactor performance with coal-derived methanol is being investigated.
- Transient operation of the reactors is being demonstrated.
- Review of clean-up methods and capabilities of competing methods is being analyzed for future experimental studies.

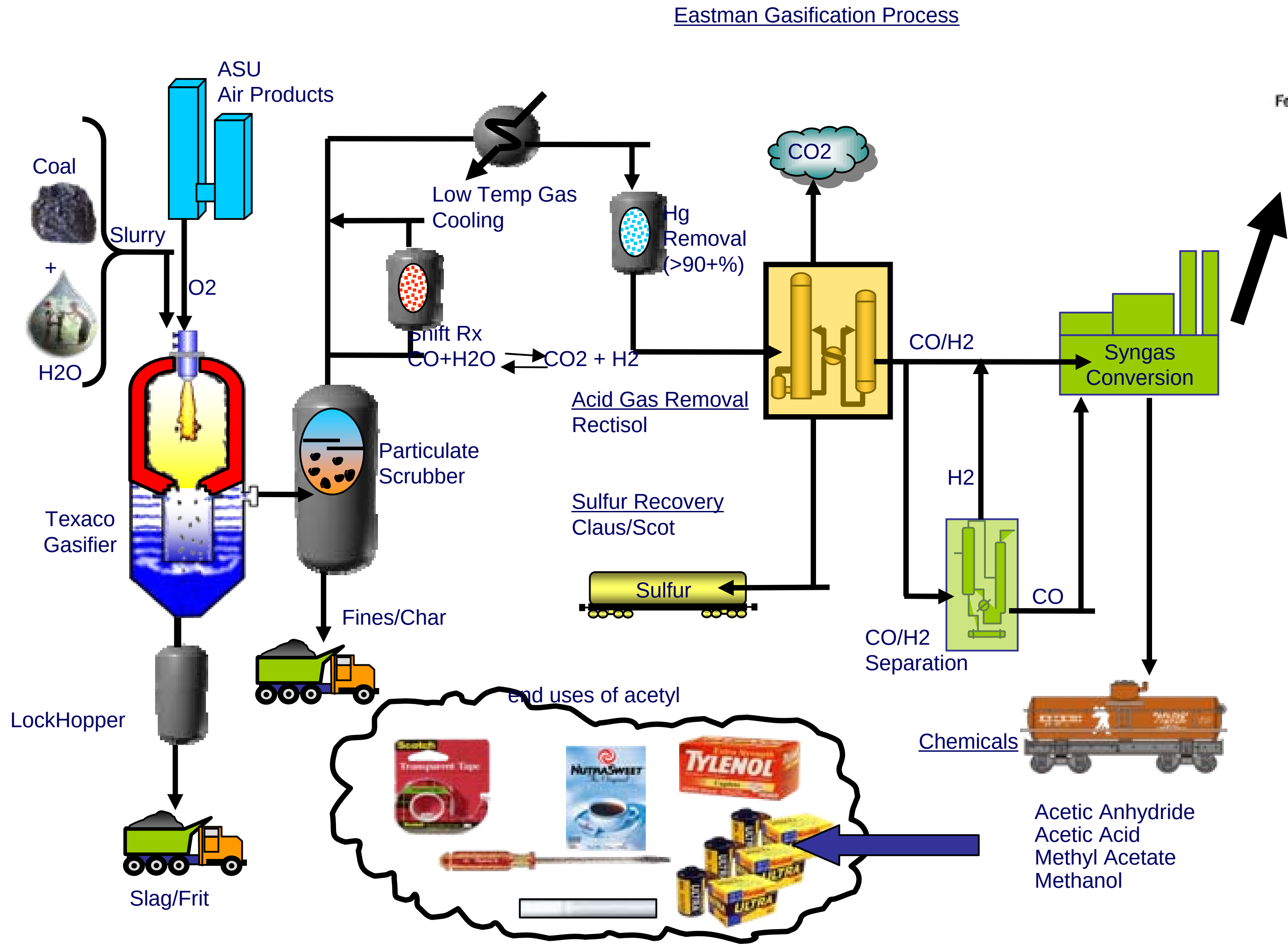
Milestones (on or ahead of schedule)

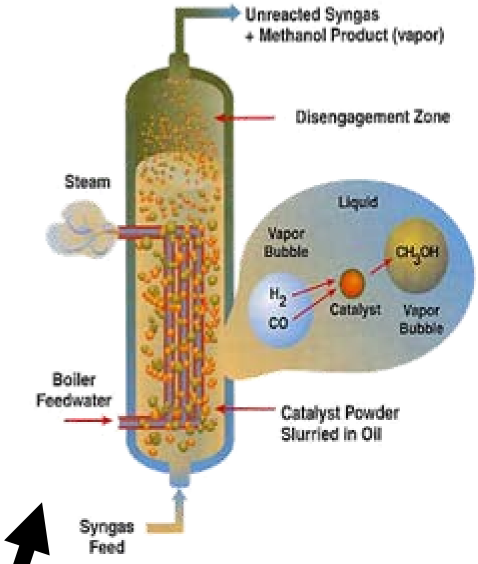
ID	Task Name	Duratio	Start	Finish
1	**Peliminary Investigation And comparison of M**	**32.4 w**	**Thu 1/1**	**Fri 8/13**
2	External Evaluation of MeOH Fuels	4 wk	Thu 1/1	Wed 1/2
3	**Internal Evaluation of MeOH Fuels**	**24 wk**	**Mon 3/1**	**Fri 8/13**
4	LCMS Testing	24 wl	Mon 3/1	Fri 8/13
5	Gravametric Testing	24 wl	Mon 3/1	Fri 8/13
6	Analysis of Coal Based MeOH Analyte Hist	24 wl	Mon 3/1	Fri 8/13
7	**Testing**	**105 wl**	**Mon 12/2**	**Fri 12/30**
8	**Steam Reforming**	**105 wl**	**Mon 12/2**	**Fri 12/30**
9	Setup	42 wl	Mon 12/2	Fri 10/1
10	**Steady State**	**41.4 w**	**Mon 10/1**	**Tue 8/2**
11	Model Development	3 wk	Mon 10/1	Fri 11/5
12	Data Collection	41.4 w	Mon 10/1	Tue 8/2
13	Transient Testing	17.2 w	Fri 4/1	Fri 7/29
14	Degradation Testing	22 wl	Mon 8/1	Fri 12/30
15	**Autothermal Reforming**	**104.2 w**	**Thu 1/1**	**Thu 12/29**
16	Setup	48.4 w	Thu 1/1	Fri 12/3
17	**Steady State**	**43.2 w**	**Mon 1/3**	**Mon 10/3**
18	Model Development	3 wk	Mon 1/3	Fri 1/21
19	Data Collection	39 wl	Tue 2/1	Mon 10/3
20	Transient Testing	17.2 w	Mon 5/2	Mon 8/2
21	Degradation Testing	17.6 w	Tue 8/30	Thu 12/2
22	**Testing the Reformate Streams in the PEM Fue**	**47.6 w**	**Mon 1/2**	**Wed 11/2**
23	Preliminary Evaluation of Enhancement Requi	26 wl	Mon 1/2	Fri 6/30
24	PEM Fuel Cell Stack Testing	26 wl	Thu 6/1	Wed 11/2
25	Analysis and Final Report Preparation	12 wl	Mon 10/	Fri 12/2



Important Background

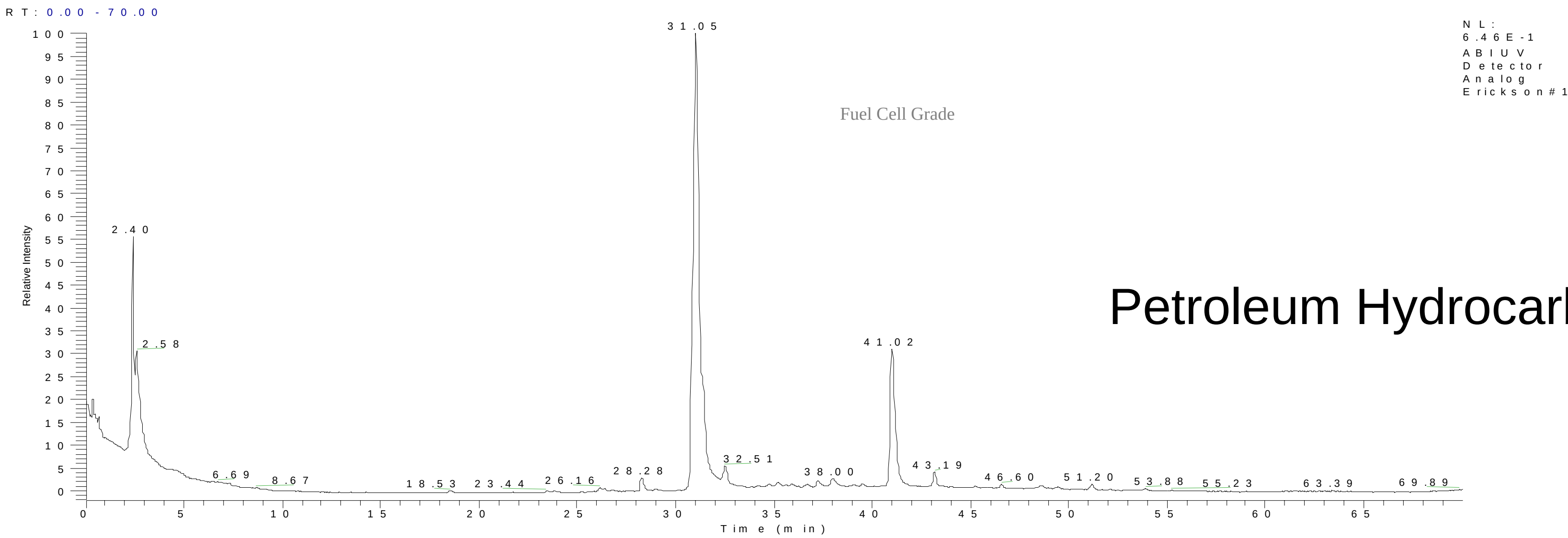
Upstream Processes (from Eastman Chemical)



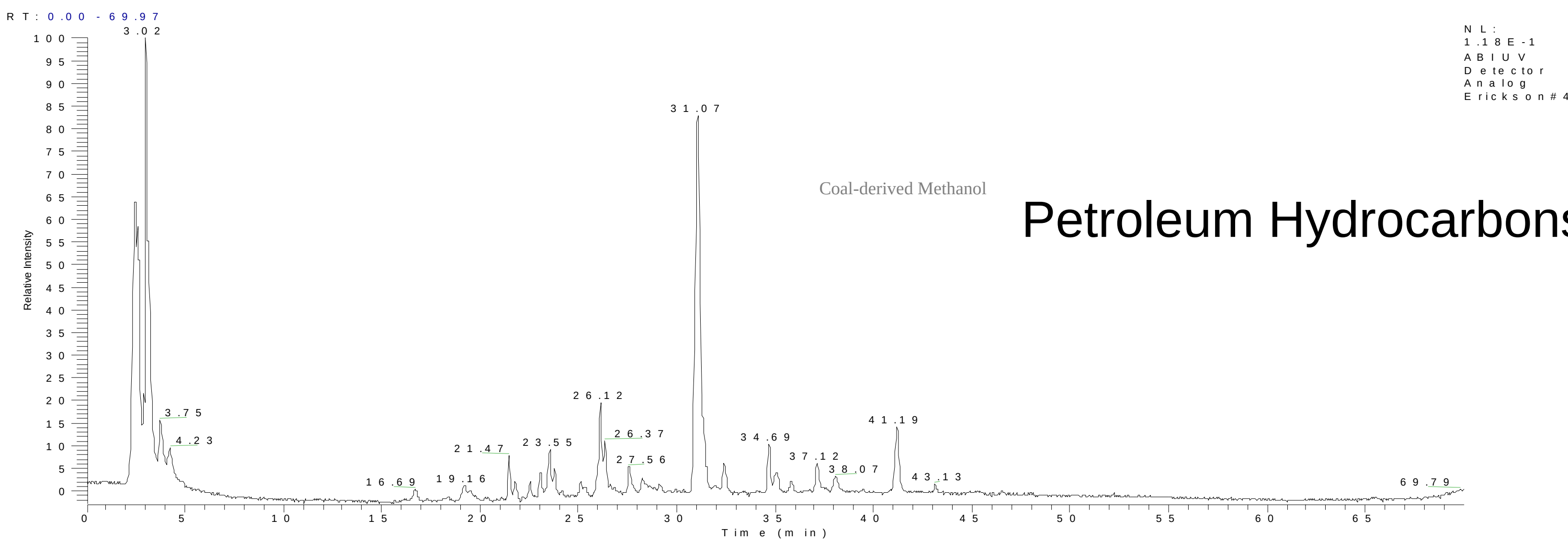


From Erickson et. al. 2004 ASME Power Conference

Differences between Eastman's Coal-derived and Fuel Cell Grade Methanol



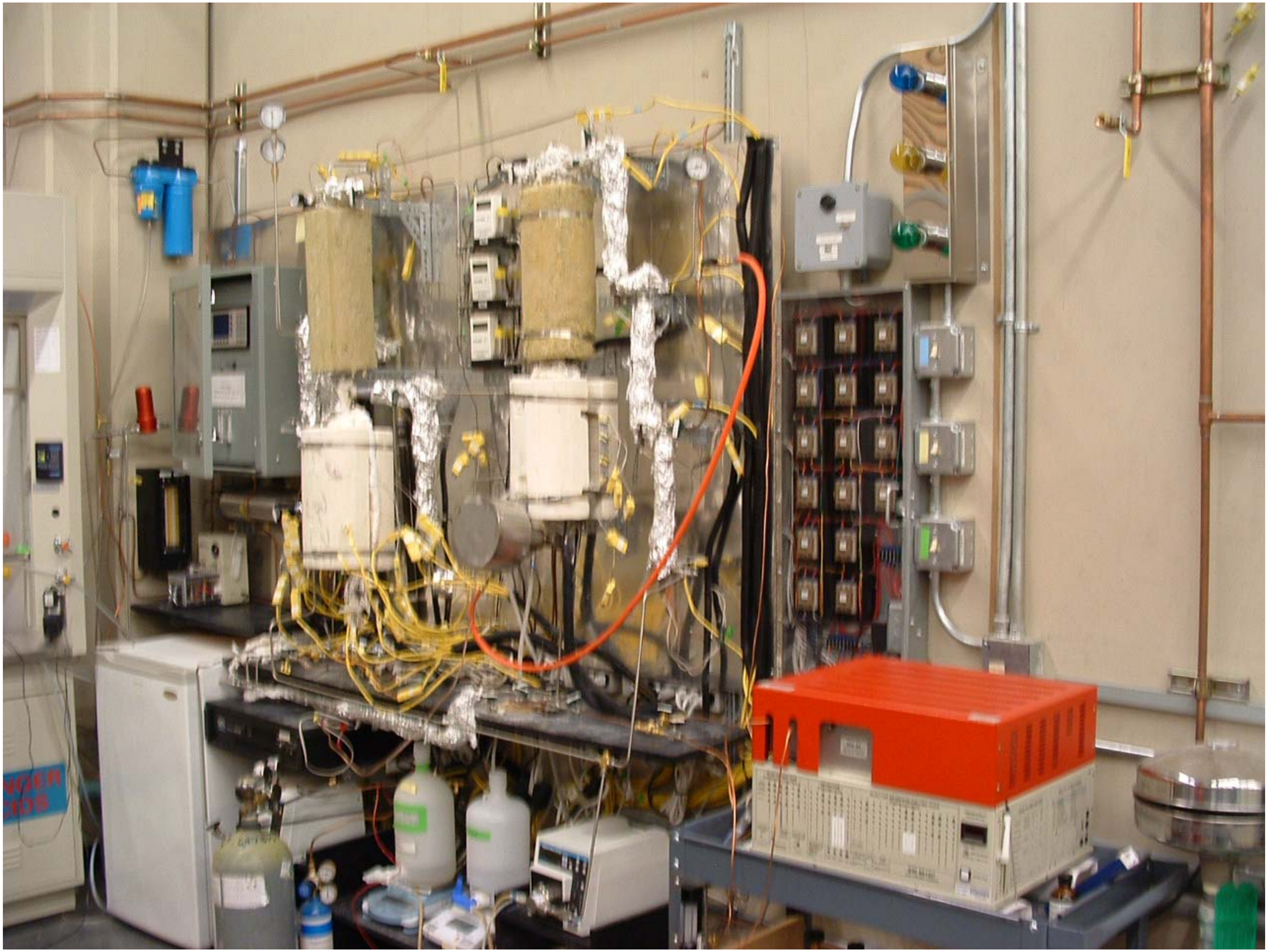
Petroleum Hydrocarbons 5.9 mg/l



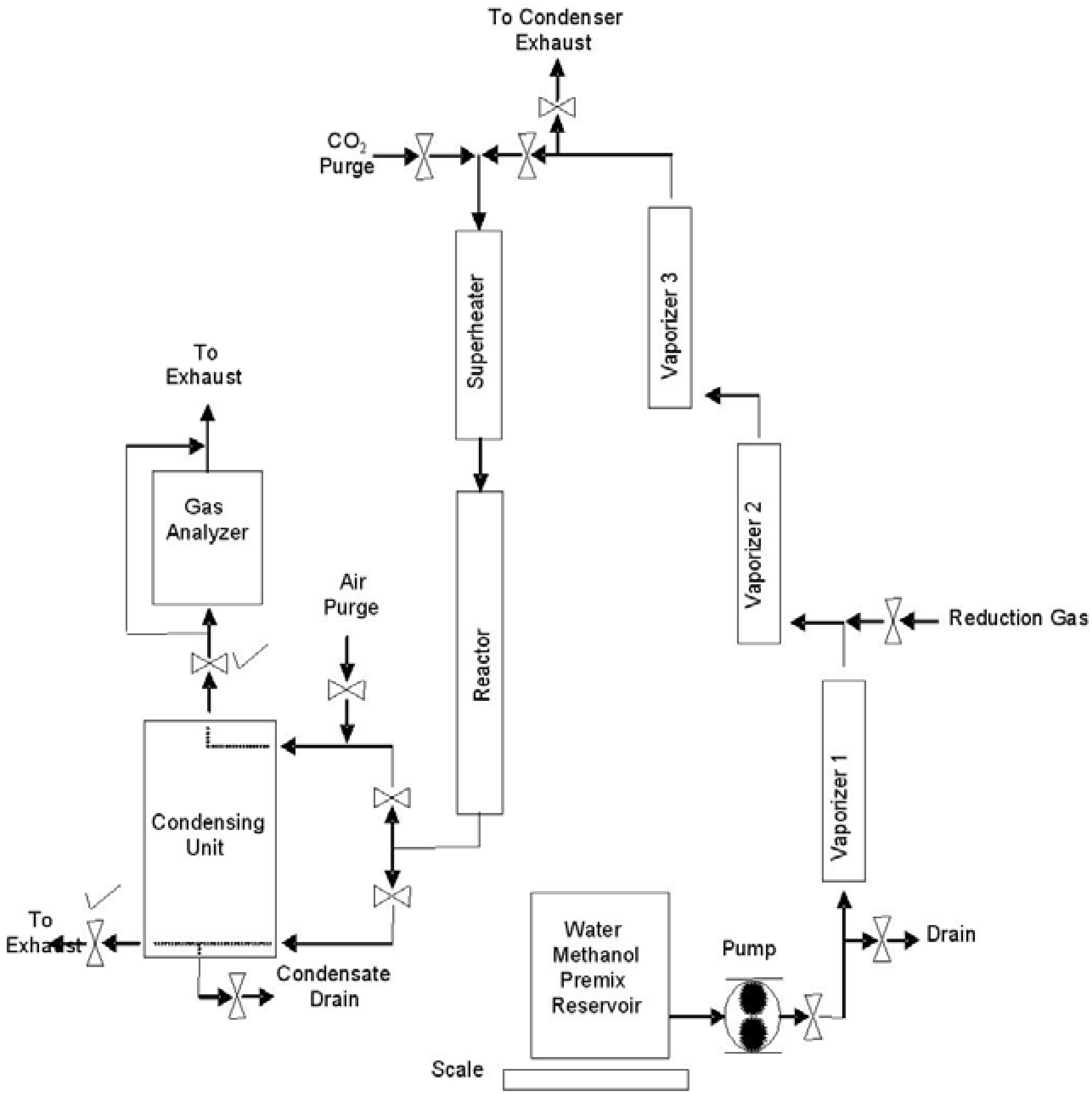
Petroleum Hydrocarbons 17.0 mg/l

Liquid Chromatography Results for both Coal-derived and Chemical Grade Methanol

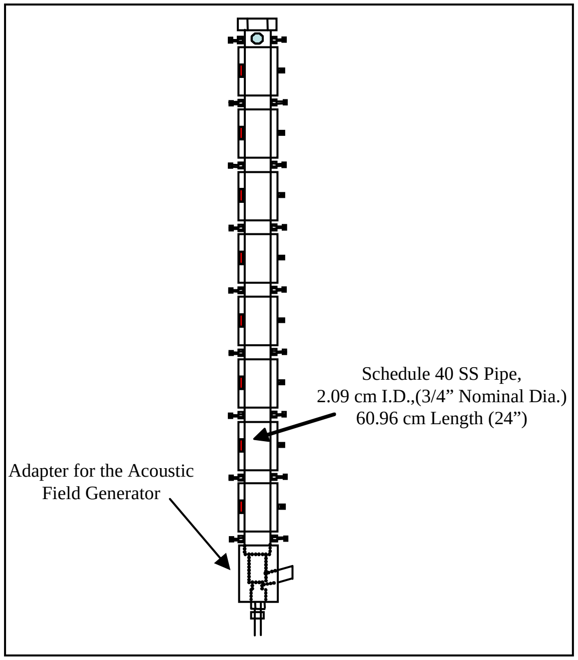
Experimental Facilities



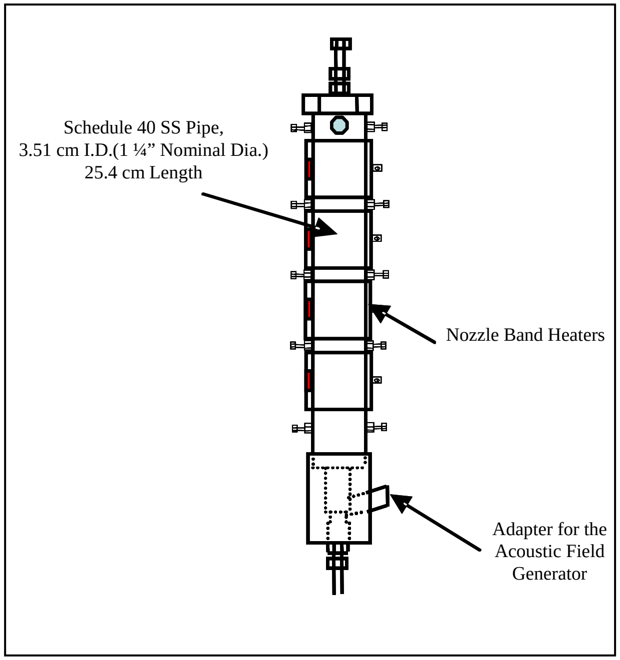
Steam Reforming Schematic



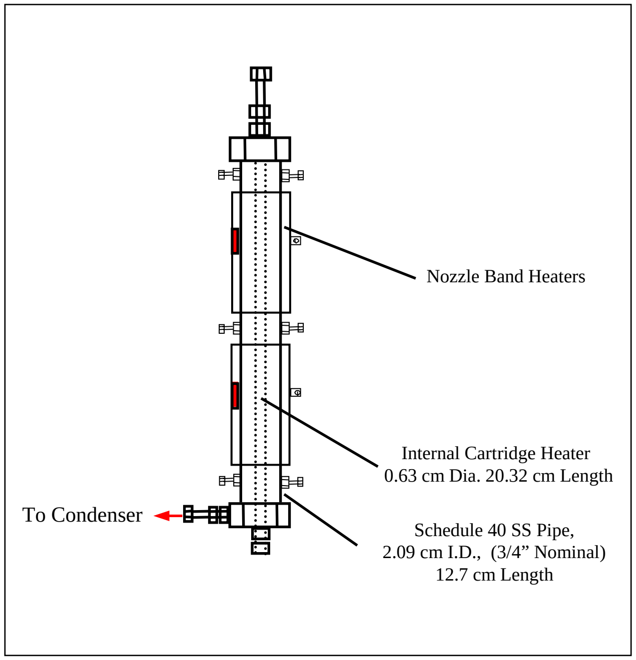
SR Reactor Geometries



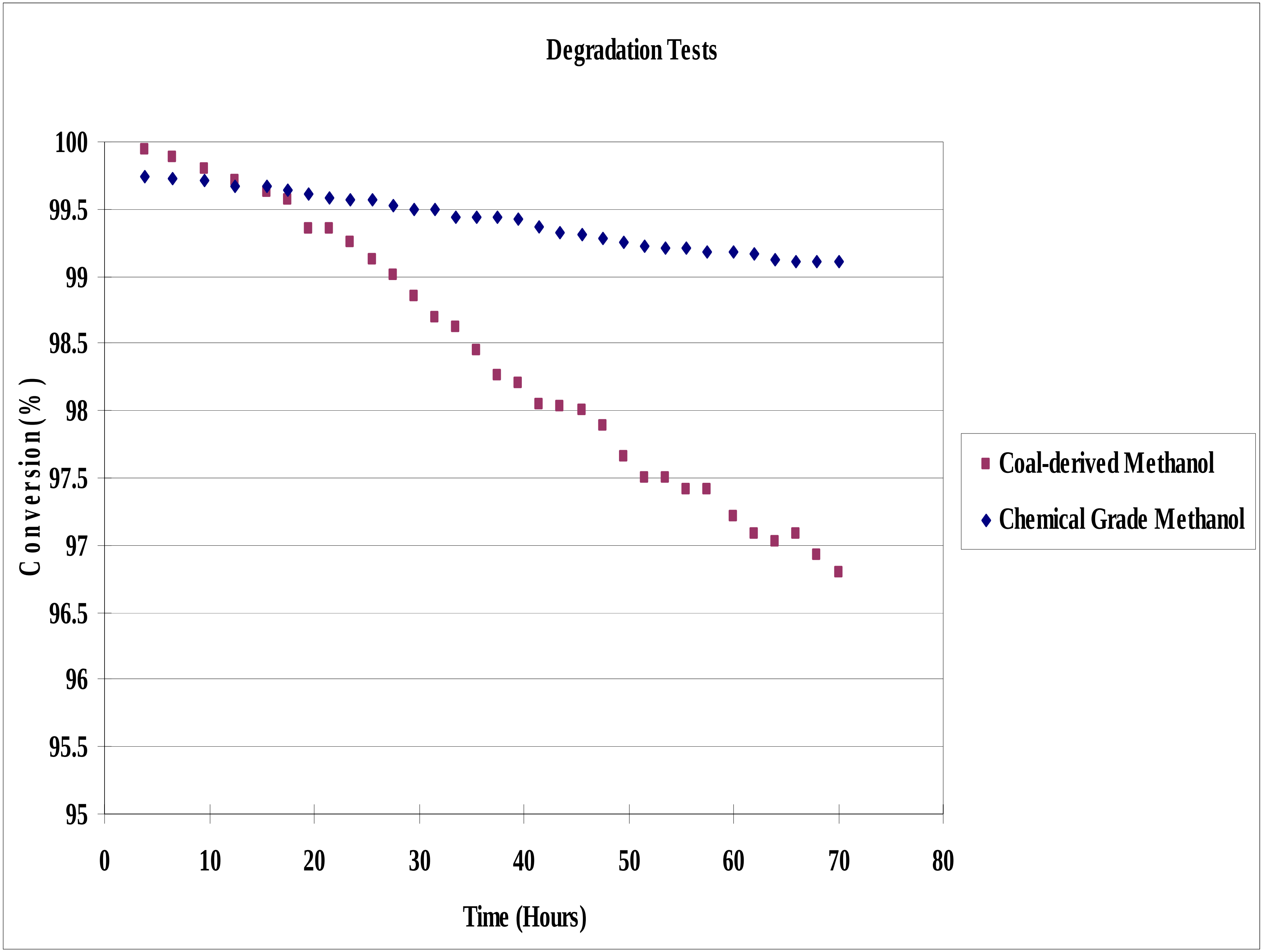
Reactor A: Large Aspect Ratio
(L/D=25.4) SR Reactor



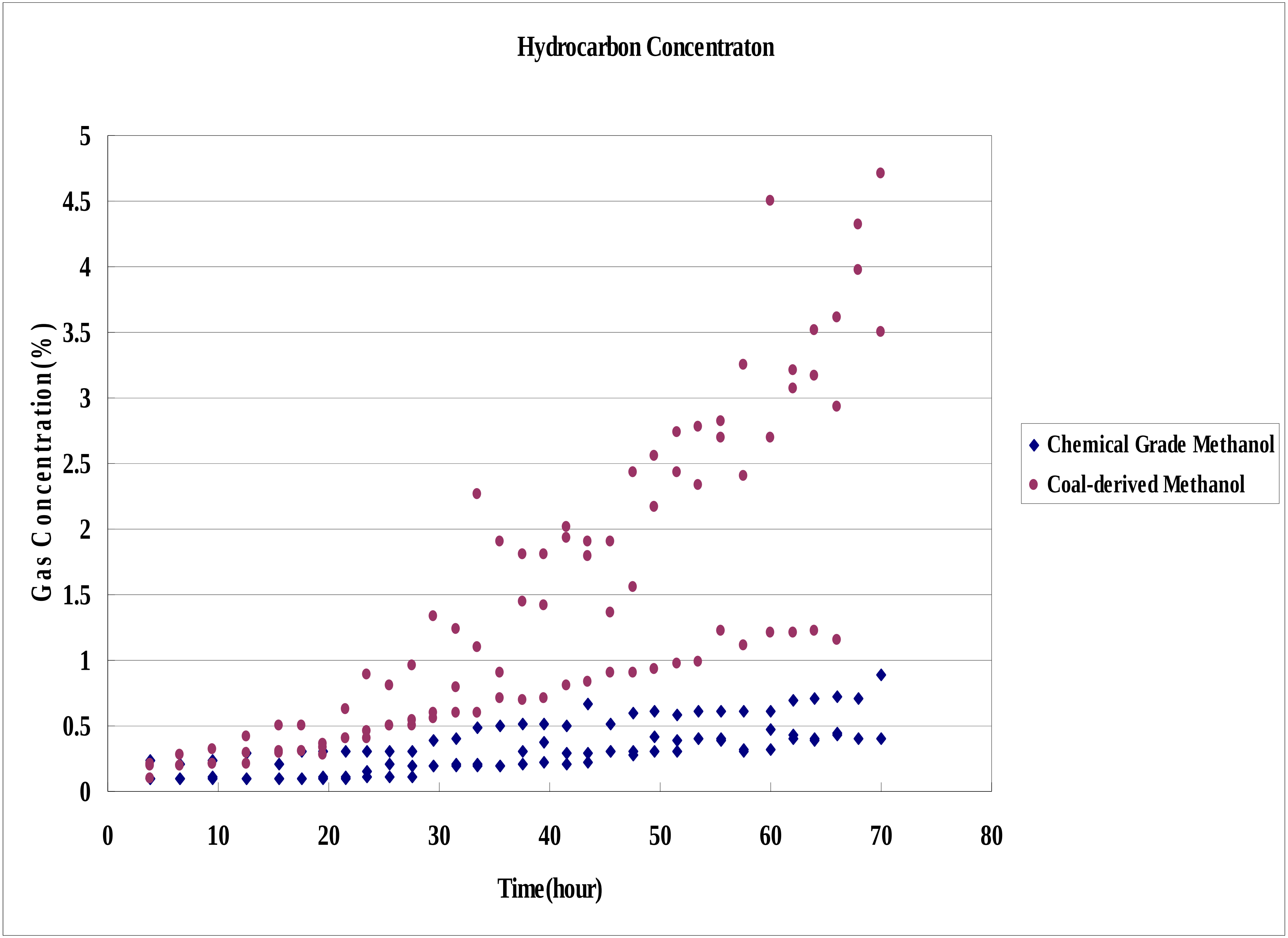
Reactor B: Small Aspect Ratio
(L/D=5.4) SR Reactor



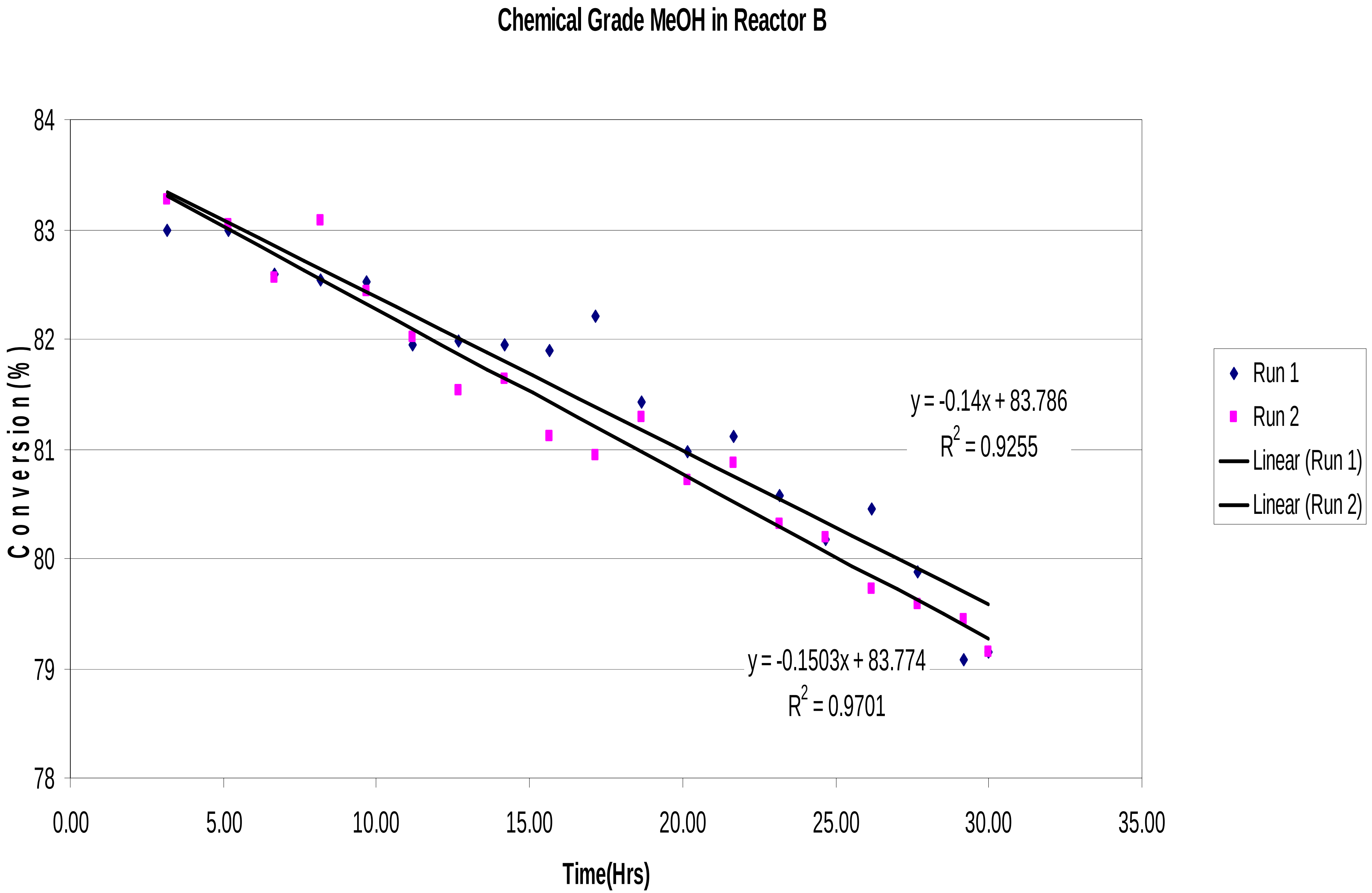
Reactor C: Cartridge Heater SR Reactor



The average results of multiple (three tests for each fuel) 70-hr Catalyst Degradation Tests in Reactor C for both fuel cell grade and coal-derived methanol (2.5 LHSV-M).



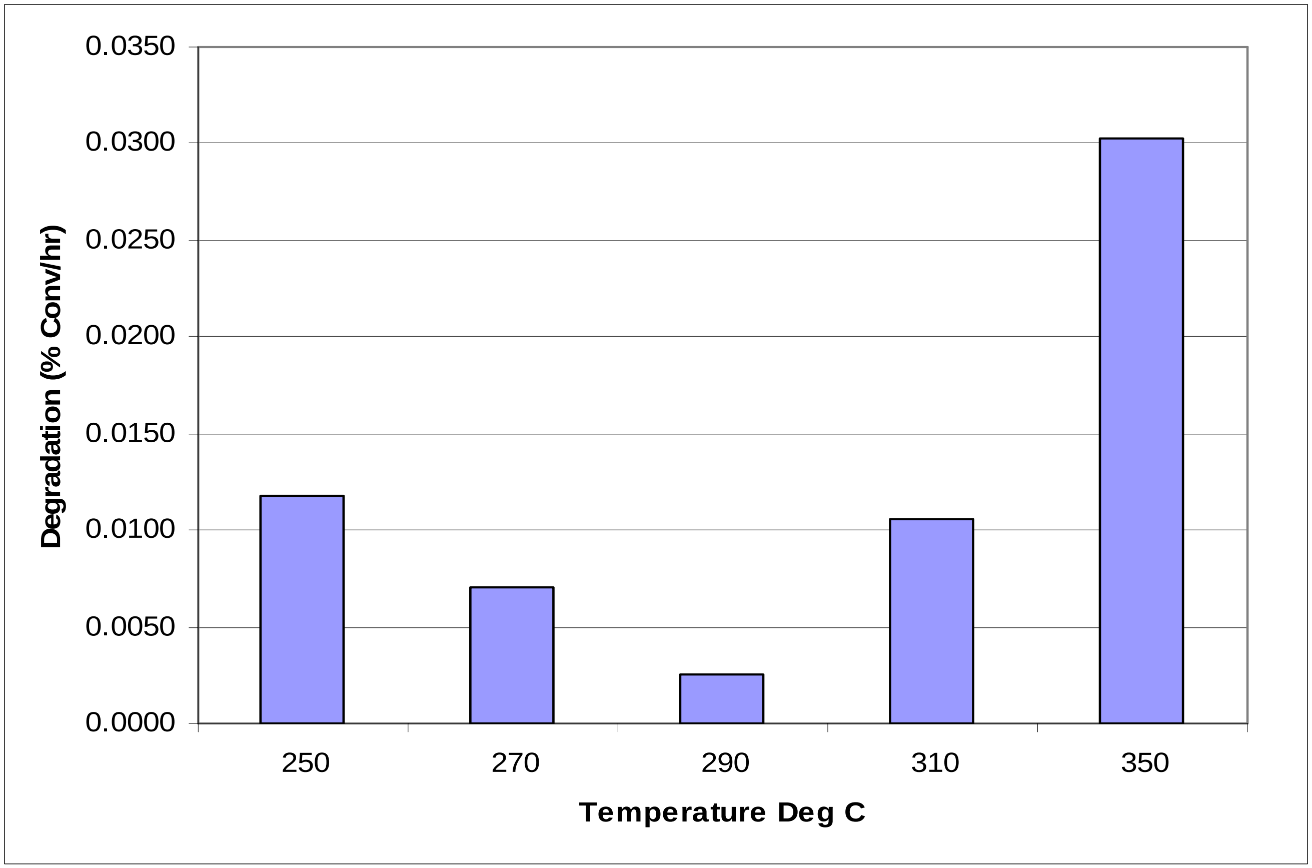
Hydrocarbon concentrations for both fuel cell grade methanol and coal-derived methanol in multiple 70 hr degradation tests.



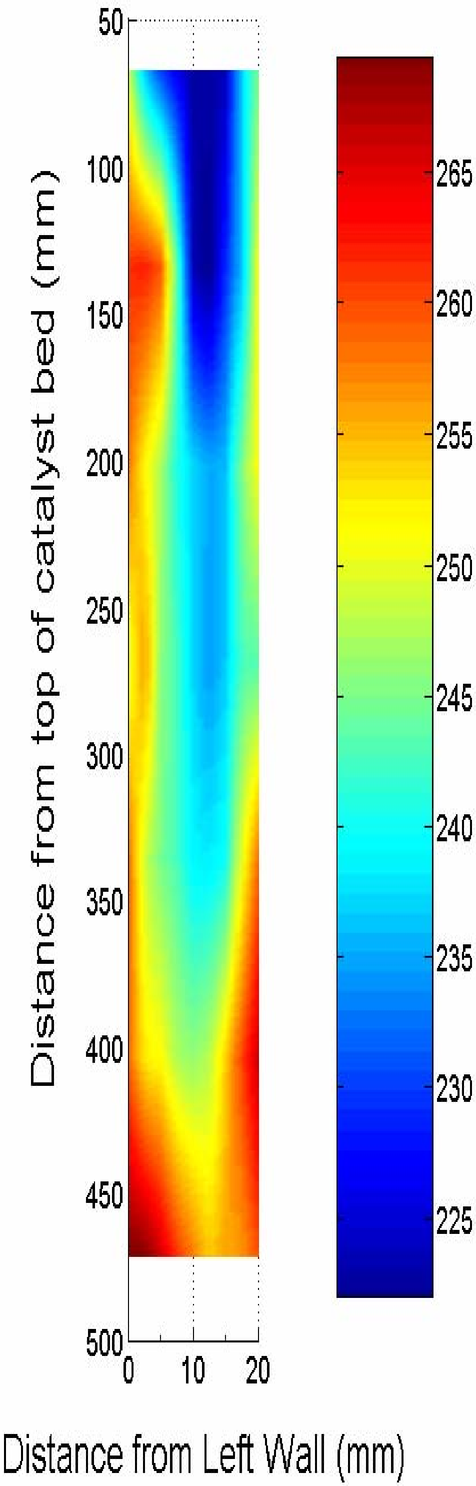
Results from two 30-hr Degradation tests in Reactor B with fuel cell grade methanol (2.5 LHSV-M). When compared to the 70-hr degradation tests in Reactor C these results show that catalyst degradation is a strong function of reactor geometry.

Understanding the Steam-Reformation Process

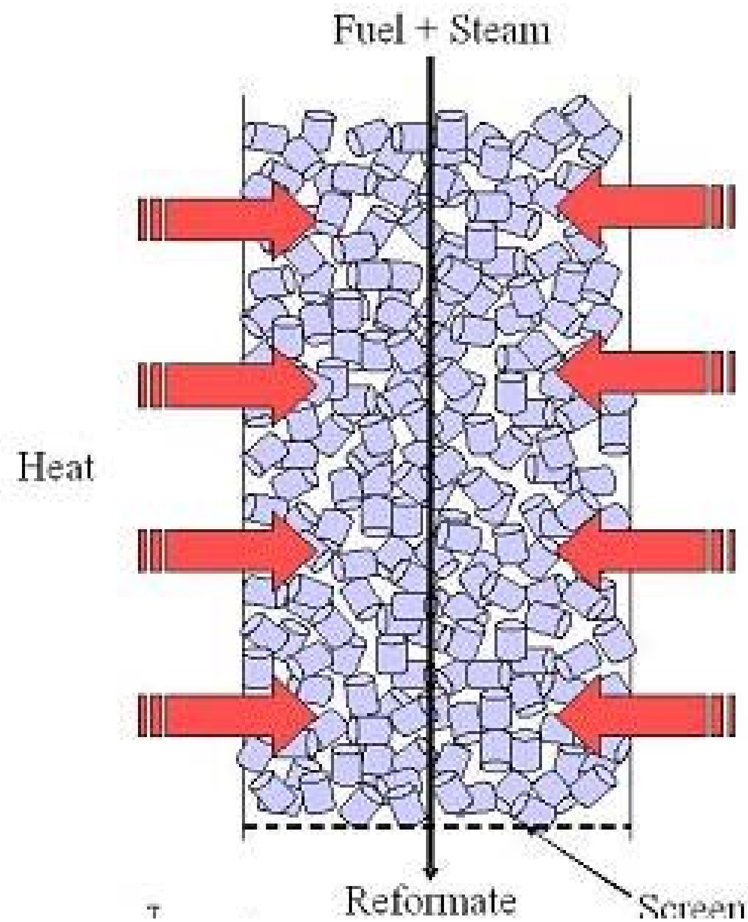
Right: Typical Reactor Temperature Profile in Reactor A (Deg C). Note that the geometry is not to scale.



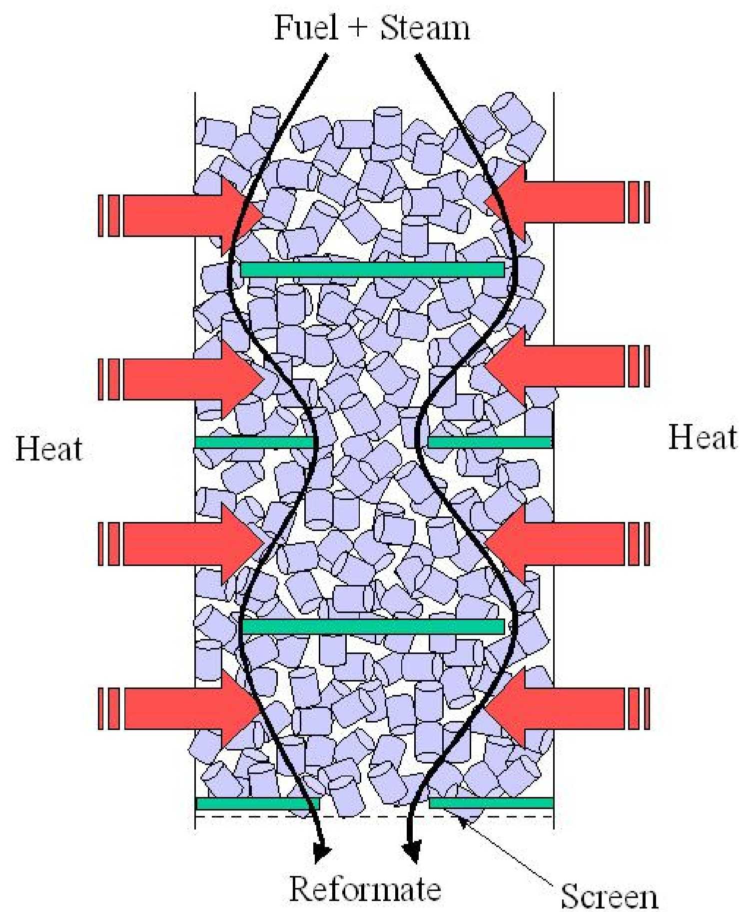
7 hour performance degradation rates (% conversion / hr) in a quasi-isothermal steam reformer using fuel cell grade methanol at different temperatures. This plot shows that degradation has a strong sensitivity to temperature variations.



Enhancing the Steam-Reformation Process

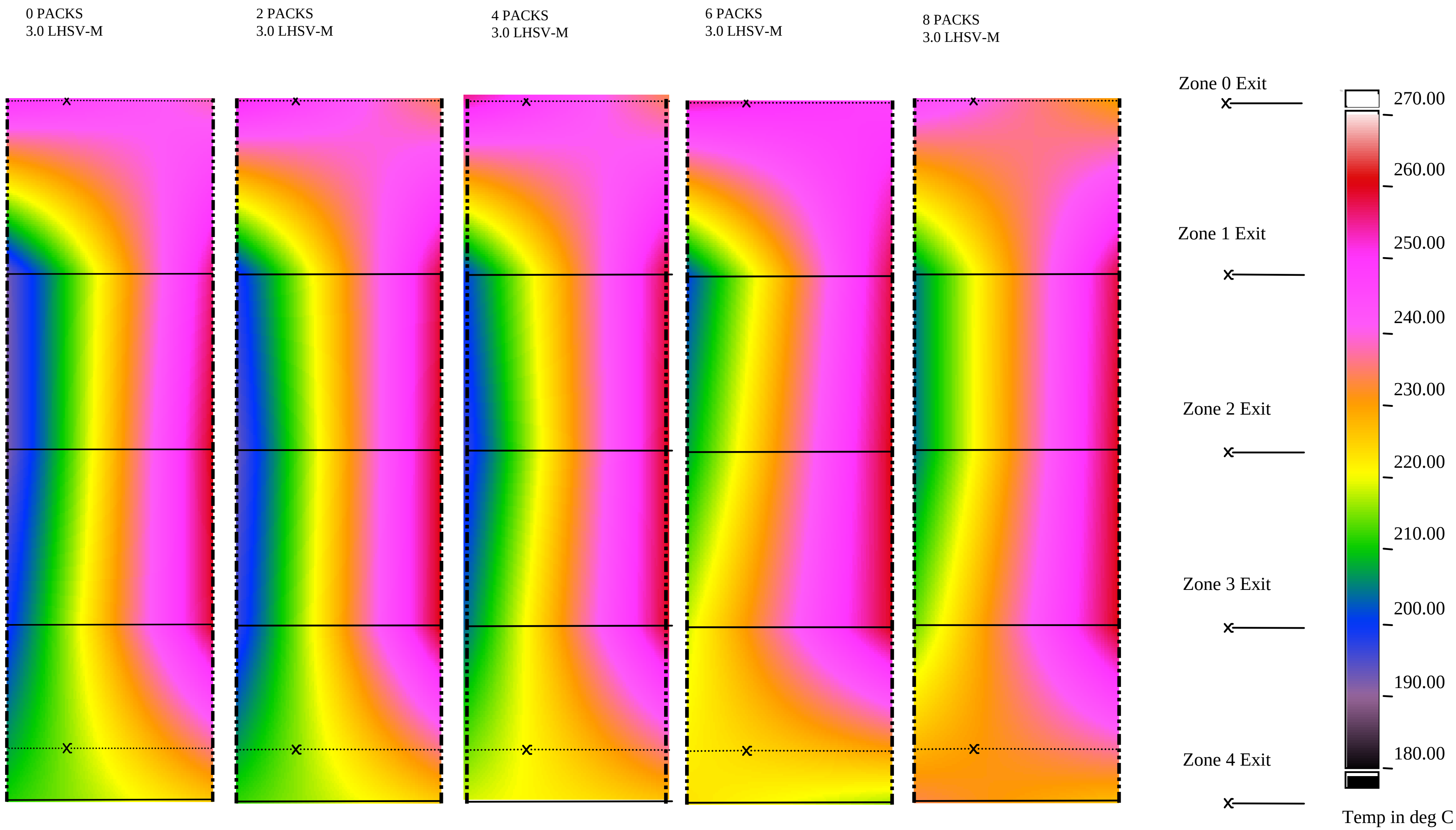


Schematic of Fluid Pathway and Heat transfer inside a Steam Reformer Catalyst Bed



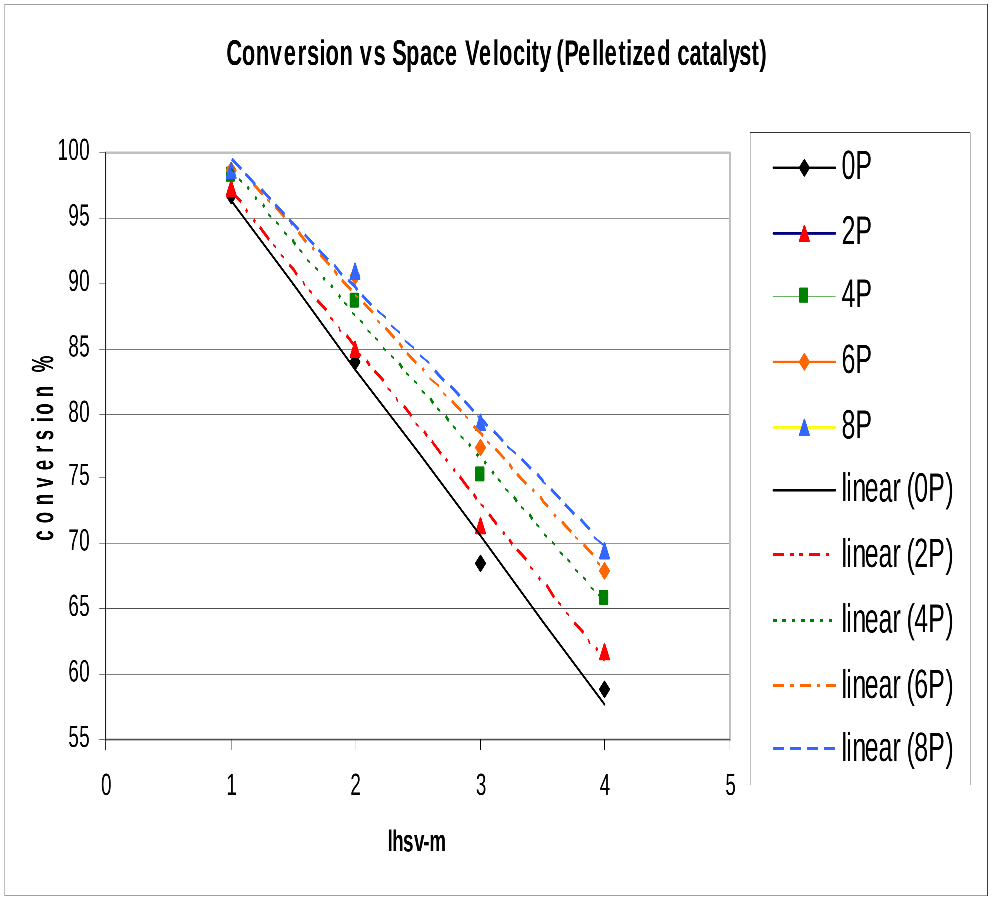
Catalyst Bed with Two Sets of Flow Disturbers

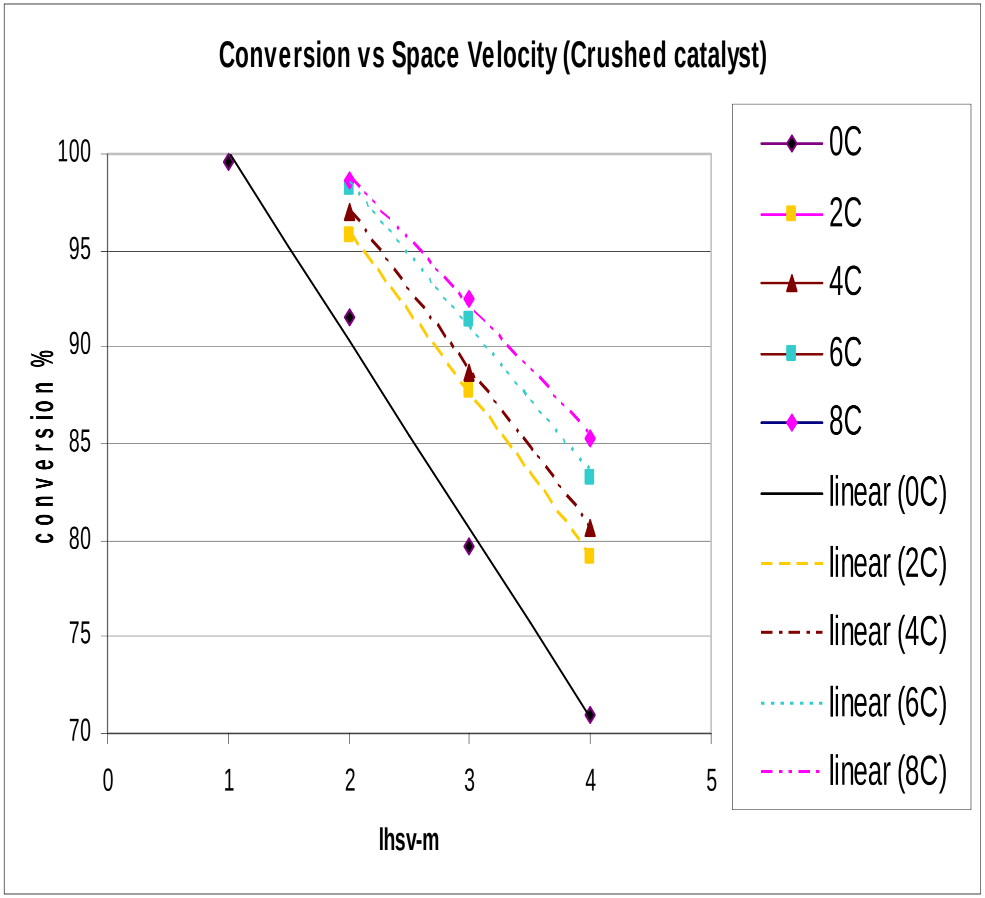
Steam Reformation: Heat Transfer Enhancement via Flow Disturbance



Temperature profiles inside the Half Radial Catalyst Bed Reactor B; Package Density of Flow Disturbers increased from Left to Right

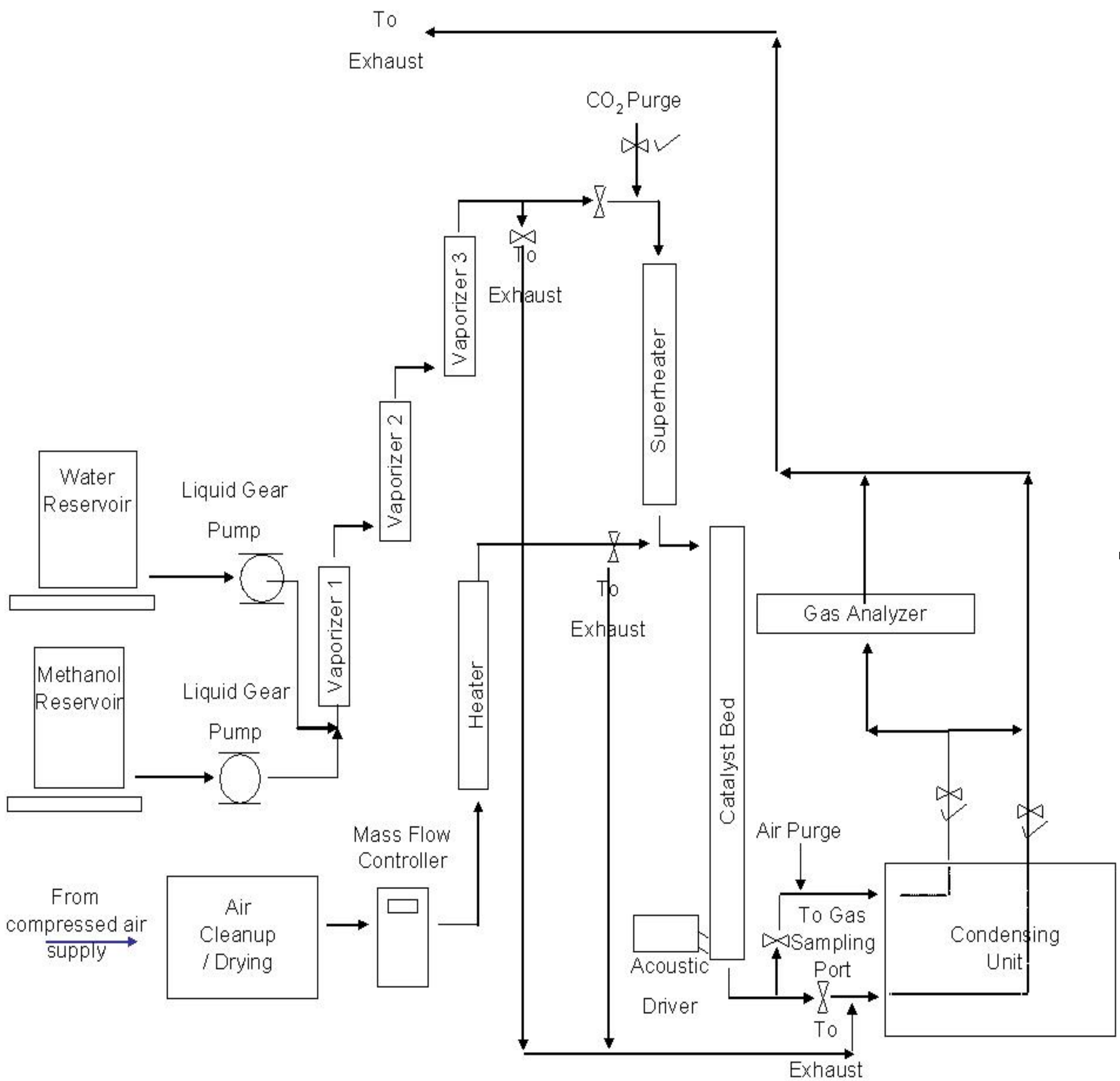
SR Reactor Performance



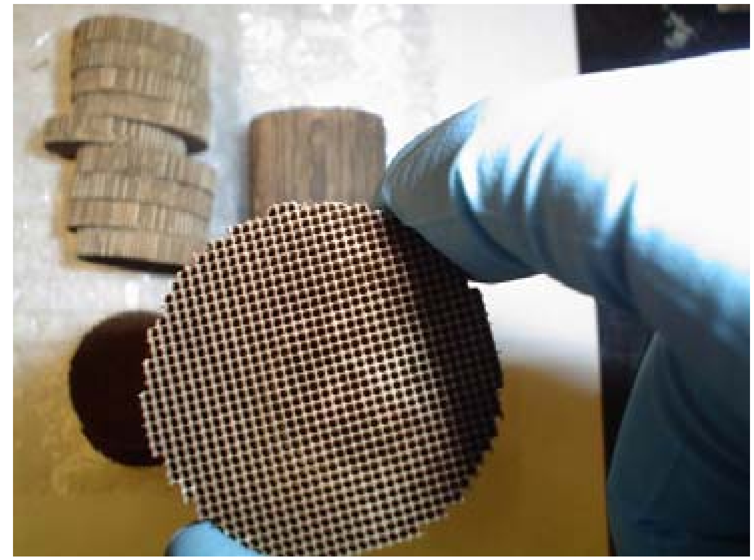


Chemical Grade Methanol Fuel Conversion (%) versus Liquid Hourly Space Velocity of Methanol at different package density of Flow Disturbers, (1)Left: Using Pelletized Catalyst; (2) Right: Using Crushed Catalyst

Autothermal Reformation

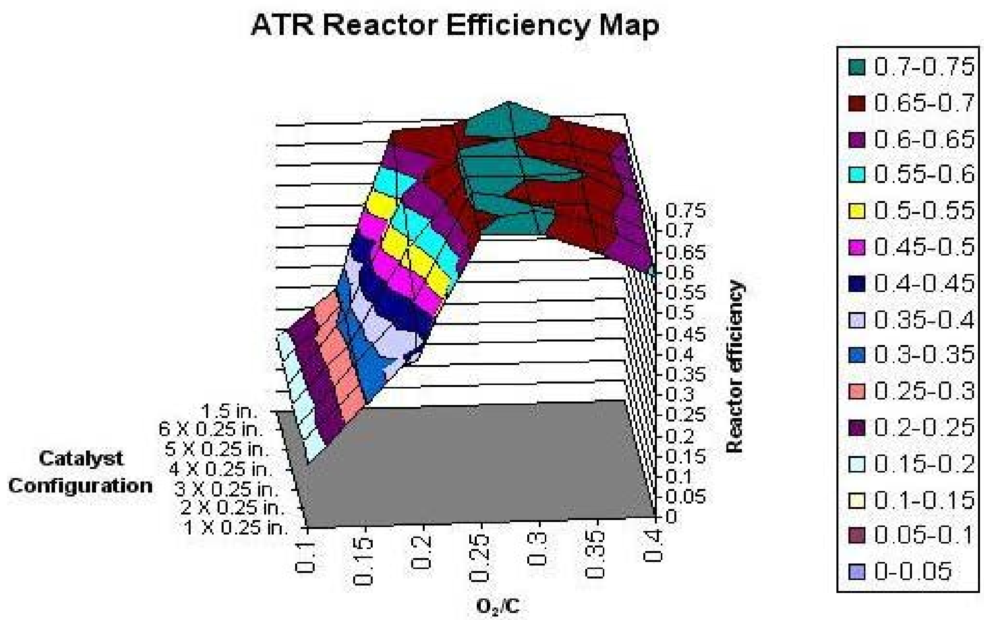


Schematic of the Autothermal-Reforming System

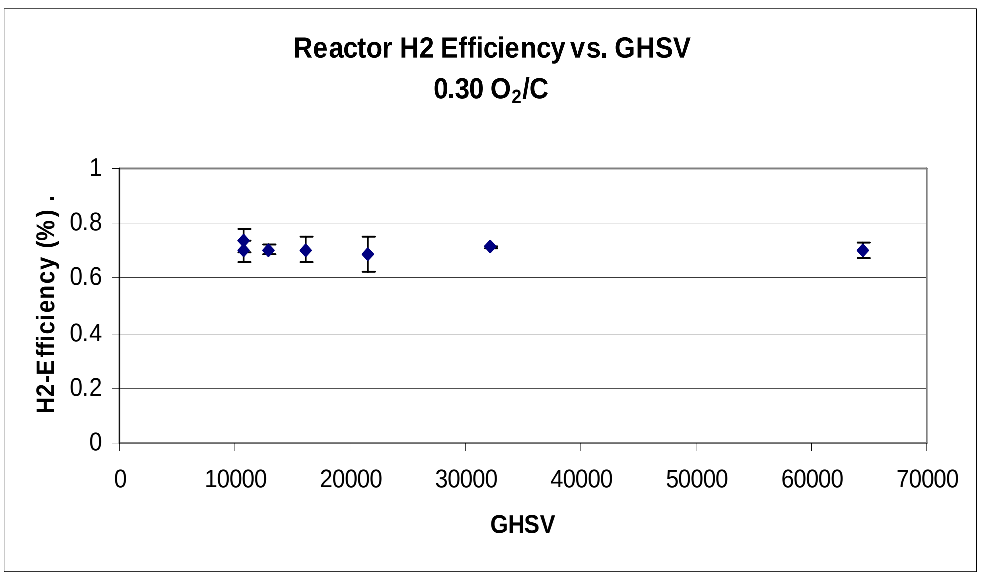


The Monolithic ATR Catalyst Tested

Autothermal Reformation of Methanol



ATR Reactor Efficiency Map from Experimental Data



- Fuel conversion was approximately 100%, when above the light off point (approx. O_2/C =0.2).
- Similar results are shown with coal-derived methanol.
- The maximum H2 output during the experiments occurred at O_2/C=0.3
- The results show that the O_2/C is a significant operating parameter in the ATR of methanol.
- Limiting space velocity has yet to be found.
- Above the light off point an equilibrium model can accurately predict the actual species concentration.
- Degradation of ATR with Coal-Derived Methanol is forthcoming.

Responses to Previous Year Reviewers' Comments

- Reviewers suggested that we check the magnitude of the reactor performance degradation due to fuel impurities in relation to this same output metric due to other variables.
- We have found that reactor geometry affects the catalyst degradation in steam-reformation much more than switching from fuel cell grade methanol to coal-derived methanol. Compare degradation rates in Slide 15 (wide diameter reactor B) to the rates shown Slide 13 (Small diameter with internal cartridge heater).

Future Work

- Present-Oct 05
  - Finish degradation rate tests for fuels in Autothermal Reactor
  - Finish transient tests
  - Review clean-up technology
- Oct 05-Oct 06
  - Integrate reformer and cleanup to PEM hydrogen fuel cell or purchase complete system
  - Quantify fuel cell performance with Coal-Derived vs. Fuel Cell grade fuel

Conclusions and Major Findings

•Coal-derived Methanol has more hydrocarbon impurities than fuel cell grade methanol. Relative levels of chlorides and sulfur are similar. (From Year 1)

•Coal-derived methanol can be used as a hydrogen feedstock with both steam reformation and autothermal reformation. Overall performance with the two fuels is comparable.

•In steam reformation with copper-based catalysts, the performance degradation with coal-derived methanol was greater than that when using fuel cell grade methanol. However, reactor geometry seems to have a much greater role in degradation than fuel impurities at this level.

•Passive flow disturbance within the steam reforming catalyst bed was investigated. From the temperature profile and fuel conversion data, it was proven that the flow disturbance made a significant heat transfer enhancement and increased the capacity of the steam reformer.

•ATR of fuel cell grade methanol has been investigated and ATR of coal-derived methanol is underway. Chemical equilibrium accurately predicts output composition above the light off point. The upper end of flow rate has not yet been determined but it is greater than 77,000 GHSV.

Publications and Presentations

Published

- Dorr, J. L., “Methanol Autothermal Reformation: Oxygen-to-Carbon Ratio and Reaction Progression” Masters Thesis, UC Davis, December 2004
- Dorr, J. L., and P.A. Erickson (2004), “Preliminary Modeling and Design of an Autothermal Reformer,” Proceedings of IMECE: 2004 International Mechanical Engineering Congress and Exposition, November 13-19, 2004 Anaheim, California, IMECE 2004-59892 pp. 1-9
- Erickson, Paul A., Robert J. Kamisky and Nate Moock (2004) “Coal-Based Methanol for Use in Fuel Cells: Research Needed” proceedings of ASME POWER 2004, PWR-Vol. 35 pp. 703-710

In Press

- Erickson, P.A. and H.C. Yoon (2005) “Hydrogen from Coal-Derived Methanol: Experimental Results” Proceedings of the 3rd International Energy Engineering Conference, 2005, Paper Number AIAA-2005-5567
- Liao, C.H. and P.A. Erickson, (2005)“Heat Transfer Enhancement of Steam-Reformation by Passive Flow Disturbance Inside the Catalyst Bed” Proceedings of the ASME 2005 Heat Transfer Summer Conference San Francisco, CA, Westin St. Francis Hotel, July 17-22, 2005 Paper number HT2005-72043 Pages 1-7

In Works

- C.H. Liao “An Analysis of the Effect of Flow Disturbers on Hydrogen Production via Steam-Reforming,” Masters Thesis, UC Davis, expected June 2005.
- H.C. Yoon “Hydrogen from Steam-Reformation of Coal-Derived Methanol,” Masters Thesis, UC Davis, expected June 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Build up and ignition of hydrogen gas or fuels from leaking valves or tubes

Hydrogen Safety

Our approach to deal with this hazard is:

- Hydrogen monitoring with appropriate alarms and evacuation procedures,
- Automatic and Manual Safety shutoffs are included at control panel location
- leak checks before and after each data run,
- real time monitoring and purging of hydrogen pathways before exposing personnel to the system,
- provide constant air flow away from reformer systems at all times, always on
- removal of potential ignition sources at most likely H_2 build up locations,
- safety training for all personnel
- CUPA audits maintained up to date

PI stays abreast of University, State and Federal regulations by being on Safety Committee for Mechanical and Aeronautical Engineering Department.