In Situ Investigation of Major and Minor Species to Support Detailed Model Development of Catalytic Chemistry in a Reformation Reactor

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Start Date = 9/30/04
Planned Completion =3/30/06

Research Goals and Objectives

- Design and construct an optical access reformation reactor enabling *in situ* study of major and minor species.
- Implement laser-based diagnostic techniques (primarily Raman spectroscopy) for quantitative measurements.
- Perform detailed measurements for methanol reformation, including spatially-resolved hydrogen, methanol, and water vapor.
- Compare measurements with detailed kinetic model (Dr. Mikolaitis).
- Extend work to similar problems, including catalytic combustion.

Relevance to Current State-of-the-Art

- Very few (if any) *in situ* experimental measurements exist for hydrocarbon reformation.
- Accurate experimental data is necessary for validation of kinetic models.
- The overall program supports an advancement of catalytic reacting flows, both reformation and direct catalytic energy conversion.

Relevance to NASA

- Extension of this work into areas like catalytic combustion of hydrogen is important for the development of low NOx/low CO2 gas turbines.

Budget, Schedule and Deliverables

Budget: $60,500 allocated/$89,300 requested

Original Schedule and Deliverables

- 1st Quarter: Design and construction of flow reactor
- 2nd Quarter: Reactor testing and validation
- 3rd Quarter: Implementation of laser-based diagnostics
- 4th Quarter: Detailed *in situ* measurements of H_2, H_2O and CH_3OH during reformation of methanol

Modified to refocus on catalytic combustion as NASA interest in reforming has shifted. Completed methanol measurements, but discontinued extension to ethanol.

Anticipated Technology End Use

- Hydrogen production and development of new catalysts for hydrogen production.
- Analysis of hydrogen production systems that use catalysts.
- Eventual application in the analysis of catalytic combustion systems for power generation, especially for low NOx/low CO2 systems.

Accomplishments and Results

Design and development of optical access reformer

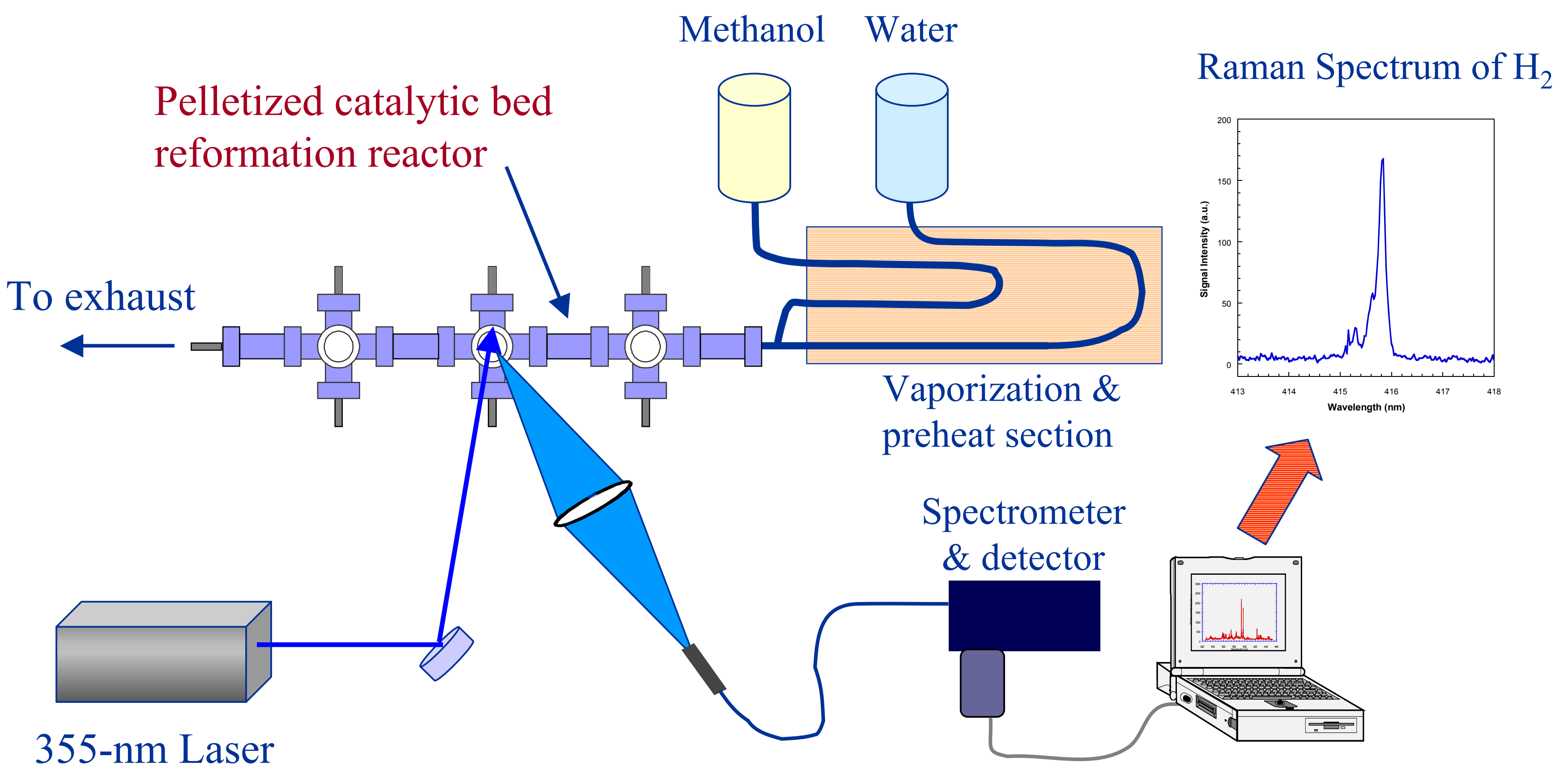
- Selection of catalyst:
  - Katalco 33-5 catalyst pellets (Johnson Matthey)
  - 64 wt % CuO, 24 wt % ZnO, 10 wt % Al_2O_3, and 2 wt% MgO
  - Widely-used low-temperature reformation catalyst
- Construct reactor from off-the-shelf components:
  - Huntington Labs vacuum flanges
  - Trade-off between optical resolution and the cost/design/manufacturing time

Accomplishments and Results

Optical Diagnostics

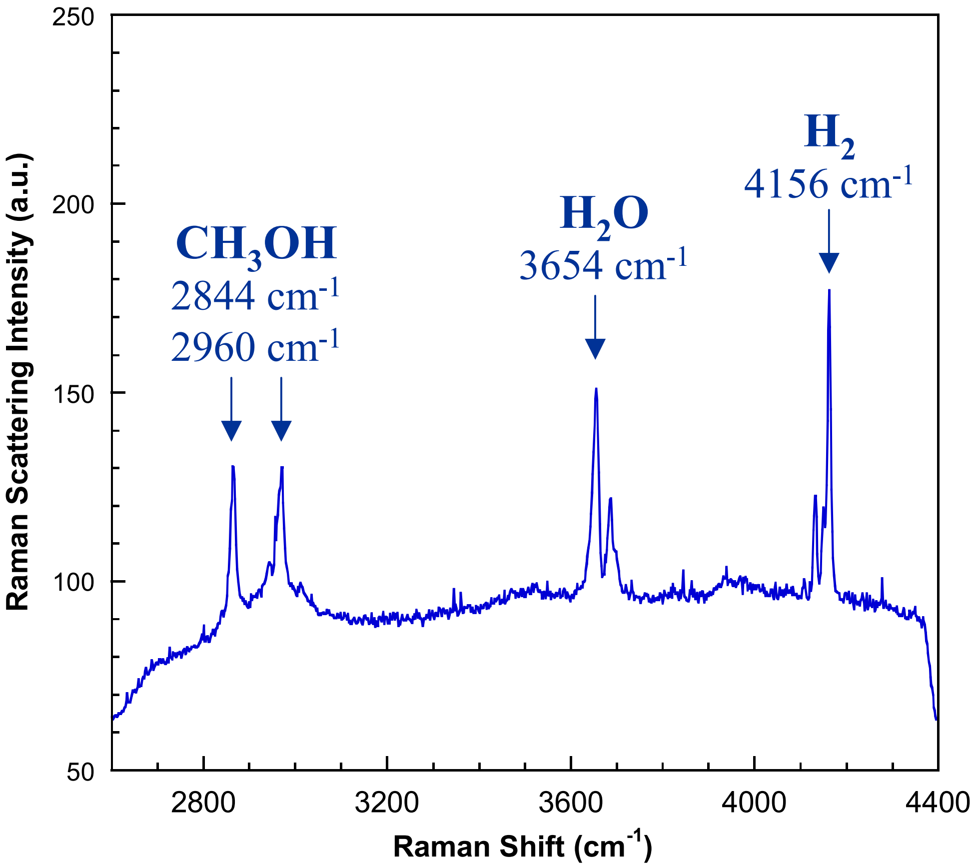
- Raman spectroscopy
  - Simultaneous measurements of hydrogen, water vapor and methanol
  - Signals are weak – detection limits ~1 percent
  - Use 355-nm excitation to maximize signal
- Considerable experience with Raman spectroscopy
  - NASA-sponsored remote leak detection
  - Have the necessary laser and detection hardware

Accomplishments and Results



Accomplishments and Results

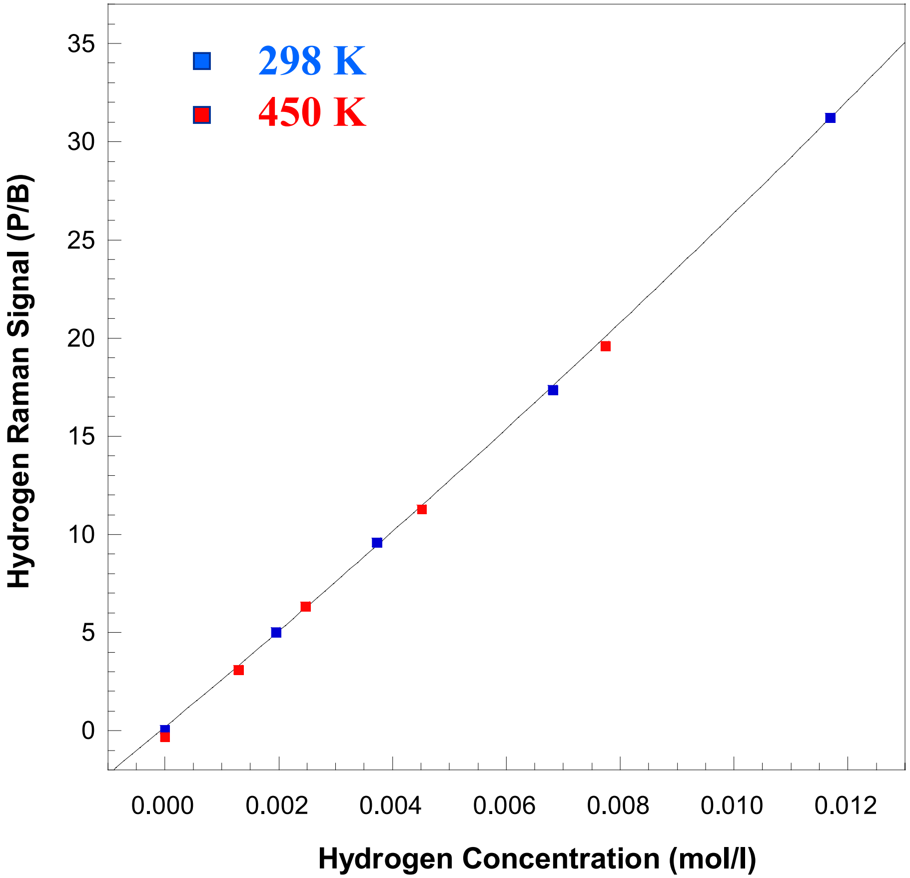
- Diagnostic implementation:



Typical Raman spectrum recorded during methanol reformation

Accomplishments and Results

- Diagnostic implementation:



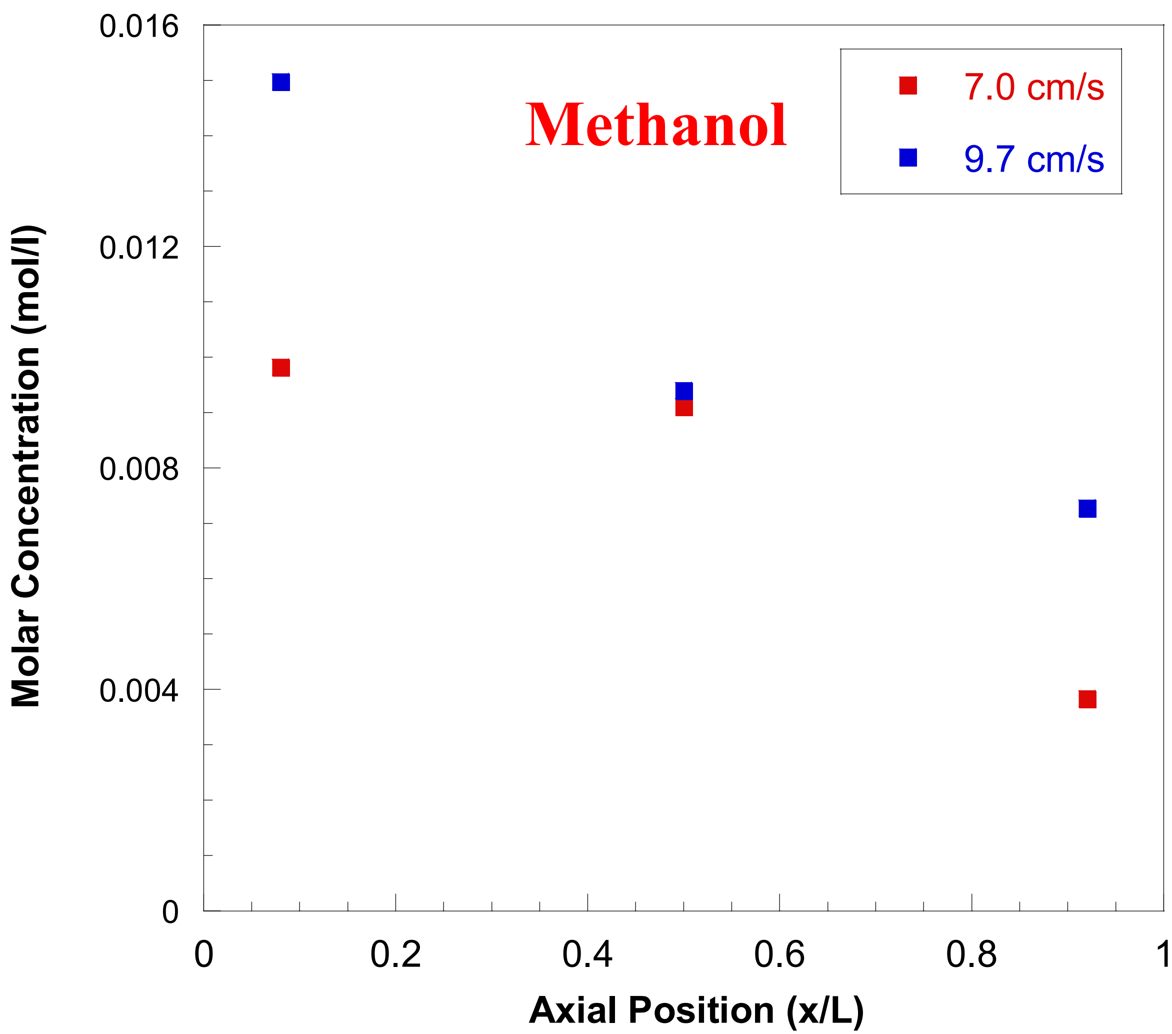
Raman calibration curve for hydrogen, showing excellent linearity and the expected independence of Raman cross-section on temperature

Accomplishments and Results

- Reformation parameters:
  - Catalyst bed temperature: 495 K
  - Gas phase temperature: 485 K
  - Steam/Methanol molar ratio: 1.05-1.08

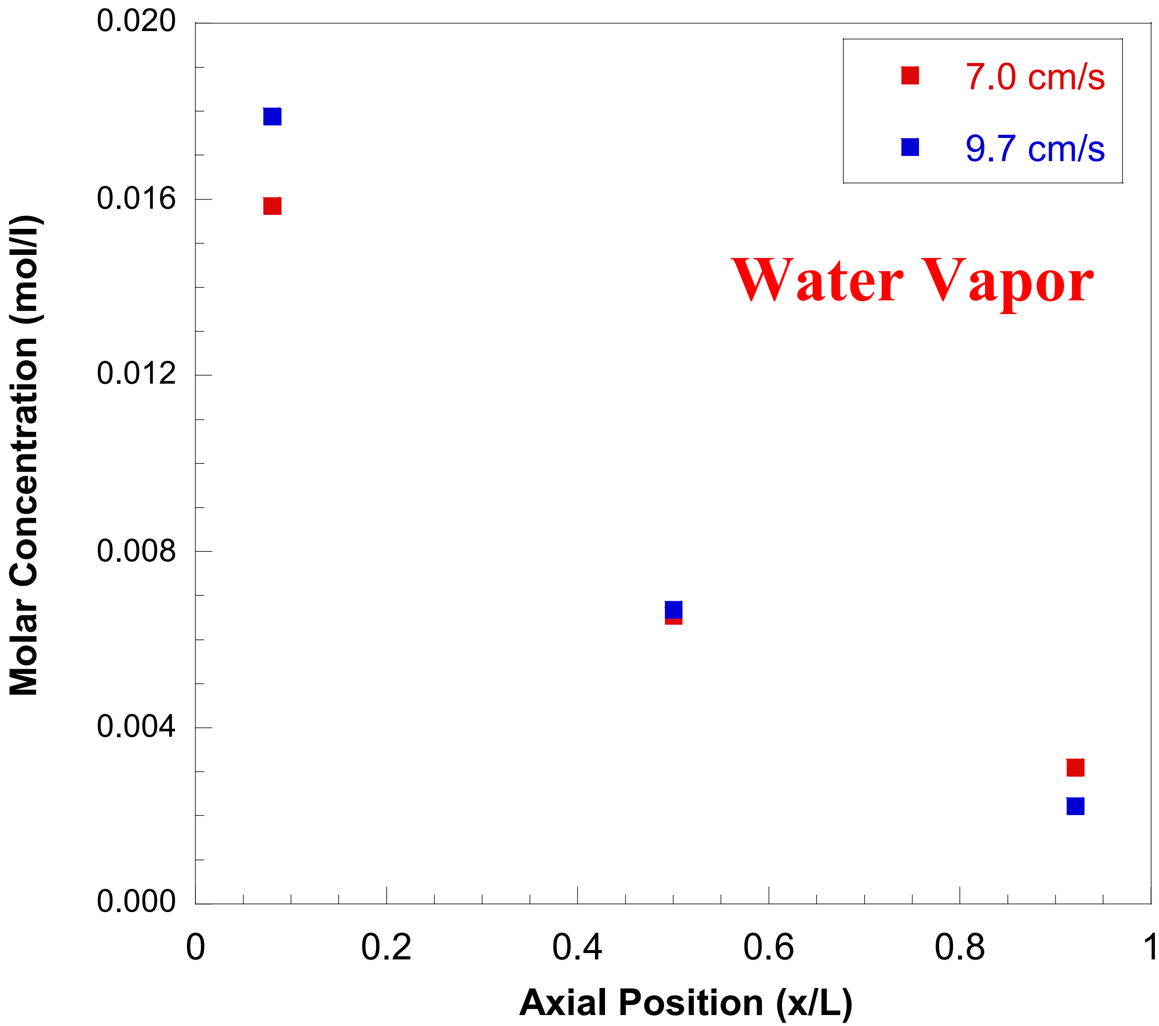
- Measurement conditions:
  - 3 axial positions (x/L): 0.08, 0.5, 0.92
  - 4 heights above reactor bed: 1.2-mm spacing
  - Flow velocity: 7.0 & 9.7 cm/s
  - Residence time: 6.3 & 8.4 s

Accomplishments and Results



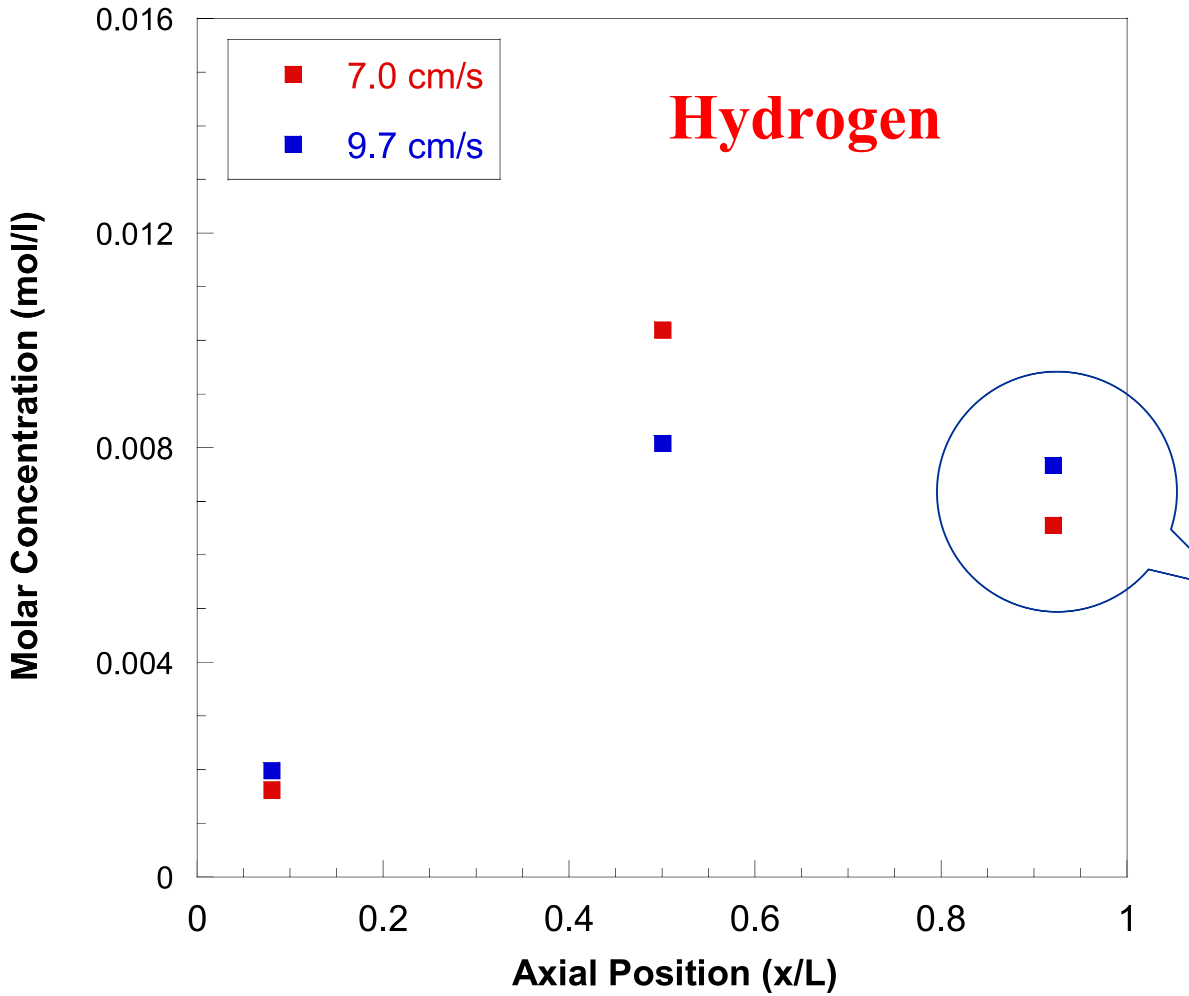
Methanol consumption with residence time

Accomplishments and Results



Water consumption with residence time

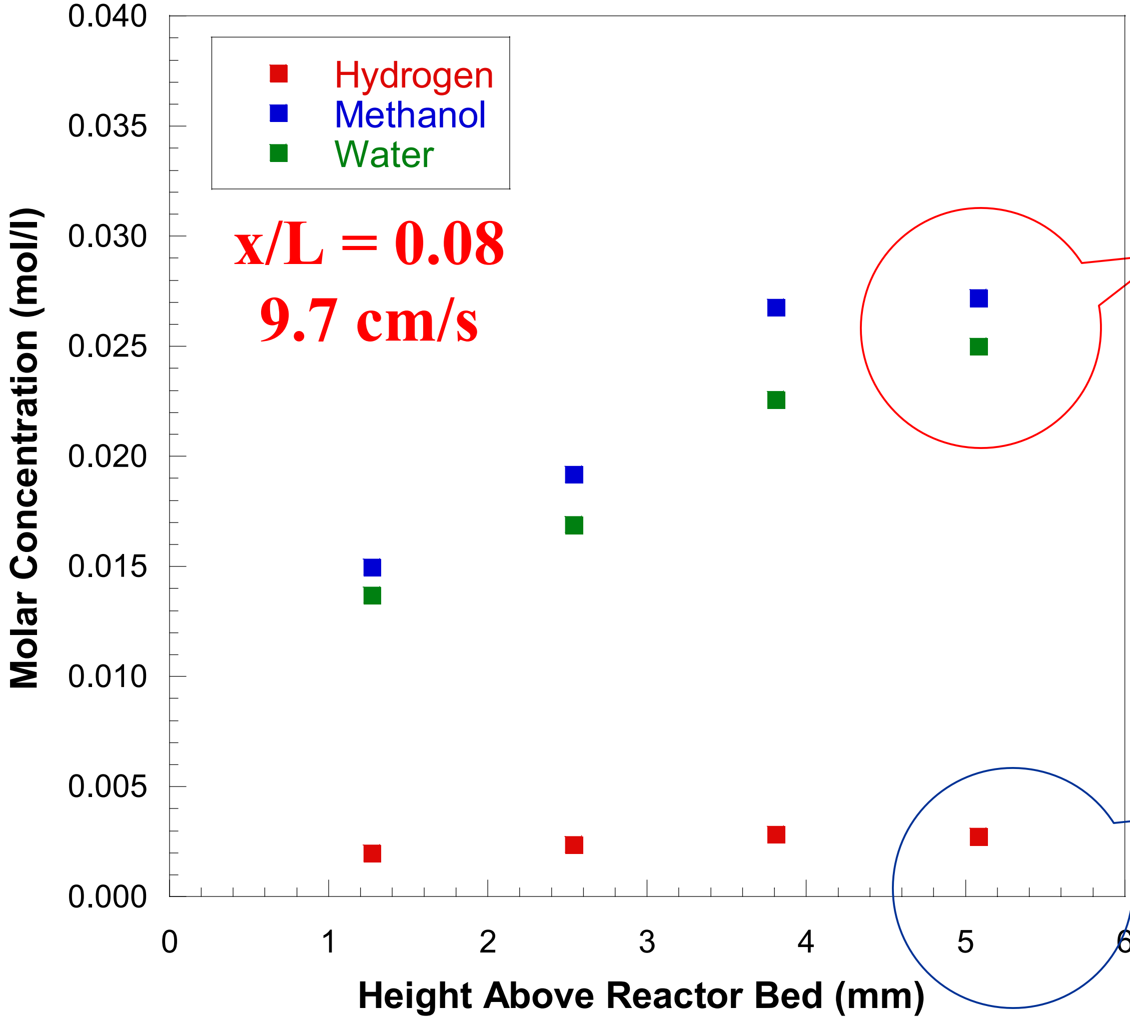
Accomplishments and Results



Hydrogen formation with residence time

Dilution effect as rate of reaction is reduced and products diffuse

Accomplishments and Results



Methanol and water gradient toward the catalyst bed

Hydrogen diffusion limits gradient

Accomplishments and Results

- Successfully detected hydrogen, methanol and water vapor during methanol reformation.
- Detection limits were consistent with experimental conditions for all three species.
- Catalytic bed and reactor configuration provided for spatially-resolved measurements for model validation.

Future Plans

- Complete experiments to improve agreement with model of Dr. Mikolaitis.
- Extend measurements to CO_2 and CO.
- Complete development of gas phase/surface reaction model for inlet flows.
- Explore feasibility of *in situ* measurements for catalytic combustion.
- Prepare scientific papers and additional proposals.
- Continue collaborations initiated with this project.