CO_2 Recycling via Reaction with Hydrogen

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EUEC Energy and Environment Conference

Phoenix, Arizona

February 4, 2009

Desert Research Institute

Outline

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B. Experimental Set-up

C. Experimental Conditions

D. Results and Discussion

- Effect of reactant stoichiometry
- Effect of catalyst temperature
- Effect of space velocity (gas flow rates)

E. Conclusions

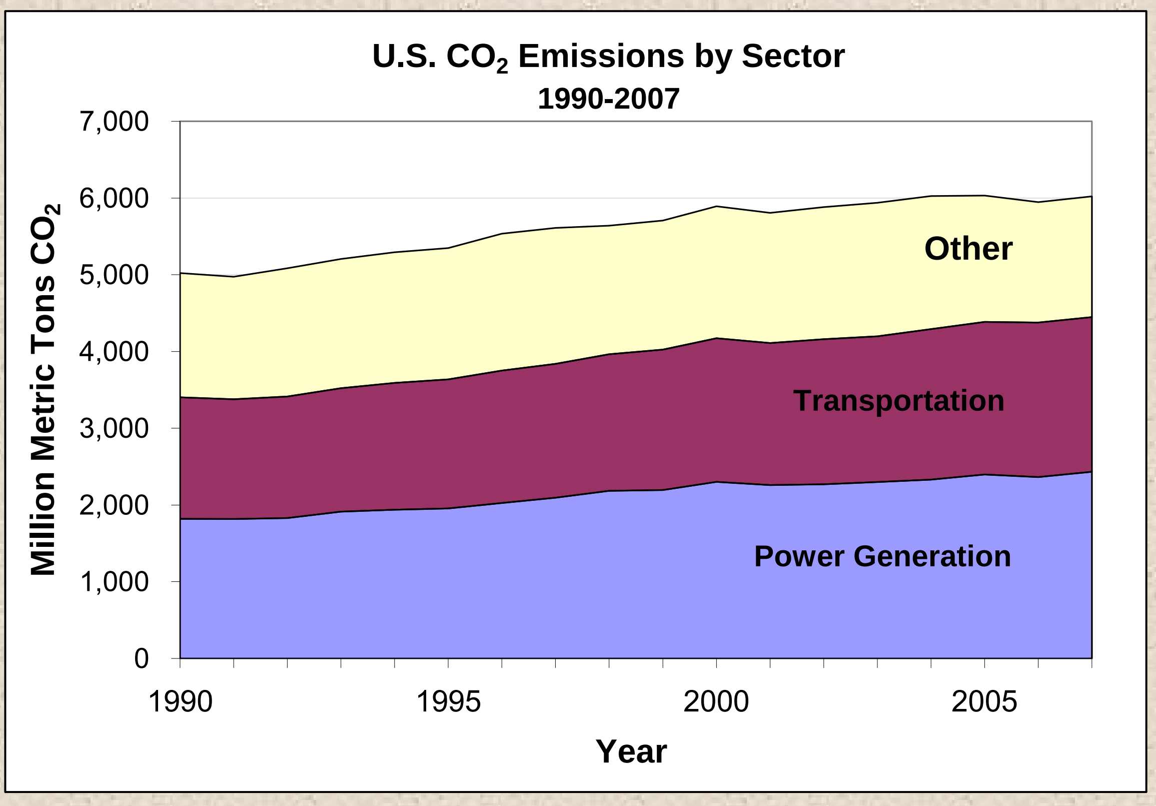
F. Next Steps

Introduction

- Power generation sector is a major contributor to total U.S. greenhouse gas emissions

- Carbon capture and sequestration (or storage), CCS, is being widely explored

- Carbon capture and recycle (CCR) is another approach for GHG mitigation



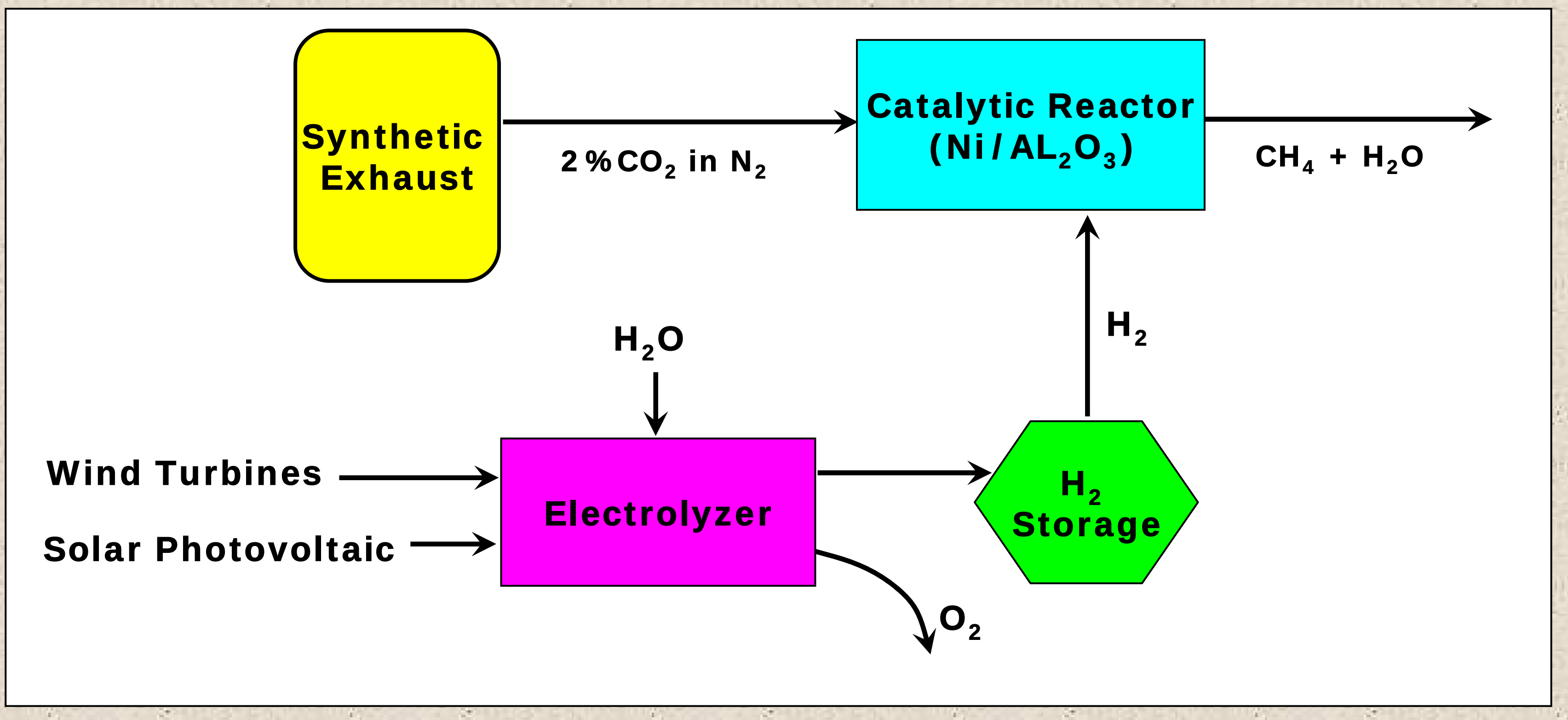
CO_2 Emissions data taken from DOE-EIA (2008)

Methanation Process: Sabatier Reaction

$$CO_2 + 4\ H_2 \underset{}{\overset{\Delta,\ \text{Catalyst}}{\rightleftarrows}} CH_4 + 2\ H_2O$$

- Reduces CO_2 to methane at modest temperatures (200-400°C)
- Reverse reaction increases at temperatures >400°C
- Highly exothermic reaction (ΔH = -167 kJ/mol)
- Catalysts commonly include Ni or Ru
- Requires supply of Hydrogen
  - H_2 must come from renewable sources (or nuclear) for GHG benefits

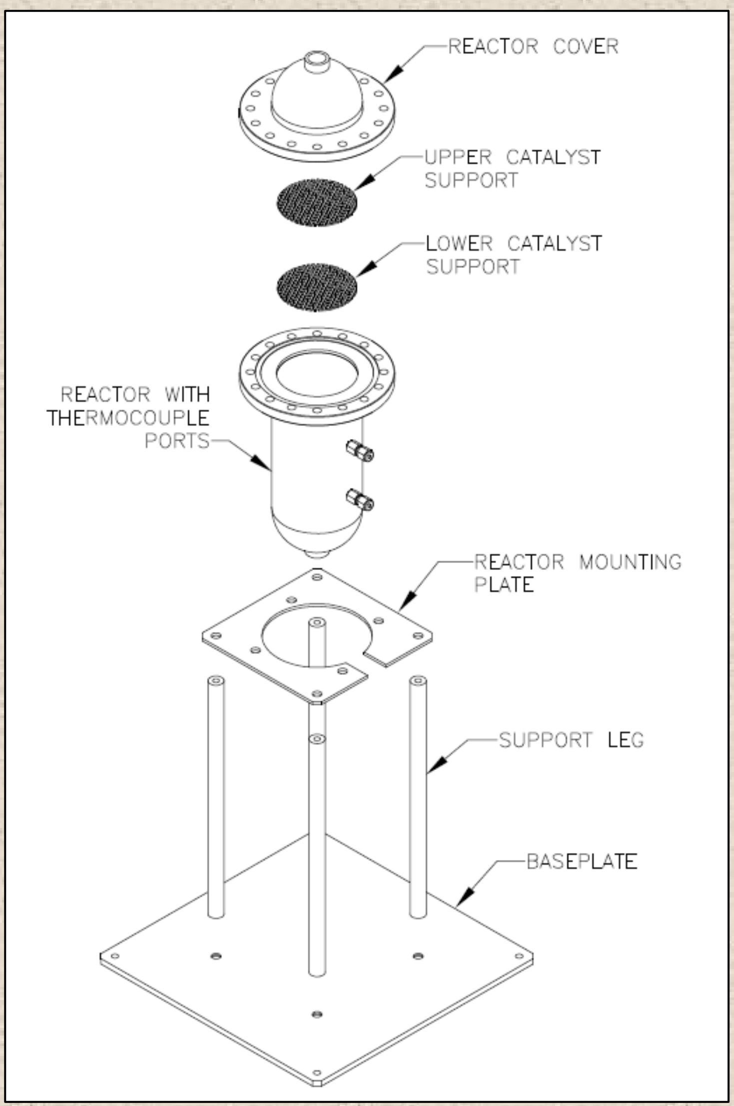
Experimental Schematic



Reactant gases: 2% CO_2 in N_2; 100% H_2

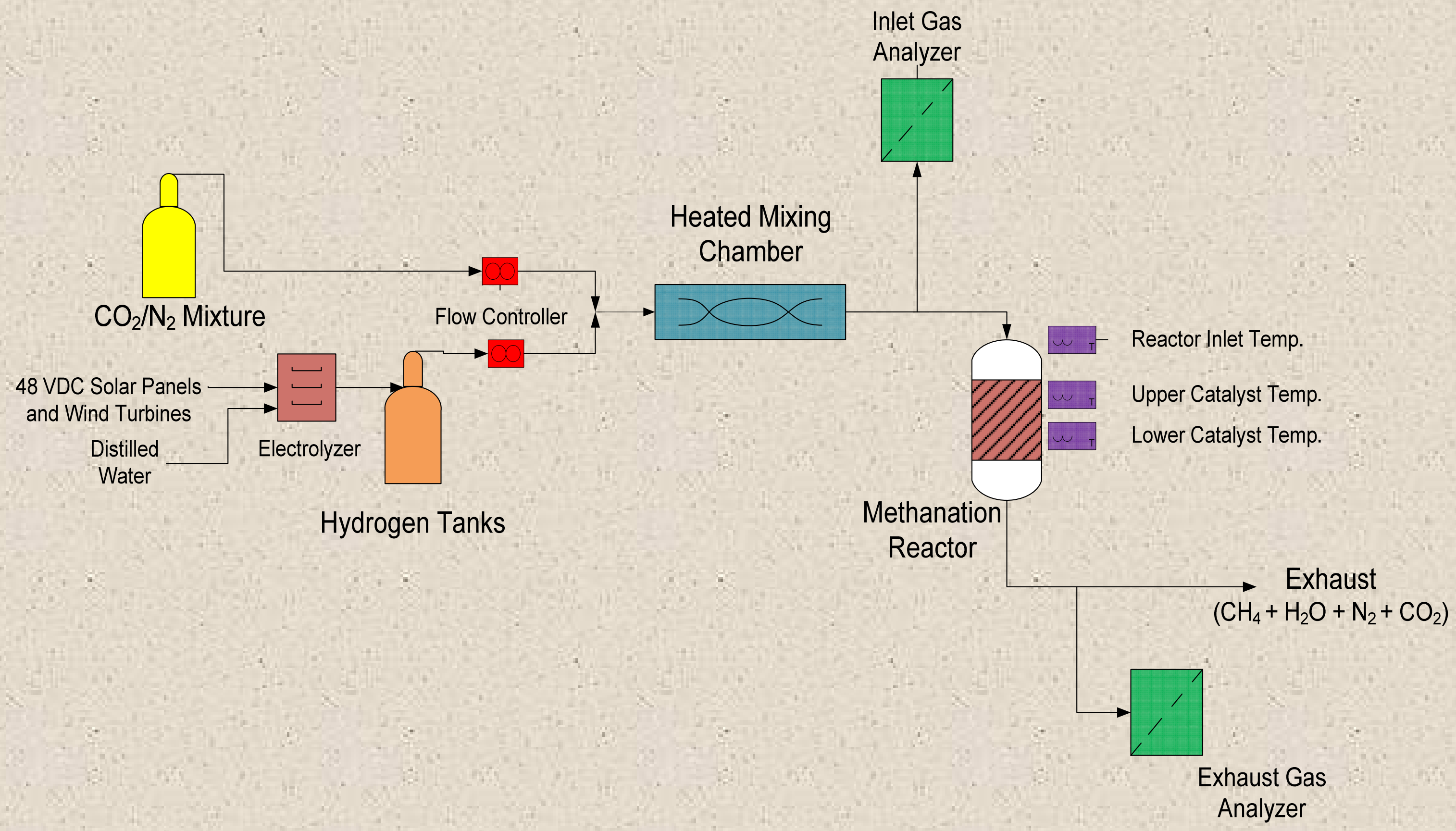
Methanation catalyst: Haldor Topsoe PK-7R

Design of Methanation Reactor



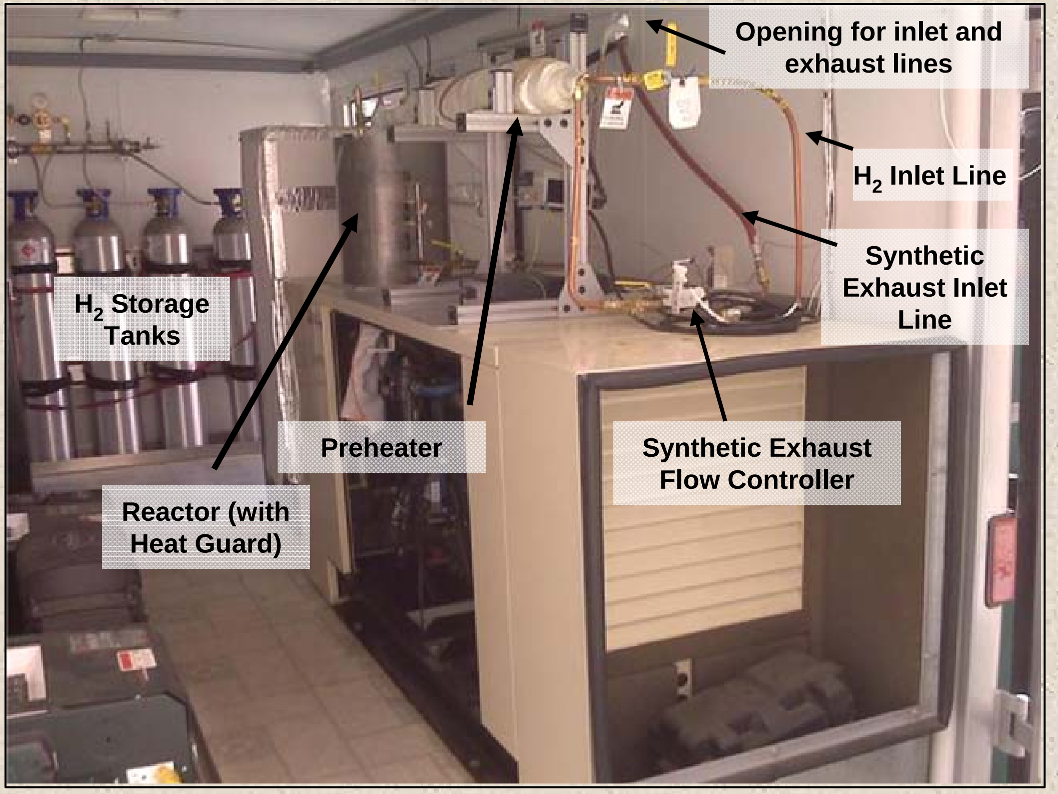
- Stainless steel tube:
  - 6.5 in. length x 3.14 in. diameter
- Catalyst packed bed:
  - 4.3 in. depth of catalyst
  - volume of 33.3 in^3 (0.55 Liter)
- Two thermocouple ports:
  - upper: 1/3 of bed depth
  - lower: 2/3 of bed depth
- Gas flow from top to bottom

Methanation Experimental Set-up



Methanation Experimental Set-up

Photo of experimental apparatus inside trailer.



Gas analyzers and synthetic exhaust cylinders located outside of trailer.

System Control and Monitoring

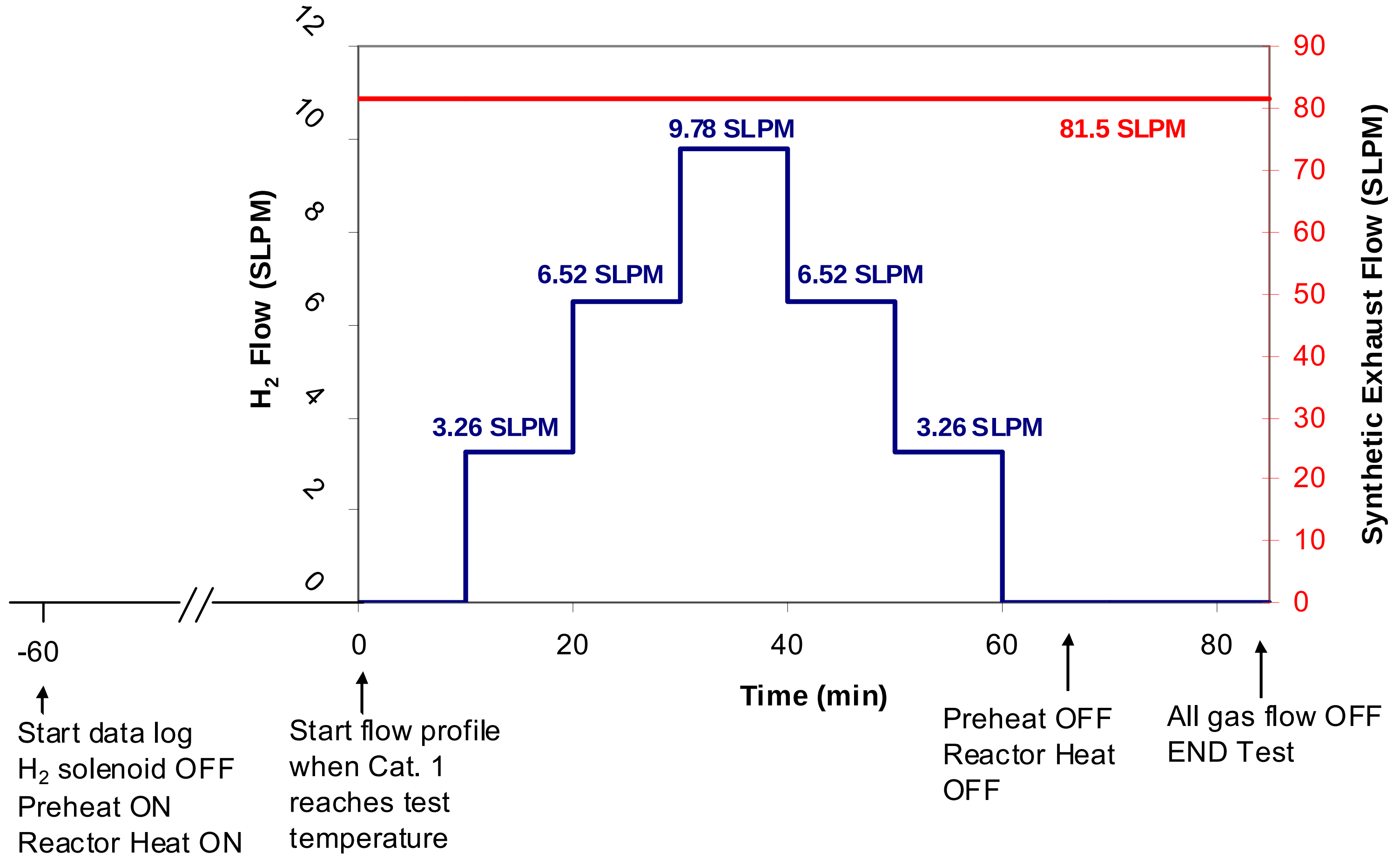
- Employed National Instruments Compact Field Point (cFP) unit:
  - Control and record temps and gas flow rates
  - Control safety shut-off

- Two continuous gas analyzers
  - Before reactor: CO, CO_2, O_2, HC, NO_x
  - After reactor: CO_2, O_2, CH_4, NO_x

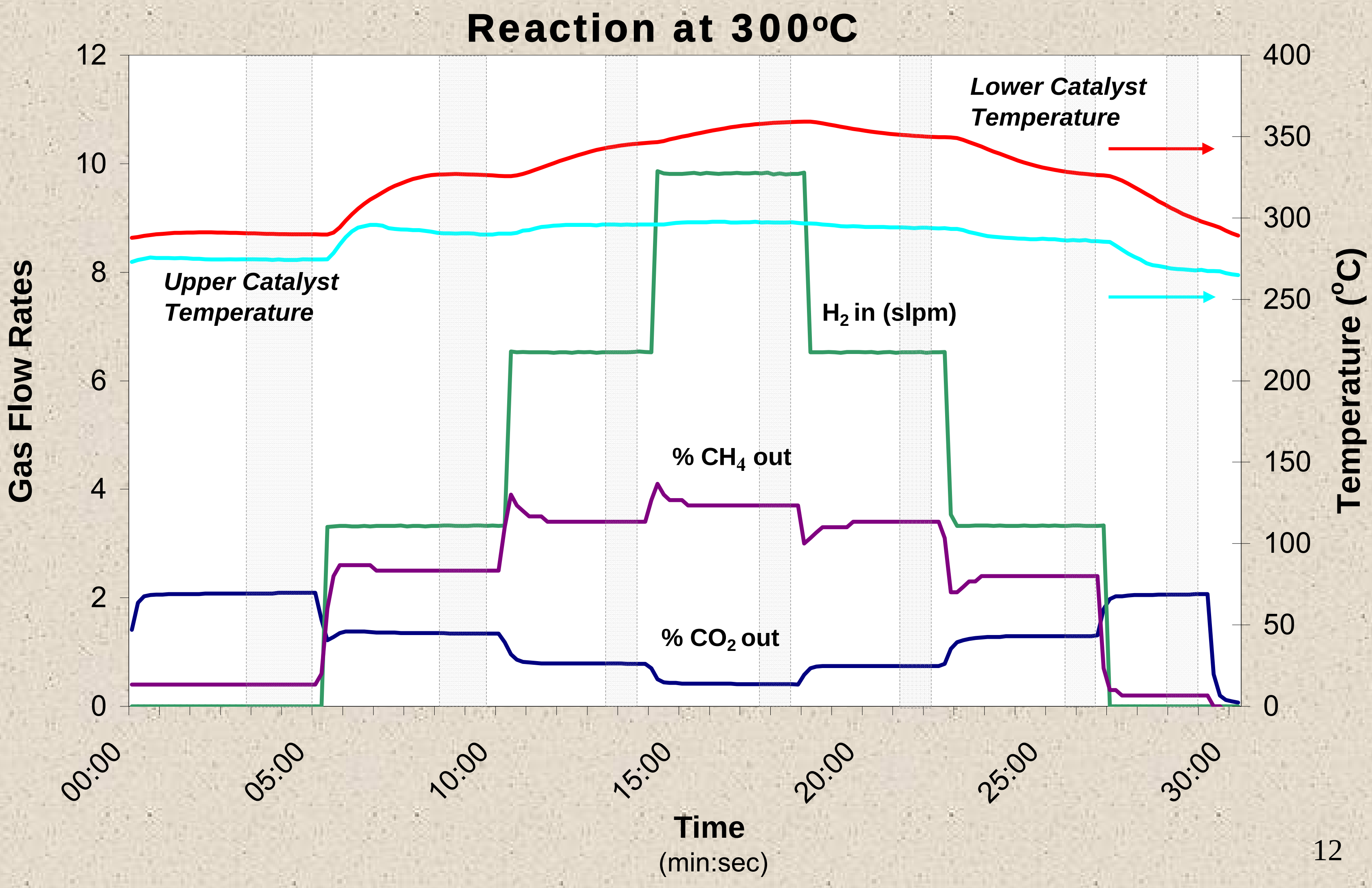
Experimental Conditions

- Stoichiometric Conditions (H_2/CO_2 = 4/1)
  - 81.5 L/min of 2% CO_2 in N_2
  - 6.5 L/min of 100% H_2
  - Total flow of 88 L/min gives space velocity of 9000 hr^{-1}
- Variations in reactant gas ratios
  - 7-step experiment
    - Hold CO_2/N_2 flow rate constant
    - Increase H_2 flow rate in discrete steps from none to excess
  - H_2/CO_2 = 0, 2, 4, 6, 4, 2, 0
- Four catalyst temperatures
  - 200, 250, 300, and 350^{o}C

7-Step Reactant Variation Experiment



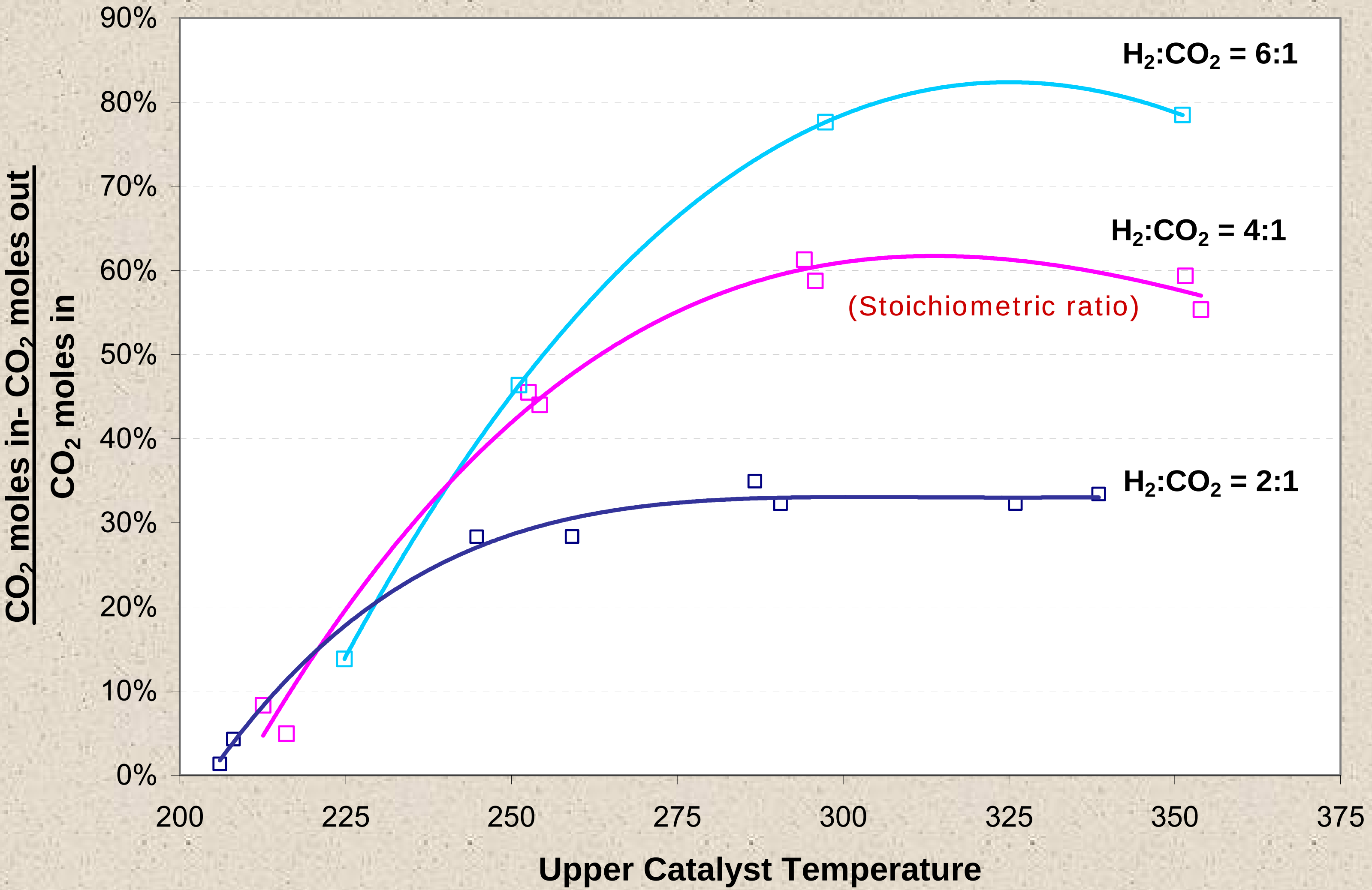
Raw Data Output



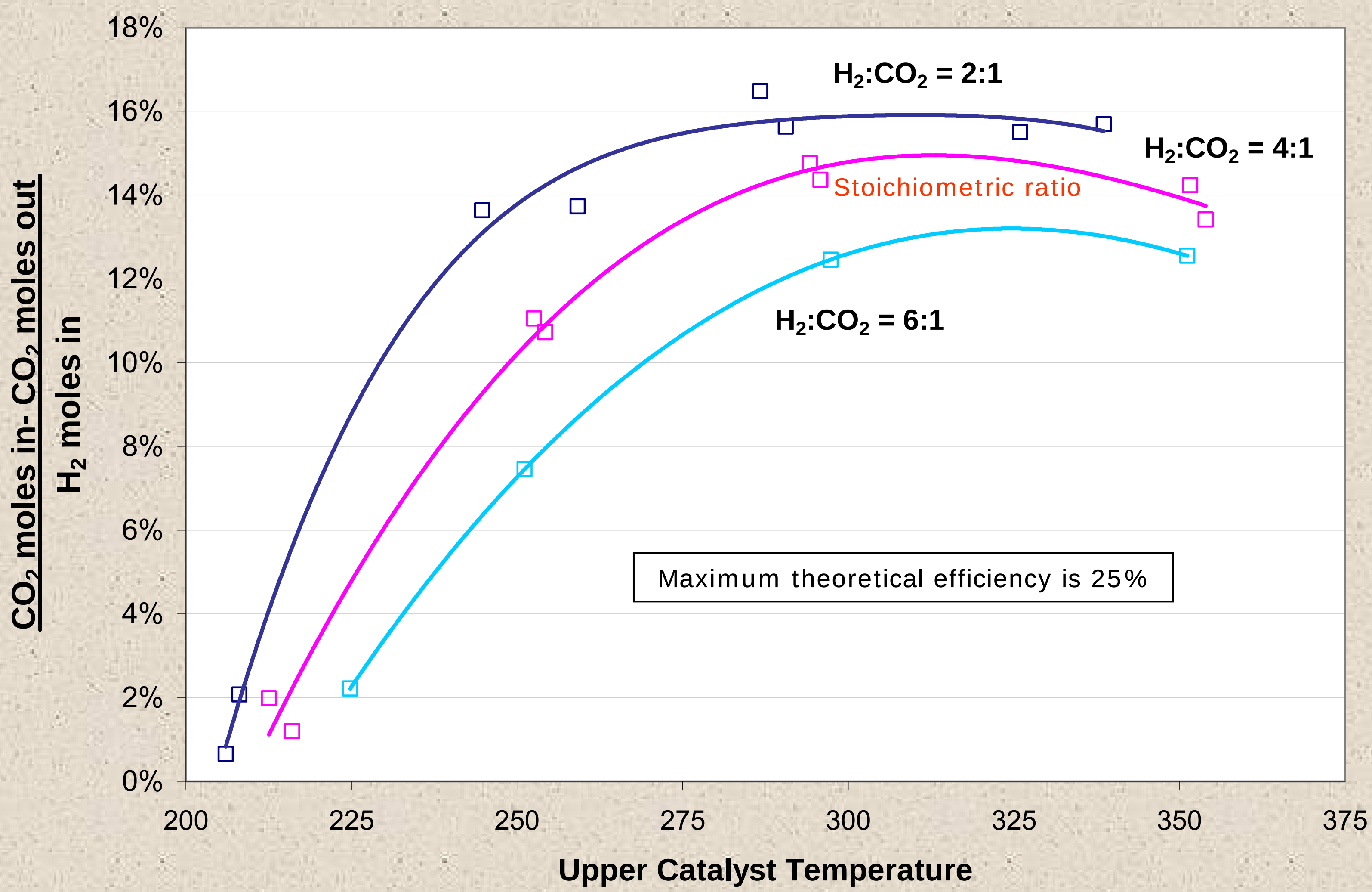
Data Analysis and Correction

- Only data from “stable periods” of operation were used (designated by shaded areas on previous plot)
- Corrected gas flows: reactor outlet flow rate does not equal inlet flow rate:
  - 5 moles of reactant produce 3 moles of product
  - Liquid water is produced during methanation
  - Some inlet flow removed for analysis
- Corrections for analyzer drift and improper zeroing

Results: Total CO_2 Conversion



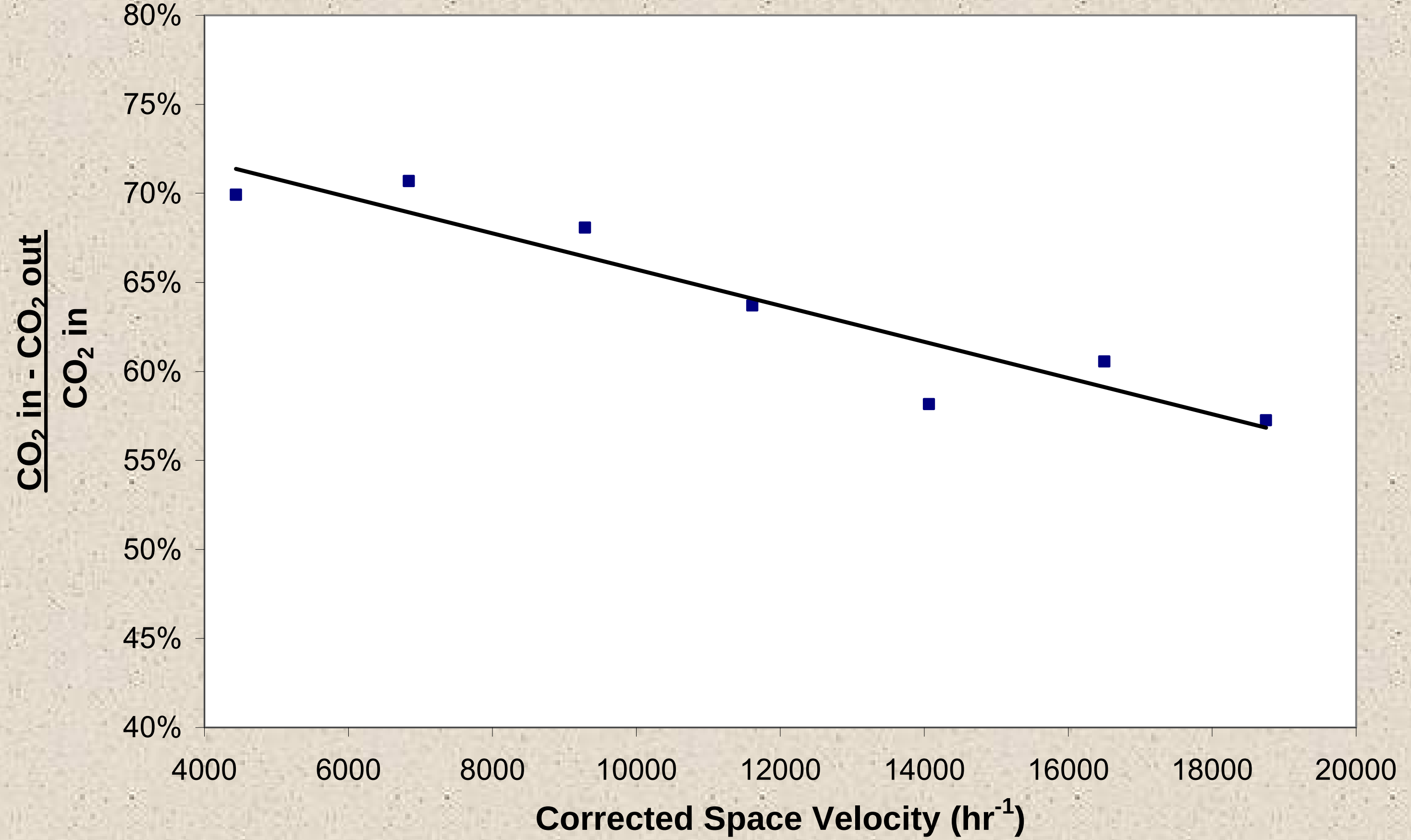
Results: CO_2 Conversion - Efficiency of Hydrogen Utilization*



Results: Effect of Space Velocity on CO_2 Conversion

Stoichiometric ratio: H_2/CO_2 = 4/1

Catalyst temperature = 300^{o}C



Summary and Conclusions

1. Sabatier reaction can be used to recycle CO_2 using renewably-produced hydrogen
2. Optimum conversion of CO_2 to CH_4 occurs at 300-350^{o}C
3. Efficiency of H_2 utilization increases at lower H_2/CO_2 ratios
   - Preferred H_2/CO_2 ratio is < stoichiometric ratio of 4/1
4. CO_2 conversion efficiency is reduced as flow rate increases
   - Observed 15% reduction in conversion over 4-fold increase in space velocity

Next Steps

1. Scale-up reactor system
   – Utilize two parallel reactors
   – Implement active cooling of reactors
2. Utilize authentic exhaust from natural gas engine
3. Develop on-line H_2 measurement capability
4. Recycle produced CH_4 back to engine as a supplemental fuel

Acknowledgements

Financial support:

- Recycle CO_2, Inc.

Technical support:

- Larry Sheetz - DRI