

This presentation does not contain proprietary or confidential information

High Pressure Distributed Ethanol Reforming

*2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review
Arlington, VA, May 23-26, 2005*

S.H.D. Lee, S. Ahmed, D. Applegate, R. Ahluwalia

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Argonne National Laboratory

Project ID# PDP7



U.S. Department of Energy
Energy Efficiency
and Renewable Energy



Overview

Timeline

- **Project start: October, 2004**
- **Project end: September, 2007**

Barriers addressed

- **Efficiency**
- **Cost**

Budget

- **Total project funding: \$225K**
- **DOE share: 100%**
- **FY05 funding: \$225K**

Partners

- **Pacific Northwest National Laboratory**

Objectives

- **Study steam reforming of ethanol at high pressure**
 - Evaluate high pressure reforming options
 - Study reforming equilibria and kinetics at elevated pressures
 - Evaluate membrane reactors

Relevance

- **Ethanol is a bio-derived renewable liquid fuel**
- **Ethanol has a high volumetric energy density**
- **Ethanol (liquid) is easy to transport**

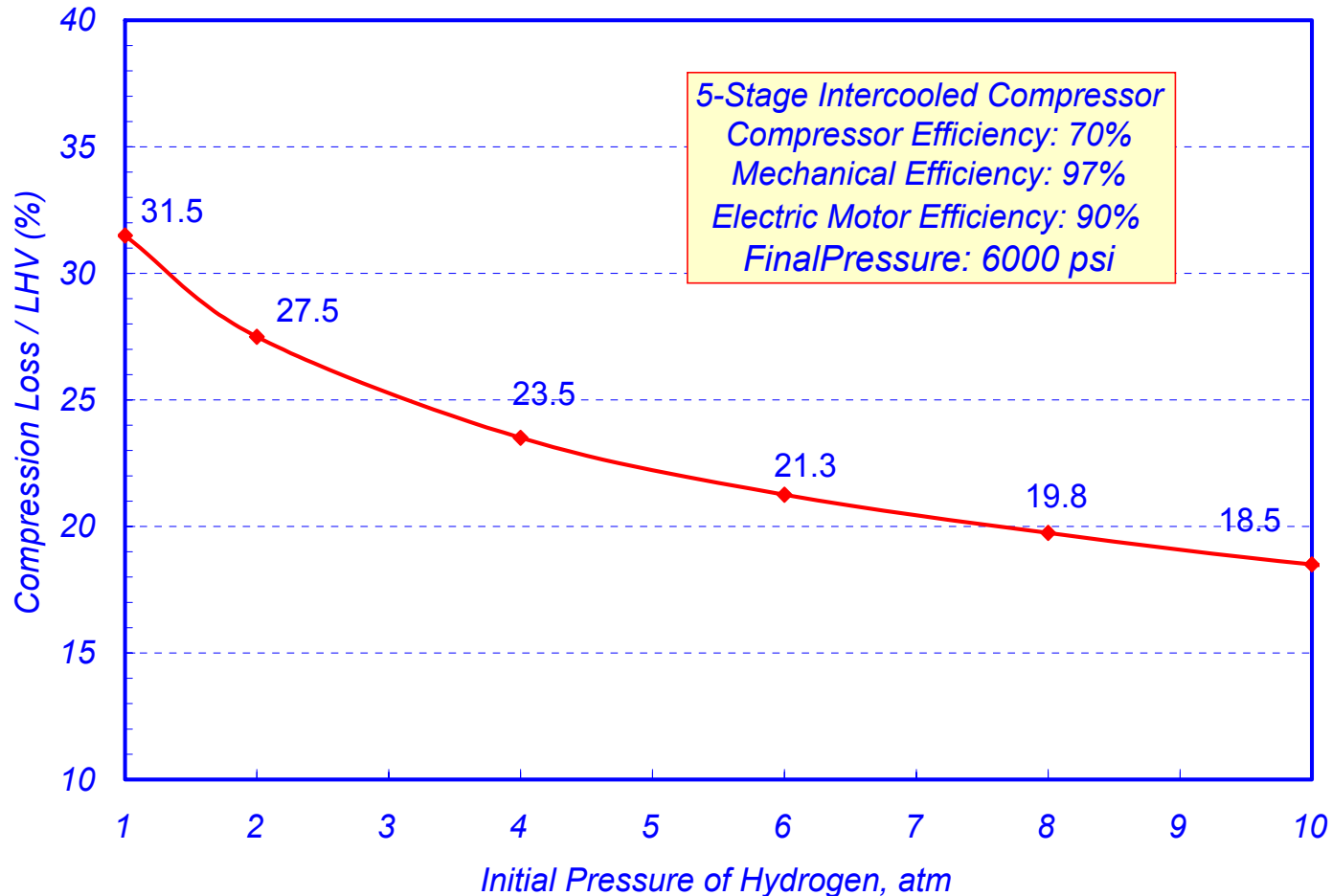
Decision Factors

- **Liquid fuels can be steam reformed at high pressure, avoiding/reducing cost of post-reformer compression**
- **Higher pressures assist membrane purification/separation**
- **Pressurized systems require high capital cost**

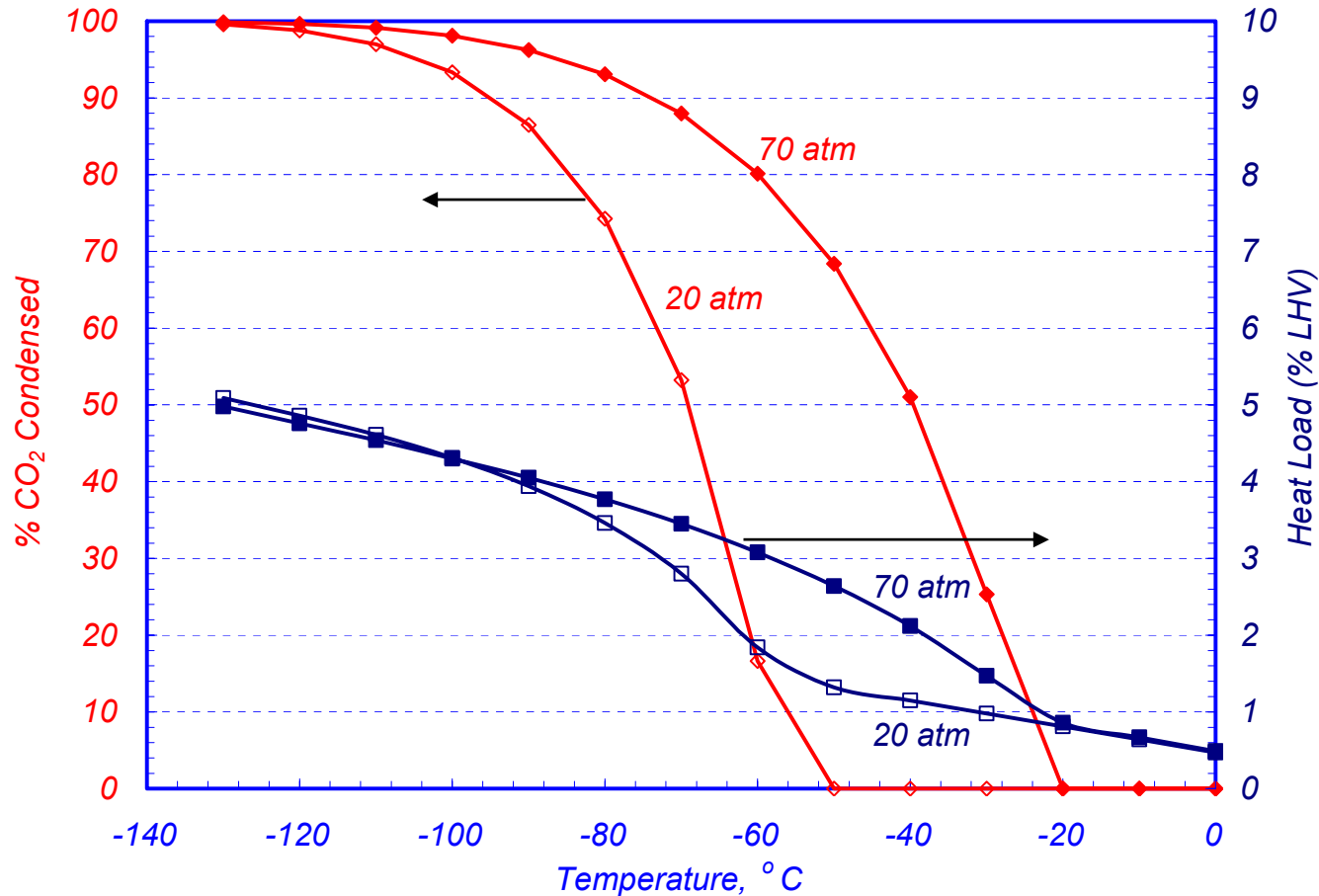
Approach

- **Study thermodynamic equilibria**
 - Effects of temperature, pressure, and steam-to-C ratio
- **Evaluate system options with respect to efficiency and cost**
 - Compare high pressure reforming, compressing reformat, compressing high purity hydrogen
 - Evaluate purification options with high pressure reformat
- **Establish reforming kinetics through experiments and models**

Hydrogen compression represents a significant power loss



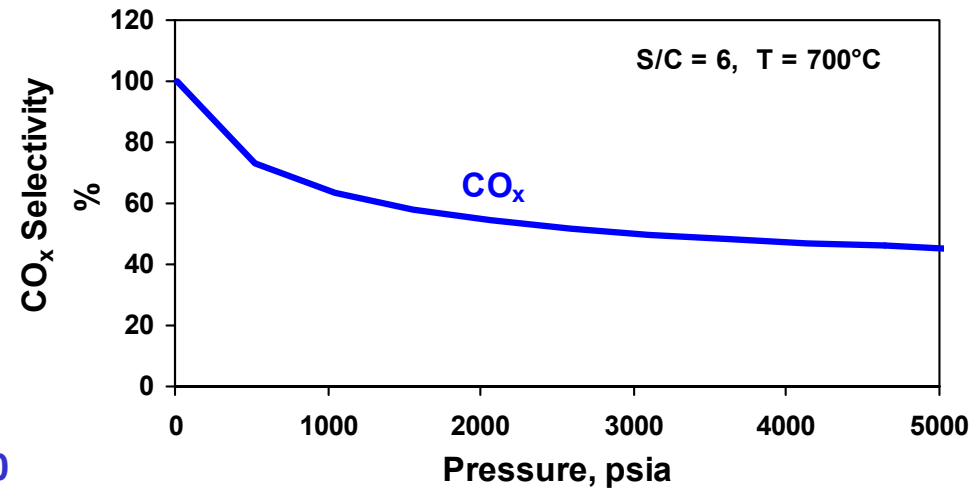
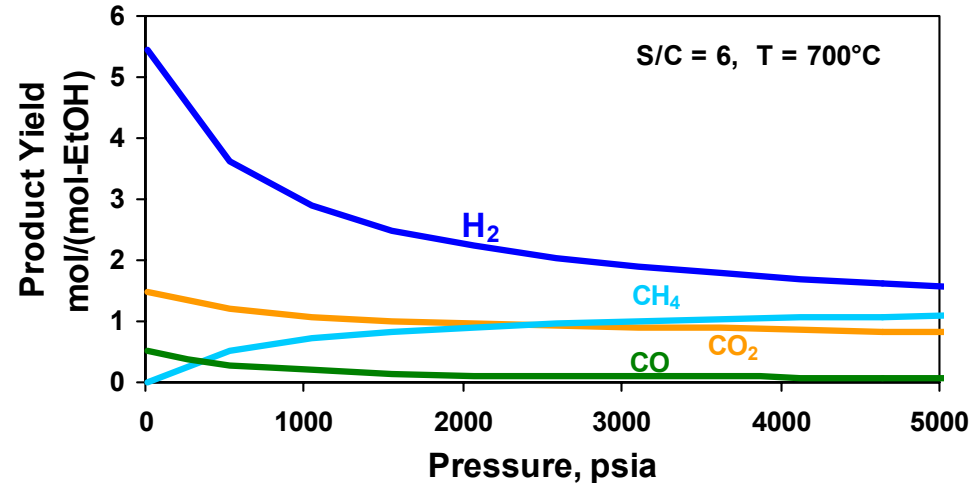
At 70 atm (1050 psi), CO₂ can be condensed out at -130°C



The energy needed to cool to -130°C represents 5% of the fuel's (ethanol) lower heating value.

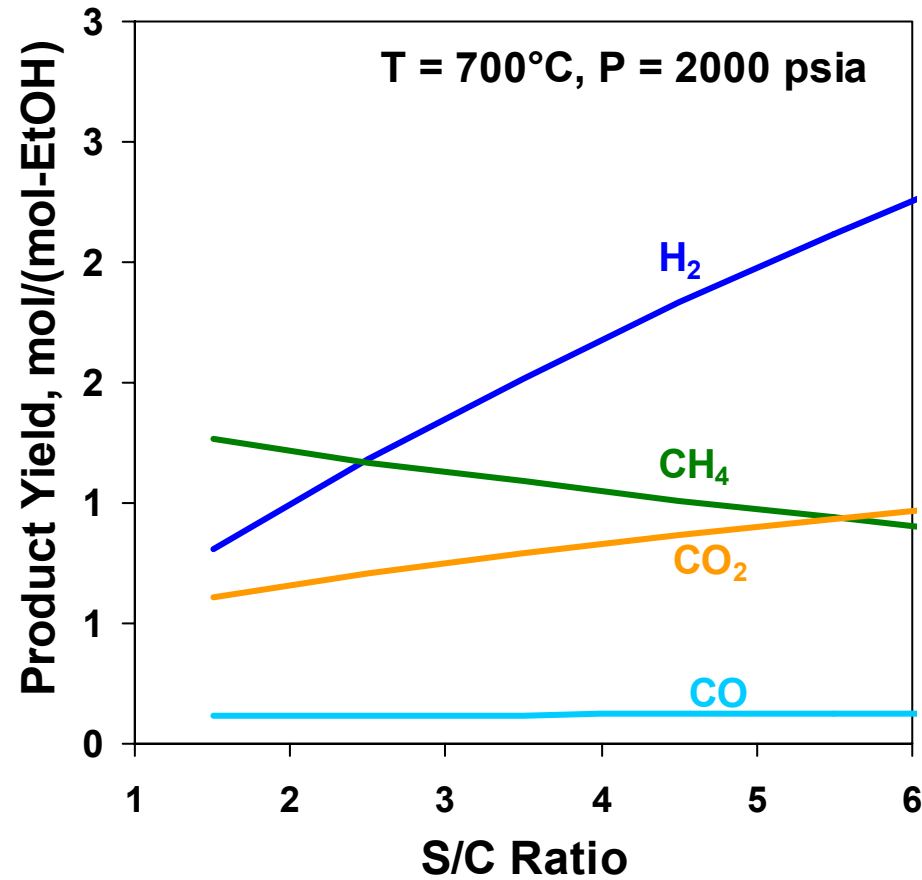
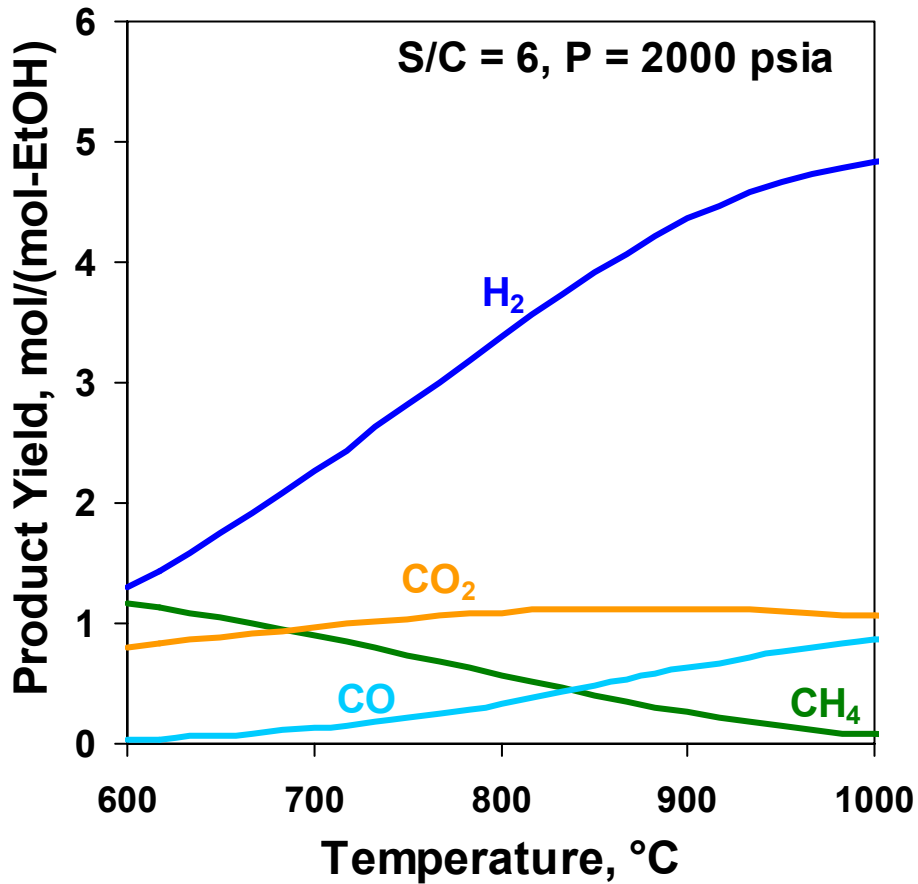
Reforming at high pressure favors more methane, less hydrogen yields at thermodynamic equilibrium

- Tendency to form carbonaceous deposits (coke) increases at higher pressures
- Coking tendency can be reduced with excess steam and/or higher temperature

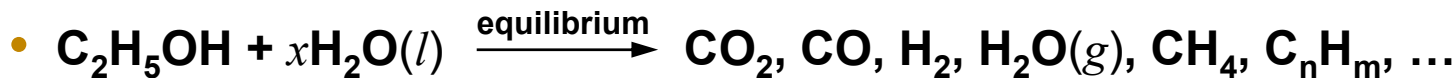


$$\text{CO}_x \text{ Selectivity, \%} = \frac{\text{Mols of CO+CO}_2 \text{ Produced}}{\text{G-Atoms of C in Feed}} \cdot 100$$

Higher temperature and excess steam favor equilibrium hydrogen yields

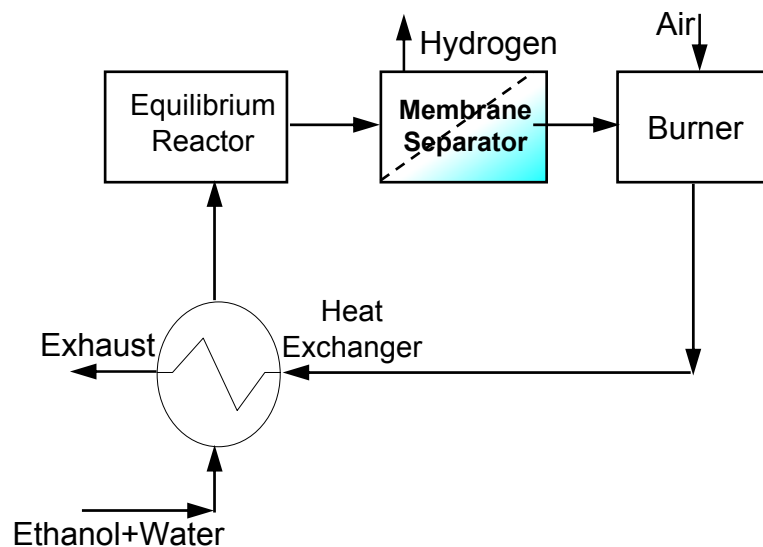
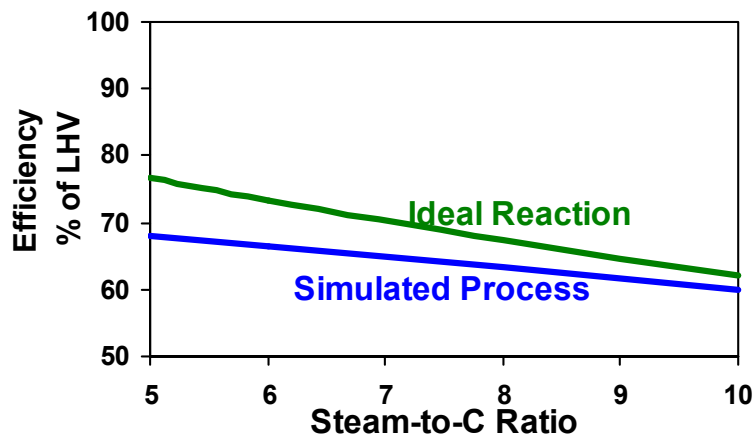


Simulated process efficiencies approach 70% at a steam-to-carbon ratio of 5



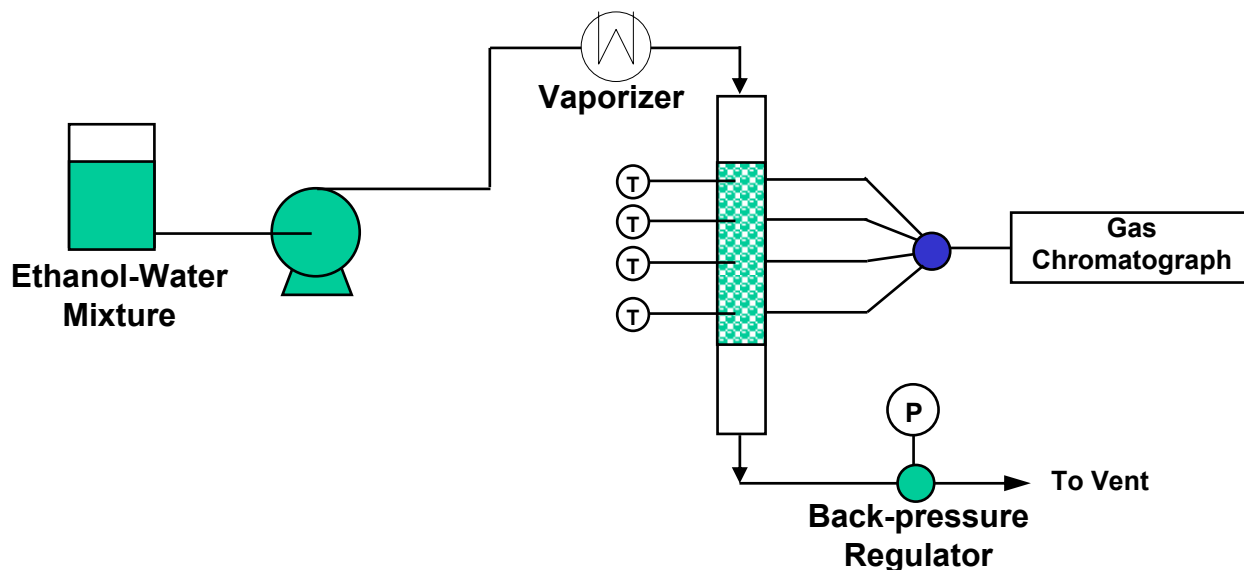
- Chemcad simulated process based on
 - steam-reformer at equilibrium
 - hydrogen separation with membrane
 - 90% hydrogen recovery
 - combustion of raffinate to generate heat
 - heat exchange to reformer feeds
 - exhaust at 200°C

- Efficiency decreases with increasing S/C



Experiments will help define suitable operating conditions

- Effects of temperature, pressure, space velocity
- Kinetic parameters, reaction pathways



Ethanol tends to decompose to carbon oxides, methane, and hydrogen in the preheating zone above the catalyst

Pressure, psig	15
Temperature, °C	525
H₂O/C in Feed	6
C₂H₅OH Conversion, %	9.7
H₂ (mol/mol EtOH)	0.206
CO (mol/mol EtOH)	0.015
CO₂ (mol/mol EtOH)	0.054
CH₄ (mol/mol EtOH)	0.0097

10% of the ethanol decomposed at 1 atm and 525°C

Preliminary experiments are confirming anticipated trends

Hydrogen concentrations in reformat gas increases with temperature and decreases with pressure.

Pressure, psig	15	1000	1000
Temperature, °C	530	530	700
H₂O/C in Feed	6	6	6
H₂ (%-dry)	71.2	45.2	53.1
CO (%-dry)	6.3	8.5	9.4
CO₂ (%-dry)	18.4	16.6	17.7
CH₄ (%-dry)	4.1	29.7	19.8

Gas composition analysis methods and equipment for condensable components are being readied

Hydrogen Safety

- **The most significant hazard of these experiments is the combination of high temperature and high pressure reactor processing combustible gases**

- **The hazard has been addressed by**
 - Appropriate design (size and materials of construction) of experimental apparatus
 - Locating apparatus within a vacuum-frame hood

Interactions and collaborations

- **Catalysts developed by Sud Chemie**
 - PNNL offered alternative formulation
- **Membrane developers expected to provide samples for testing**
 - Synkera

Accomplishments

- **Thermodynamic equilibrium analysis has been done**
- **Simple process models are being evaluated**
 - System models will explore efficient and cost-effective pathways
- **An experimental apparatus has been designed and fabricated to evaluate reaction data**
 - Apparatus has been safety approved
 - Experiments have been initiated to establish kinetic parameters

Future Work

- **System modeling will identify suitable processes**
 - Compare separation options (operation/process, and location), such as for example,
 - *high pressure reforming followed by hydrogen separation vs.*
 - *compressing hydrogen purified after low pressure reforming*
 - Assess CO₂ sequestration options
- **High temperature membranes will be evaluated**
- **Membrane reactor will be designed and tested**

Publications/Presentations

- **Abstract submitted to 2005 Fuel Cell Seminar**