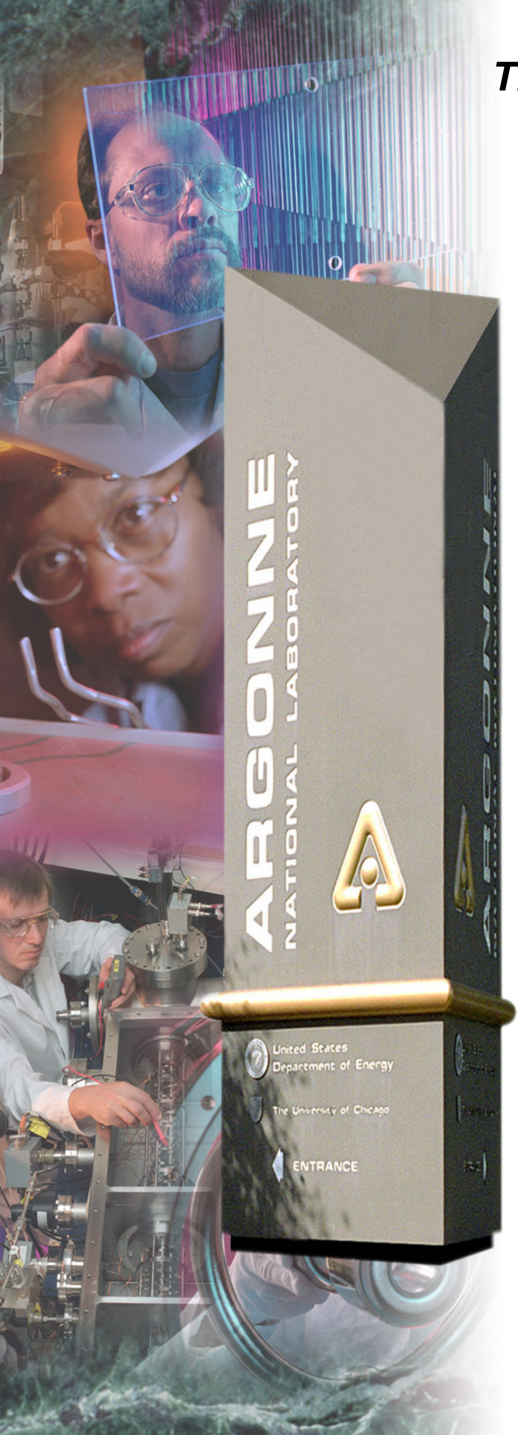

High Pressure Distributed Ethanol Reforming

2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

Arlington, VA, May 23-26, 2005

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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**

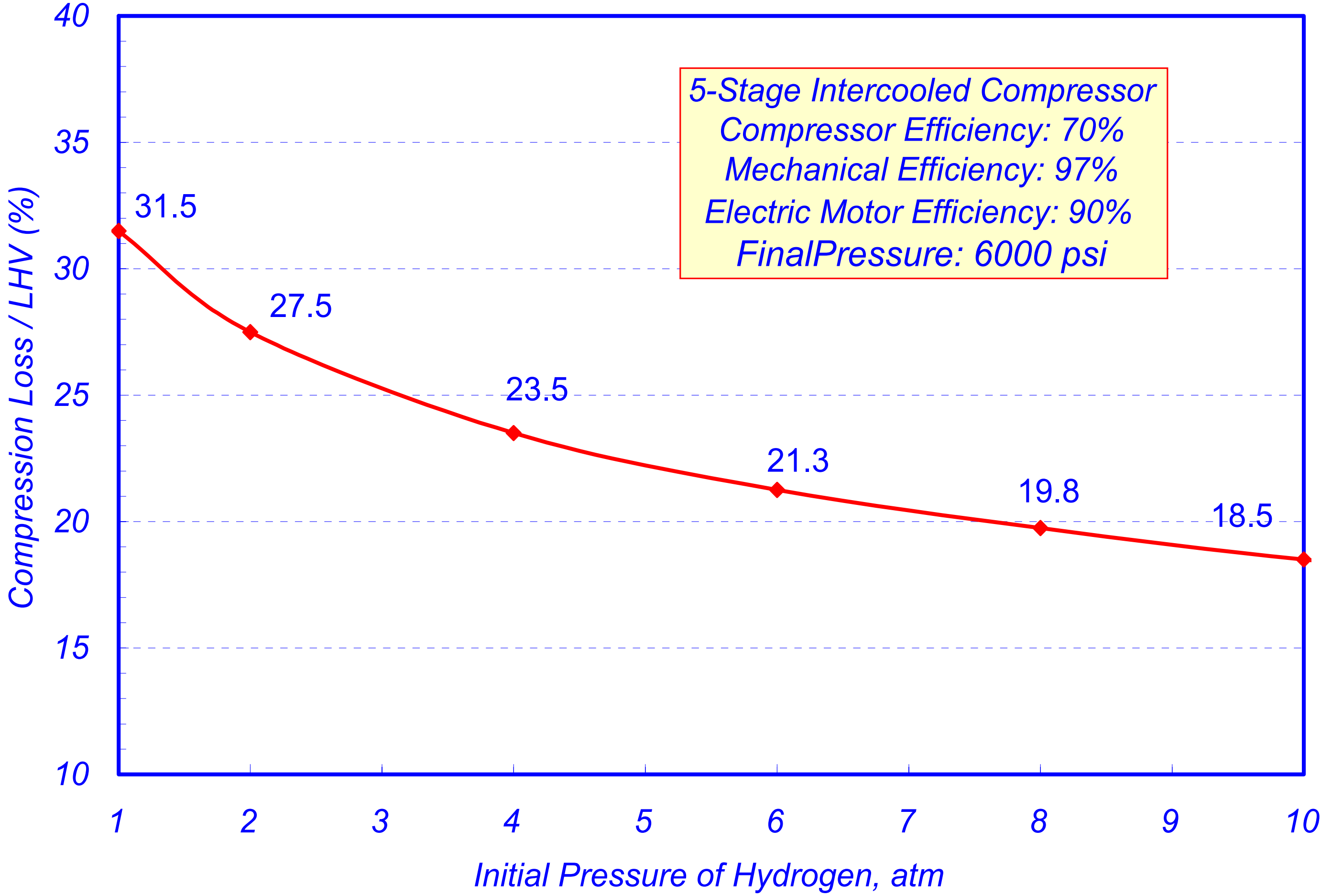
Decision Factors

- **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**

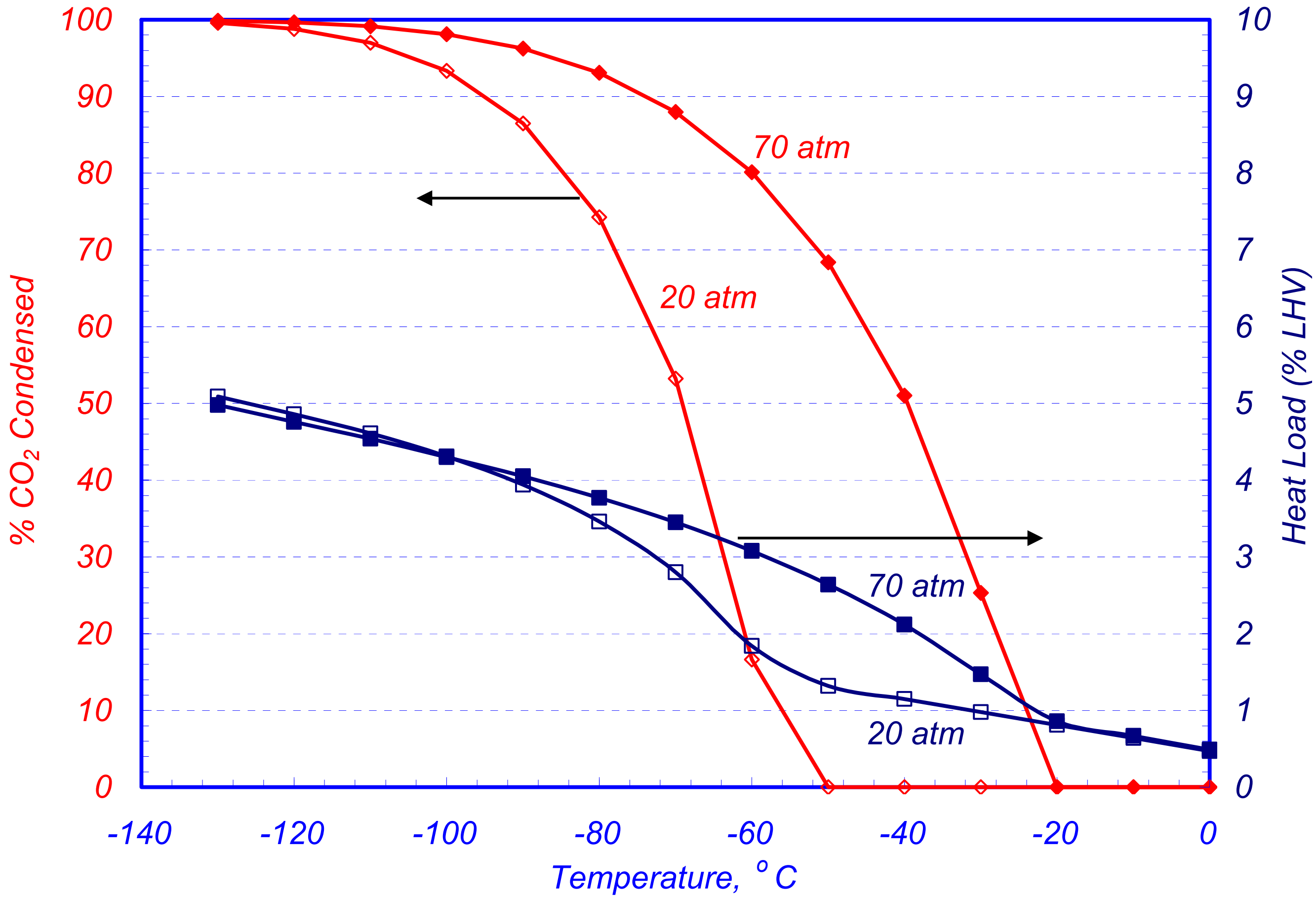
Approach

- **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 reformate, compressing high purity hydrogen
  - Evaluate purification options with high pressure reformate
- **Establish reforming kinetics through experiments and models**

Hydrogen compression represents a significant power loss



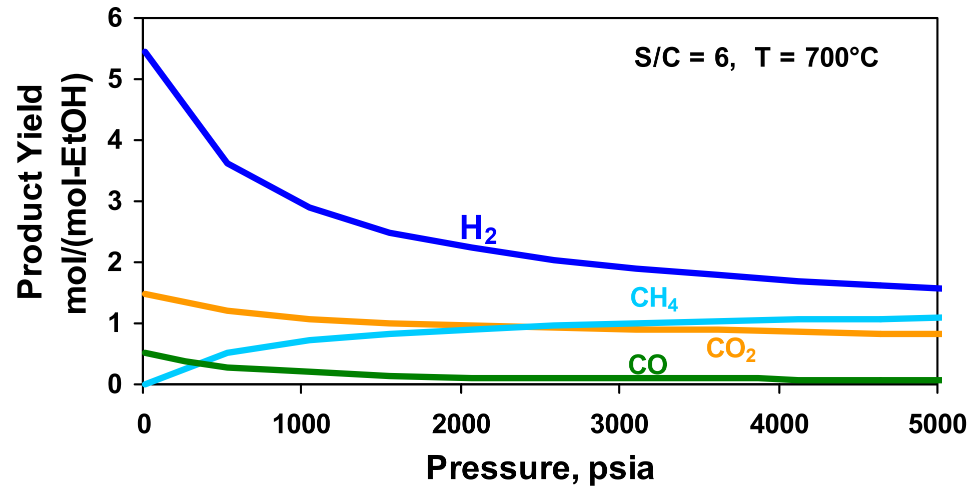
At 70 atm (1050 psi), CO_2 can be condensed out at -130°C

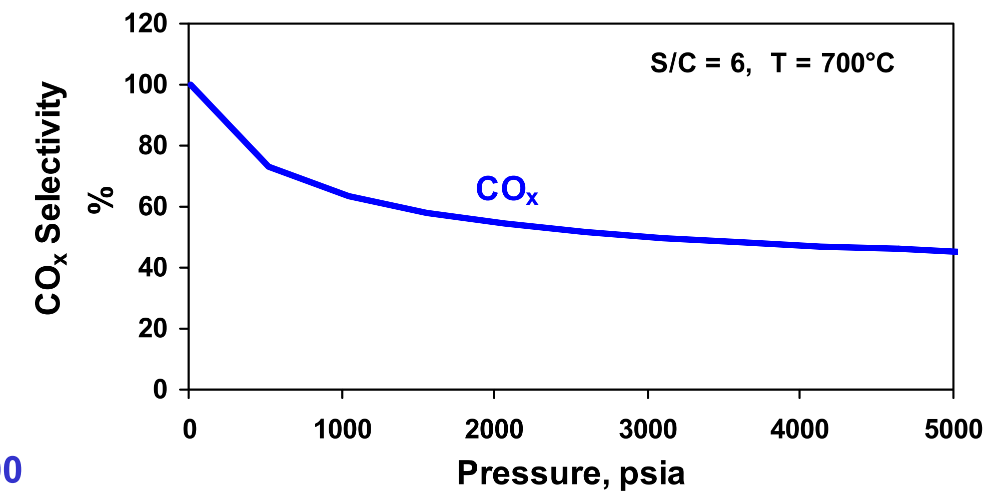


The energy needed to cool to -130°C represents 5% of the fuel's (ethanol) lower heating value.

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

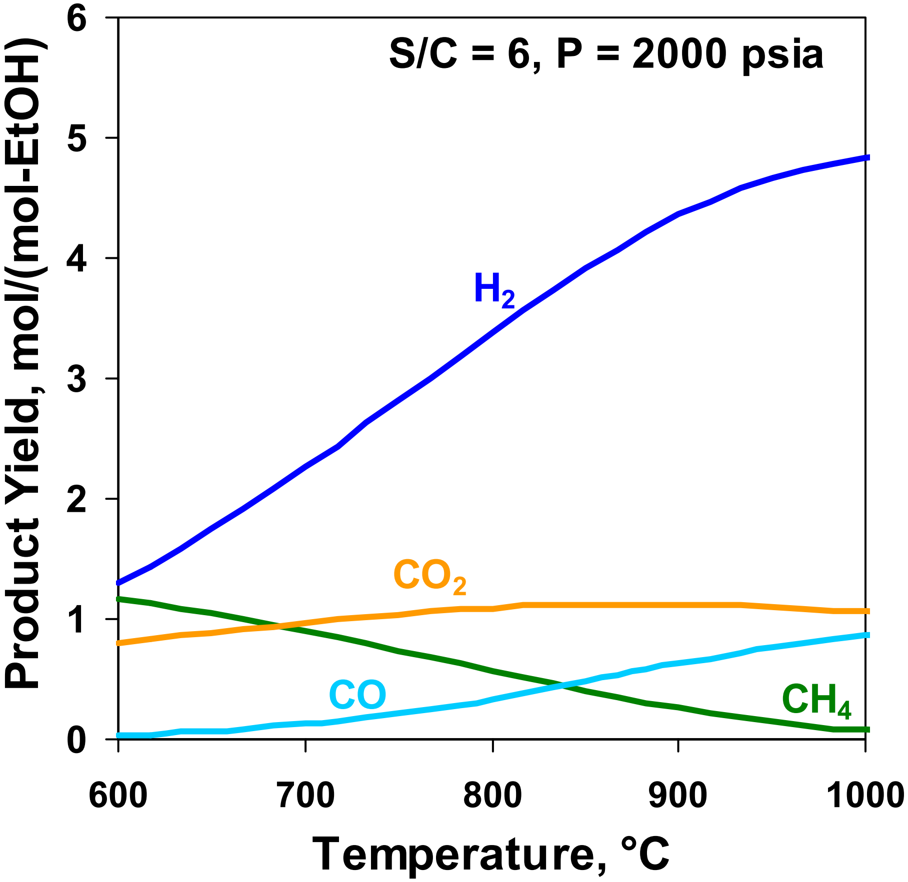
- **Tendency to form carbonaceous deposits (coke) increases at higher pressures**
- **Coking tendency can be reduced with excess steam and/or higher temperature**

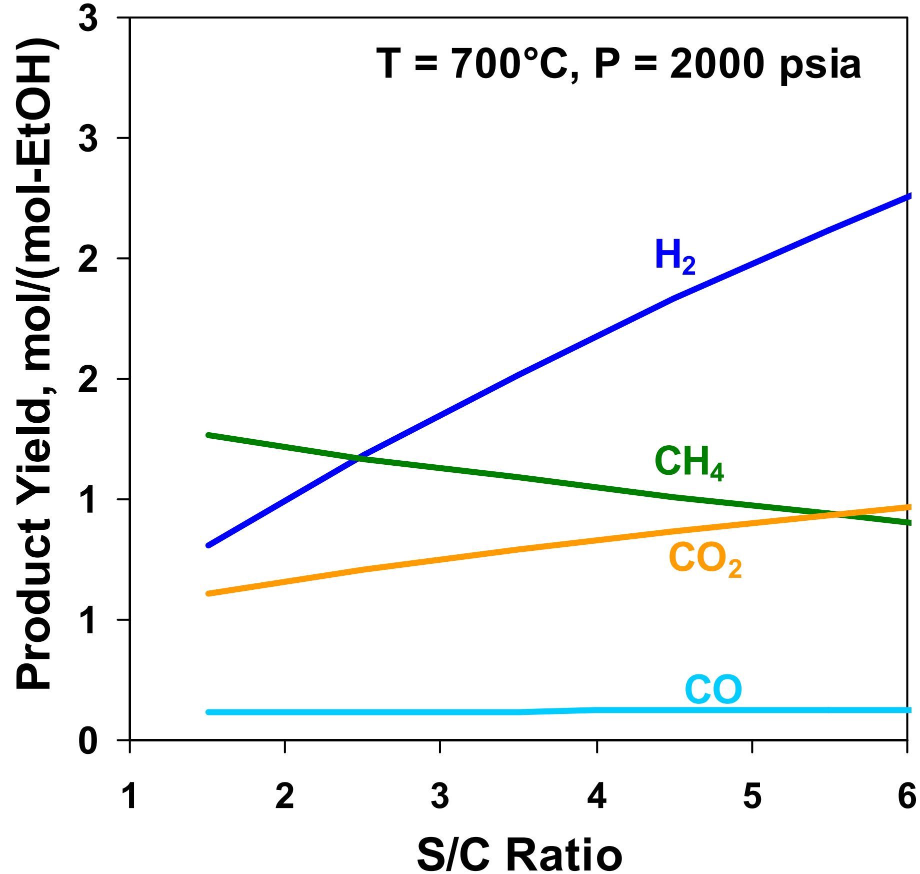




$$CO_x \text{ Selectivity, \%} = \frac{\text{Mols of } CO + CO_2 \text{ Produced}}{\text{G-Atoms of C in Feed}} \cdot 100$$

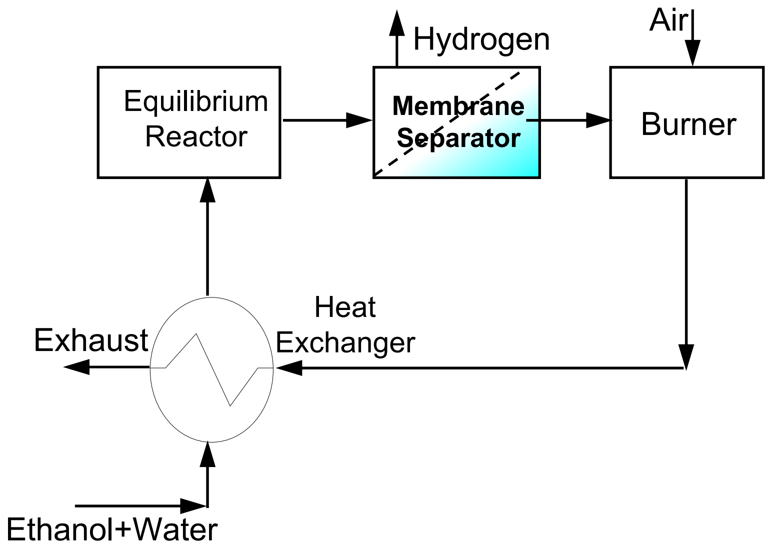
Higher temperature and excess steam favor equilibrium hydrogen yields

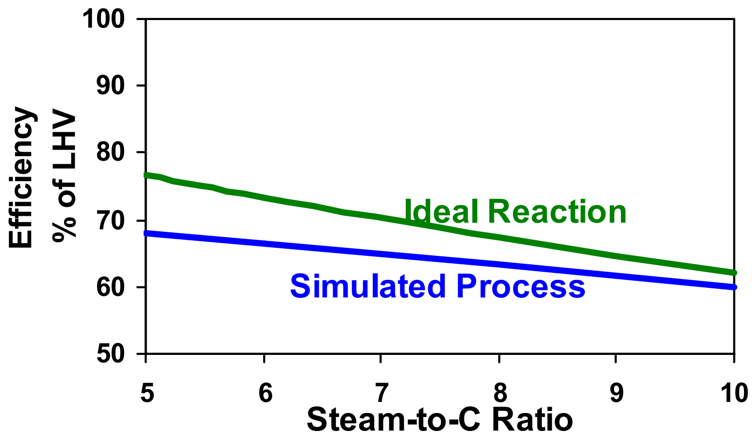




Simulated process efficiencies approach 70% at a steam-to-carbon ratio of 5

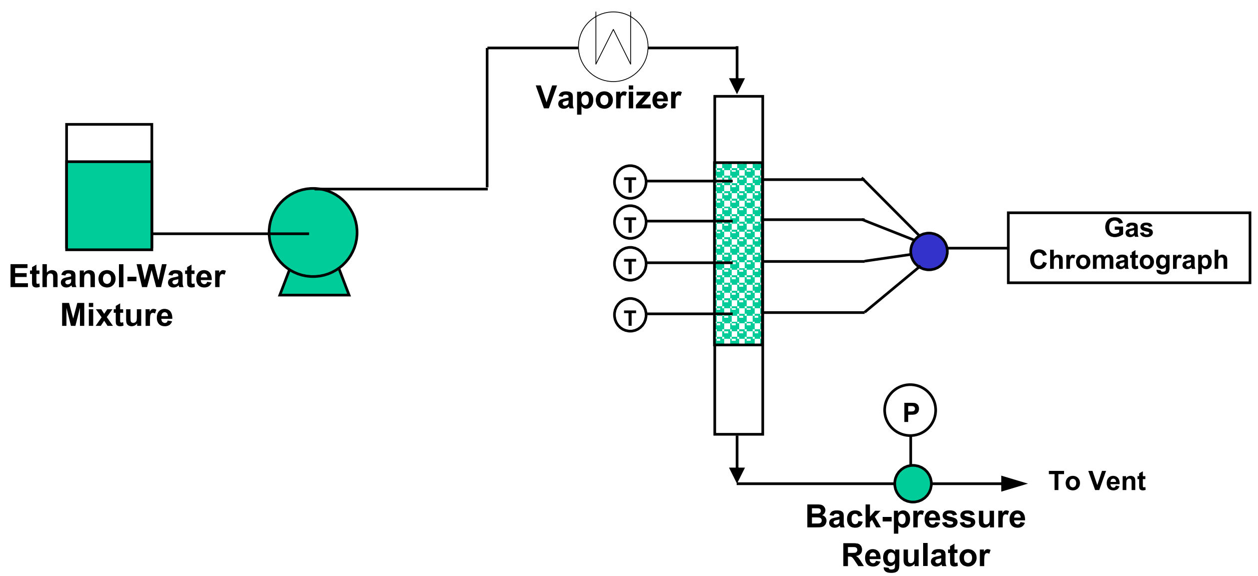
- **$C_2H_5OH + xH_2O(l) \xrightarrow{\text{equilibrium}} CO_2, CO, H_2, H_2O(g), CH_4, C_nH_m, \ldots$**
- **Chemcad simulated process based on**
  - steam-reformer at equilibrium
  - hydrogen separation with membrane
    - *90% hydrogen recovery*
  - combustion of raffinate to generate heat
  - heat 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**
H_2O/C in Feed	**6**
C_2H_5OH Conversion, %	**9.7**
H_2 (mol/mol EtOH)	**0.206**
CO (mol/mol EtOH)	**0.015**
CO_2 (mol/mol EtOH)	**0.054**
CH_4 (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 reformate gas increases with temperature and decreases with pressure.

Pressure, psig	15	1000	1000
Temperature, °C	530	530	700
H_2O/C in Feed	6	6	6
H_2 (%-dry)	71.2	45.2	53.1
CO (%-dry)	6.3	8.5	9.4
CO_2 (%-dry)	18.4	16.6	17.7
CH_4 (%-dry)	4.1	29.7	19.8

Gas composition analysis methods and equipment for condensible 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 CO_2 sequestration options
- **High temperature membranes will be evaluated**
- **Membrane reactor will be designed and tested**

Publications/Presentations

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