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High Pressure Ethanol Reforming for Distributed H_2 Production

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Bio-Derived Liquids to Hydrogen Distributed Reforming Working Group Kickoff Meeting

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U.S. Department of Energy

UChicago Argonne LLC

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Background

- Compressed hydrogen is needed for storage and delivery
  - Compressed gas tanks at 5,000-10,000 psig
  - Metal hydride (150-450 psig)

- Pressurized reformate is needed for many purification and enrichment paths
  - Membrane separation
    - *Hydrogen permeation, e.g., Pd-membrane*
    - *By-product removal, e.g., COx (CO & CO_2)*
  - Pressure Swing Adsorption (PSA)

- Gas compression is energy intensive

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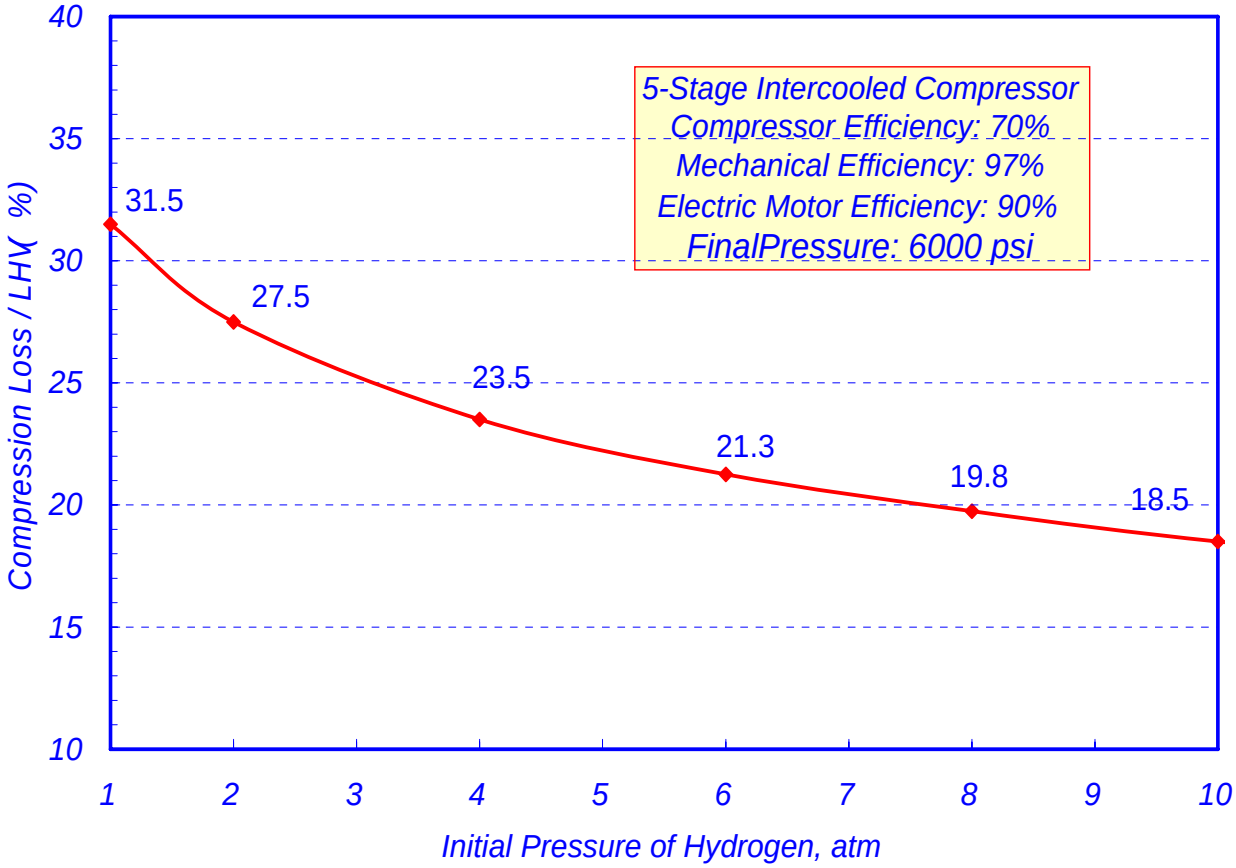
The energy required to compress hydrogen to 6,000 psig can be as high as 31% of the LHV of hydrogen



Electricity Generation Efficiency = 40%

- Starting with a pressurized hydrogen / reformate stream lessens the energy required by the compressor

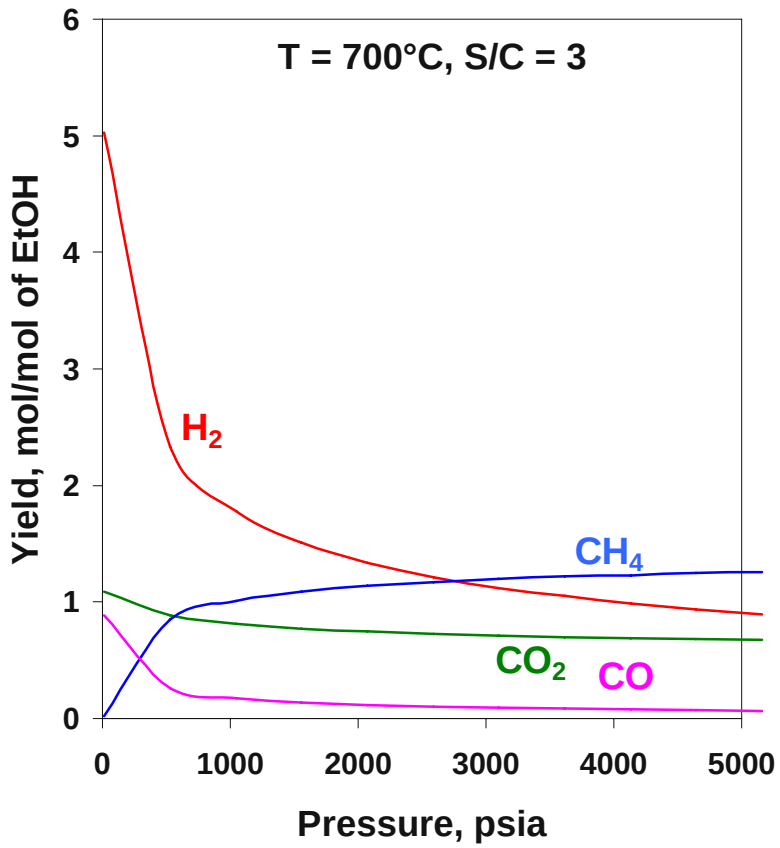
Note: Hydrogen from SMR-PSA processes may be available at 200 psig

(SMR- Steam Methane Reforming; PSA – Pressure Swing Adsorption)

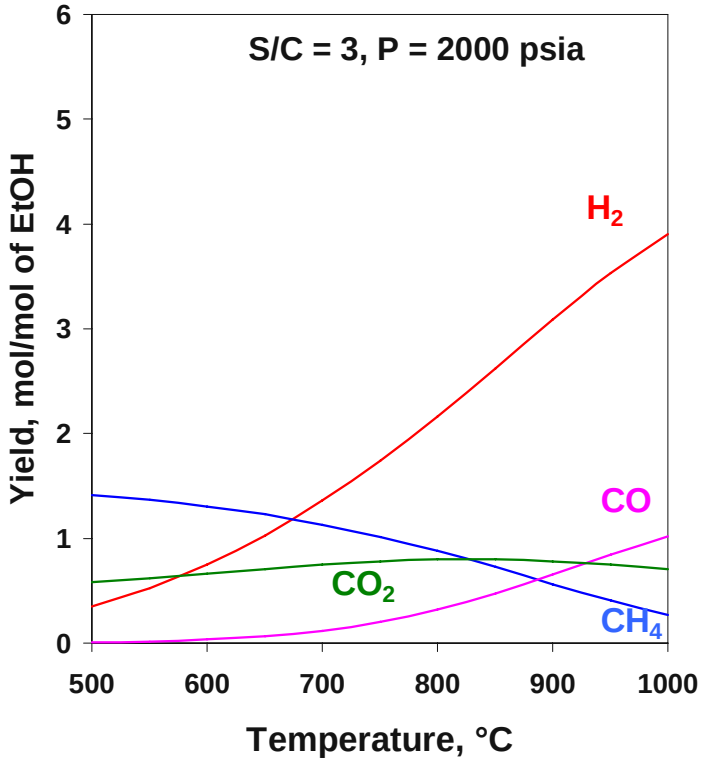
Steam reforming of liquid fuels generates a pressurized reformate with little energy penalty

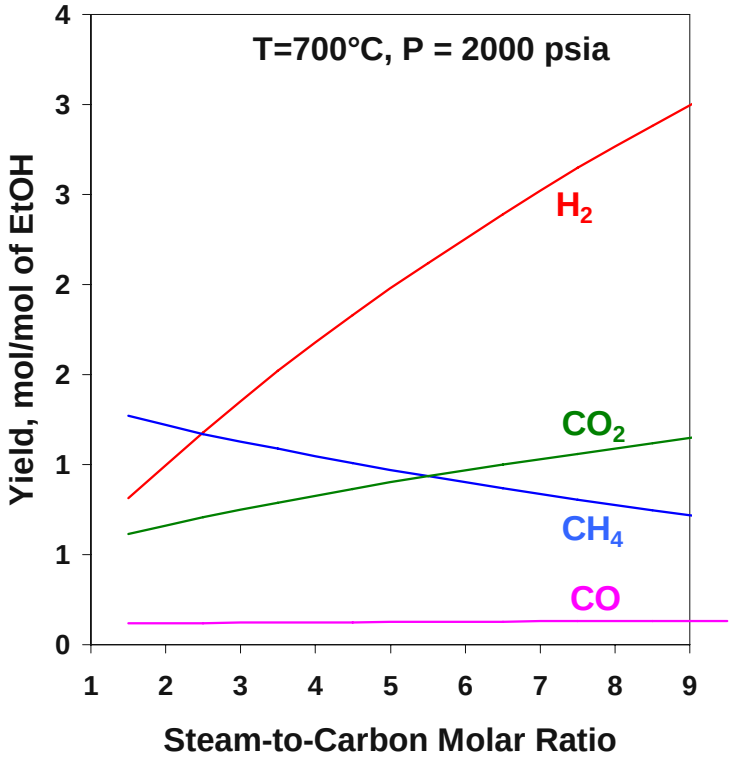
- Injecting liquid (ethanol + water) feeds into a high pressure reactor requires little energy
- Hydrated ethanol is less expensive than fuel-grade ethanol
  - Available upstream before water separation (distillation, adsorption, membrane)

- Steam reforming of ethanol at elevated pressure does not favor hydrogen yield, however
  - Equilibrium predicts increasing methane yields with increasing pressures



The negative effect of pressure on hydrogen yield can be offset with higher temperature and steam-to-carbon ratio





- High pressure-temperature combinations add to hardware cost
- High steam-to-carbon ratio reduces overall process efficiency

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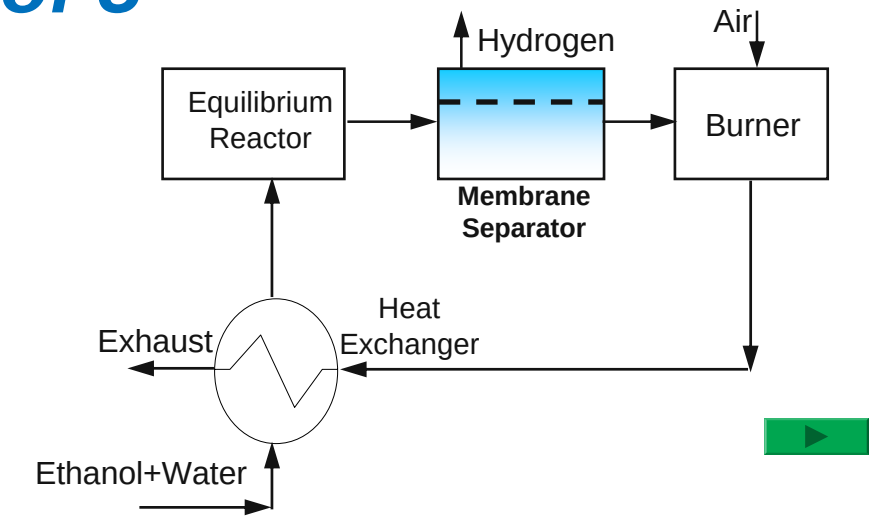
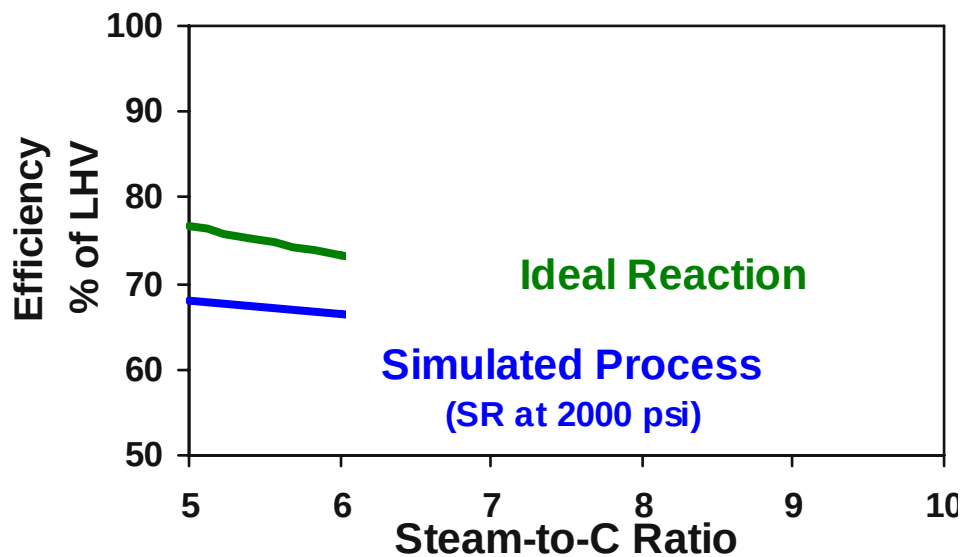
Simulated process efficiencies approach 70% at a steam-to-carbon ratio of 5

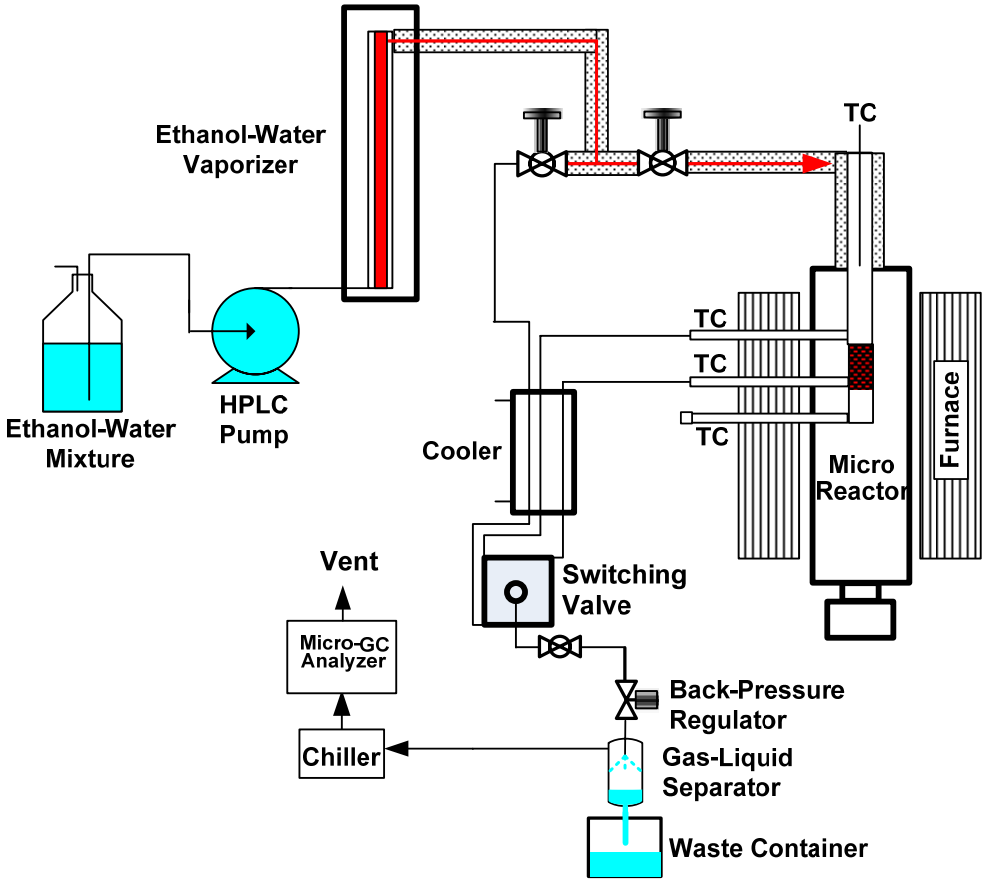
- $C_2H_5OH + xH_2O(l) \xrightarrow{\text{equilibrium}}$
  CO_2, CO, H_2, $H_2O(g)$, CH_4, C_nH_m, …
- Chemcad simulated process based on
  - steam-reformer at equilibrium
  - hydrogen separation with membrane
    - *90% hydrogen recovery*
  - combustion of raffinate to generate heat
  - heat exchange to reformer feeds
  - exhaust at 200°C
- Efficiency decreases with increasing S/C
- Various alternative and more detailed system solutions need to be evaluated





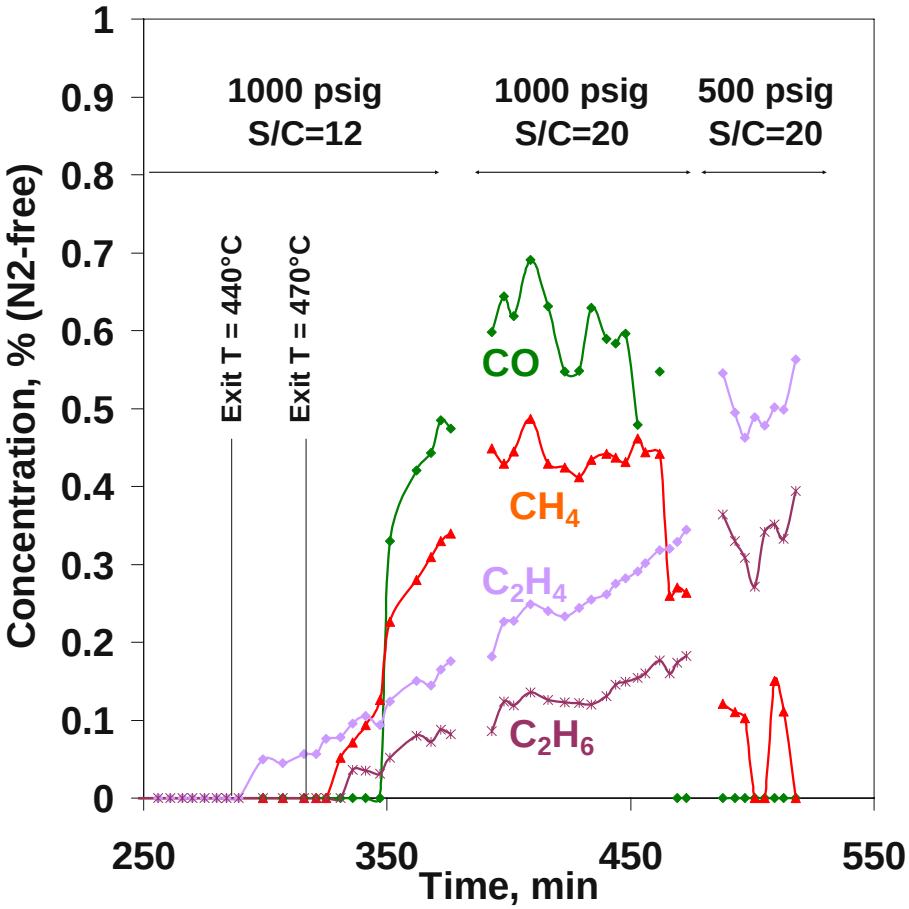
A micro-reactor apparatus is being used to generate yield data

- Rated for 1,000 psi, 900°C
- 63.5-mm (0.25-in) ID reactor tube
- 4 wt% Rh/ La-Al_2O_3
- Powder, 150-250 μm
- 0.35 g of catalyst
- 20-mm long-catalyst bed



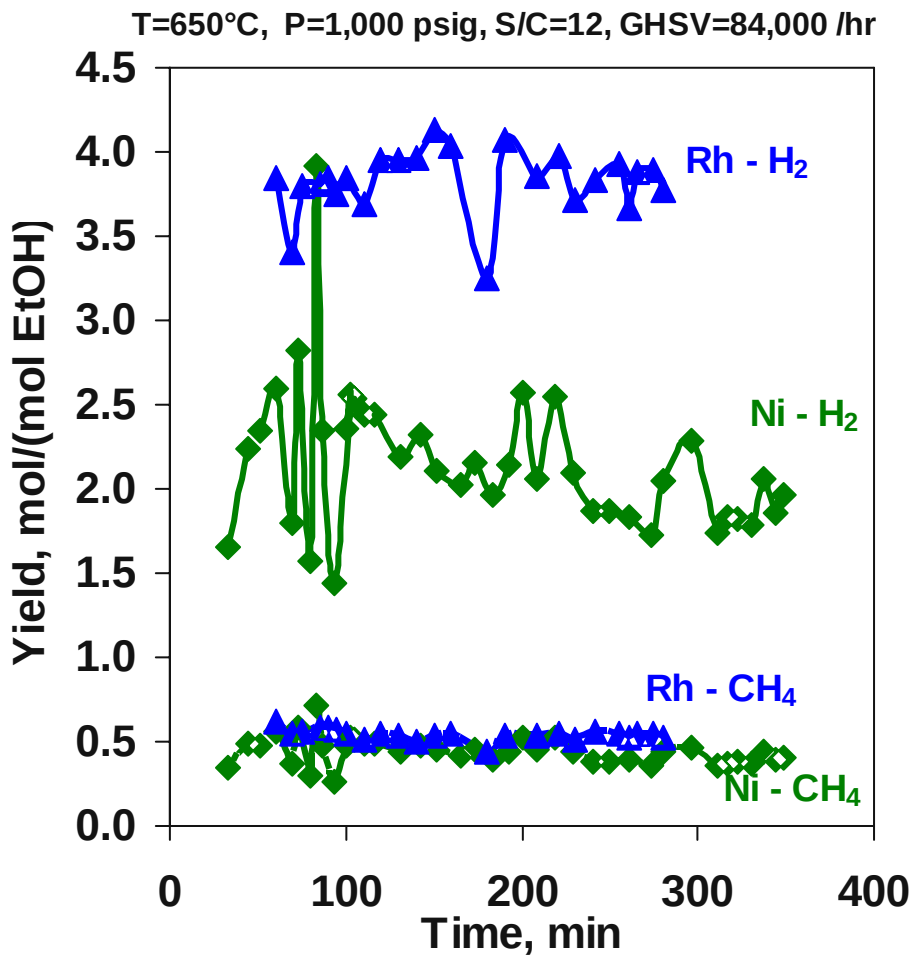
Vaporizer tests indicate the ethanol starts decomposition above 440°C

- At 1000 psig, S/C = 12-20
  - BP = ~310°C
- At 500 psig, S/C = 12-20
  - BP = ~255°C



The hydrogen yield with the nickel catalyst decreased with time, indicating deactivation of the base metal catalyst

- The nickel catalyst deactivated with time
  - Bed pressure drop increased
  - Carbonaceous deposits were observed in the reactor
- The reactor was re-packed with a rhodium catalyst
  - 4 wt% Rh / La-Al_2O_3
- The rhodium catalyst performed better
  - Higher hydrogen yield
  - Maintained activity



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The nickel catalyst yielded a considerable fraction of condensable products

- The Ni catalyst yielded more undesirable hydrocarbons
  - Mass balance accounted for 76% of the carbon
    - *Condensable products and carbon deposits could not be factored in*
- The Rh catalyst yielded more hydrogen and COx, the desired product species

Catalyst	**Ni**	**Rh**
Temperature, °C	650	650
Pressure, psig	1000	1000
GHSV, /hr	83,000	83,000
Steam-to-Carbon	12	12
Product Yield		
H_2, mol/(mol EtOH)	2.4	3.9
CO, mol/(mol EtOH)	0.2	0.1
CH_4, mol/(mol EtOH)	0.5	0.6
CO_2, mol/(mol EtOH)	0.8	1.4
C_2H_4, mol/(mol EtOH)	0.006	ND
C_2H_6, mol/(mol EtOH)	0.029	ND
Carbon Balance, %	76	101

ND – not detected

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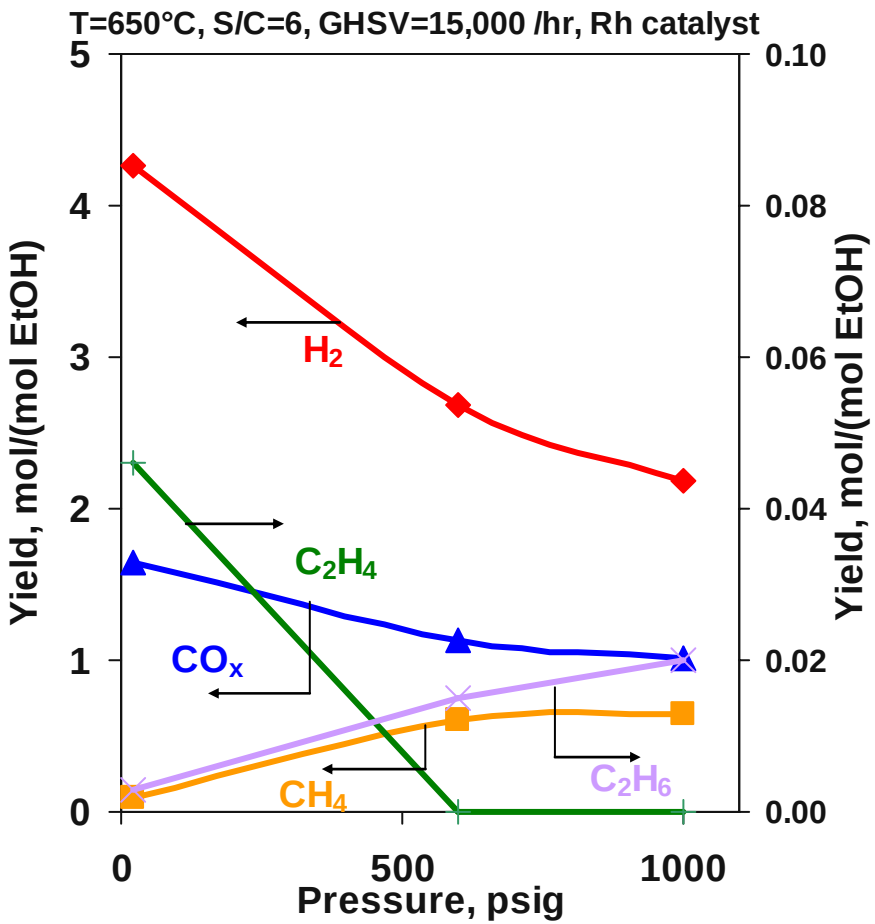
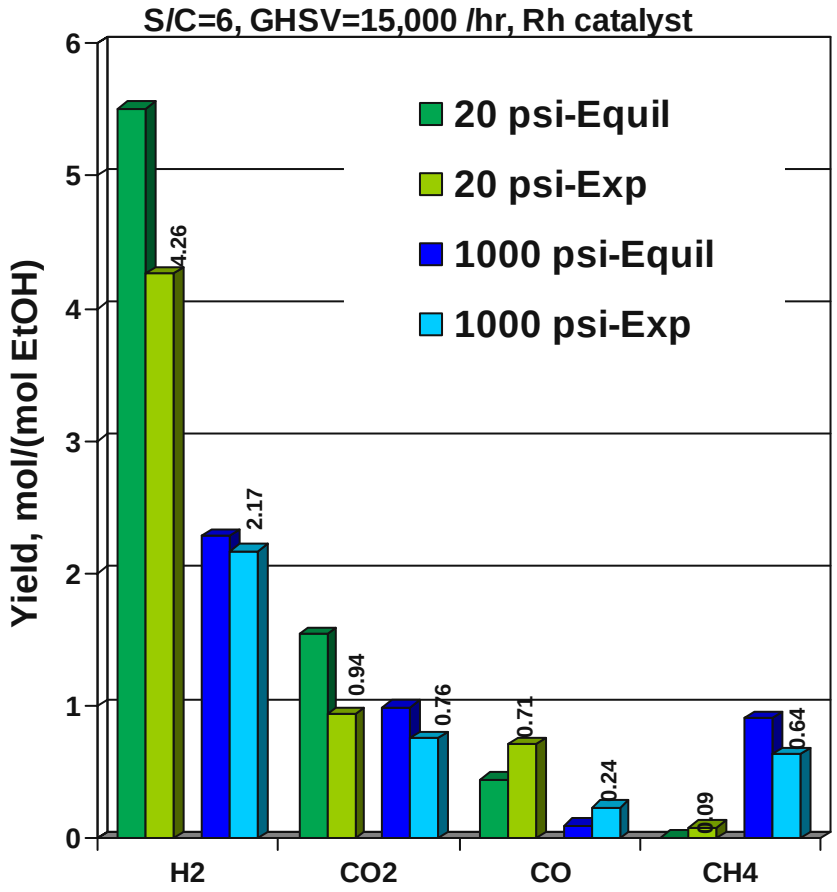
Experimental data show multiple hydrocarbon species in the product stream

- With increasing pressure
  - Hydrogen yield decreases
  - Methane yield increases
  - Ethylene is hydrogenated to produce ethane



The experimental hydrogen yield approaches equilibrium predictions at 1000 psi

- At a constant GHSV, equilibrium is approached at higher pressures
  - Faster reaction rates



The product species can be explained through a combination of reactions

1. Ethanol Dehydrogenation : $C_2H_5OH = CH_3CHO + H_2$
2. Ethanol Dehydration : $C_2H_5OH = C_2H_4 + H_2O$
3. Dissociative Ads. of Water : $C_2H_5OH + H_2O = CH_3COOH + 2H_2$
4. Acetaldehyde Dissociation : $CH_3CHO = CO + CH_4$
5. Ethanation : $C_2H_4 + H_2 = C_2H_6$
6. Dissociation of Acetic Acid : $CH_3COOH = CH_4 + CO_2$
7. Methane Steam Reforming : $CH_4 + H_2O = CO + 3H_2$
8. Water Gas Shift : $CO + H_2O = CO_2 + H_2$

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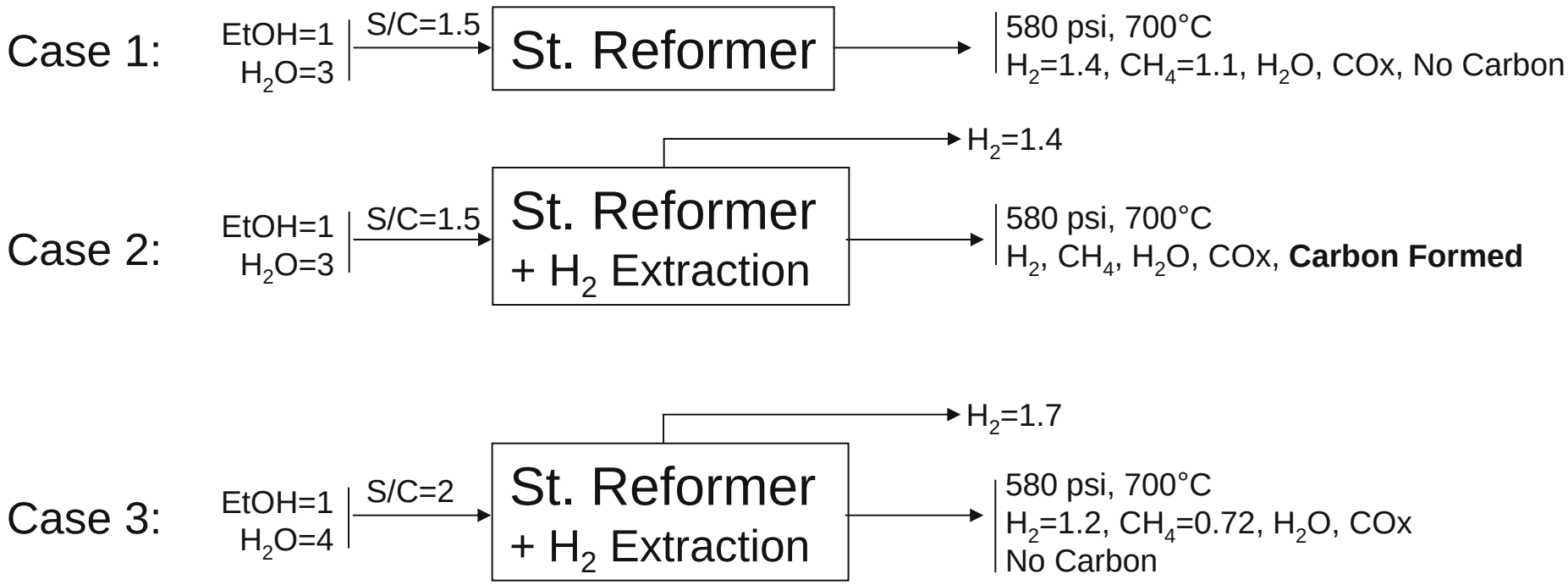
FY07 work directed at yield and kinetics of pressurized reforming

- Experimental yields and kinetics are being determined
- Using a micro-reactor with a Pd-membrane separator
- Hydrogen extraction exacerbates coking



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How worthwhile is the pressurized steam reforming of bio-liquids?

- We are currently seeking an answer for ethanol
  - Experimental yields and kinetics are being determined
    - *Using a micro-reactor with a Pd-membrane separator*
  - Reactor models will help extract kinetic information
  - Supported by new generation of catalysts
    - *Improve durability and reduce cost*

- System model and analysis
  - Simple membrane reactor concept
  - Alternative purification / enrichment options
  - Go / NoGo determination on pressurized reforming with ethanol

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