Analysis of Ethanol Reforming System Configurations

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10 June 2008

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Overview

Timeline

• Contract Period:
  • May 2007 to September 2008
  • 75% complete

Budget

• Total project funding: $150k
• Funding for FY 2007: $150k

Barriers

• Distributed H$_2$ Production from Renewable Liquids:
  • A: Reformer Capital Costs
  • B: Reformer Manufacturing

DOE Cost Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>2006</th>
<th>2012</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Efficiency</td>
<td>70%</td>
<td>72%</td>
<td>65-75%</td>
</tr>
<tr>
<td>Prod. Unit Capital Cost (uninstalled)</td>
<td>$1.4M</td>
<td>$1.0M</td>
<td>$600k</td>
</tr>
<tr>
<td>Total H$_2$ Cost</td>
<td>$4.40/kg</td>
<td>$3.80/kg</td>
<td>&lt;$3.00/kg</td>
</tr>
</tbody>
</table>

Collaborations

• Interaction/Data-Transfer between PNL, OSU and multiple DOE contractors (H$_2$Gen, Pall Corp., Virent)
Objectives

• Assess cost of H₂ from bio-derived liquids
  • Distributed forecourt scale systems: 1500kgH₂/day
  • Emphasis on Ethanol
  • Both “conventional” and “advanced” systems

• Reflect Recent Research
  • Interact with DOE Labs and Contractors
  • Researchers supply catalysts composition, performance, potential configurations
  • Ground in reality but forward looking

• Output of work is:
  • System/Configuration Definition
  • Performance specification & optimization
  • Capital cost estimation
  • Projected hydrogen $/kg
Methodology

- **Catalyst/Reforming Reactions**
  (from Researchers, Industry, thermodynamics)

  - **System Configuration**

  - **Performance Assessment & Sizing**
    (Efficiency, flow rates, temp., pressures)
    (Hysys and modeling)

  - **Mechanical Configuration**

    - **Bill of Materials**

      - **Capital Cost Estimates**
        (DFMA-style analysis, scaling factors)

  - **Separations Technology**
    (from Researchers, Industry)

  - **Feedstock Consumption Data**

    - **H2A Model**
      to determine H₂ $/kg
Ethanol Reforming Hierarchy

Reforming Options

Gas Phase

Steam Reforming
- High Temp >550°C
- “2-Step” Ref. (ie. methanation followed by SMR)
  - H₂Gen
  - With WGS
- Med. Temp 300-550°C
  - “1-Step” Ref.
    - PNNL
    - OSU
    - With or Without WGS

Liquid Phase
- Virent (glycerol/sugars feedstock)

Partial Oxidation
- GE (SCPO)
- With WGS
- MRT/Linde (fluidized bed)
- With WGS

“2-Step” Ref.
- Methanation followed by SMR

H₂ Purification

H₂Gen

PSA

Separate Membrane Section

Membrane/WGS

Membrane Reactor
Multiple Configurations Examined

- Many configurations/variations are possible
- Arrows mark focus for today’s presentation

<table>
<thead>
<tr>
<th>Config. Number</th>
<th>Fuel</th>
<th>Temperature</th>
<th>Key Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NG</td>
<td>High Temp. (900°C)</td>
<td>SMR → WGS → PSA</td>
</tr>
<tr>
<td>2</td>
<td>NG</td>
<td>Med. Temp. (550°C)</td>
<td>Integrated Reformer/WGS/Membrane Separator</td>
</tr>
<tr>
<td>6</td>
<td>NG</td>
<td>High Temp. (900°C)</td>
<td>Pre-Reformer → SMR → WGS → PSA</td>
</tr>
<tr>
<td>11</td>
<td>Ethanol</td>
<td>High Temp. (900°C)</td>
<td>Pre-Reformer → SMR → WGS → Membrane Separator</td>
</tr>
<tr>
<td>12</td>
<td>Ethanol</td>
<td>High Temp. (900°C)</td>
<td>Pre-Reformer → SMR → Integrated WGS/Membrane Separator</td>
</tr>
<tr>
<td>9</td>
<td>Ethanol</td>
<td>Med. Temp. (550°C)</td>
<td>Reformer (NPM Catalyst) → WGS → PSA</td>
</tr>
<tr>
<td>15</td>
<td>Ethanol</td>
<td>Med. Temp. (550°C)</td>
<td>Reformer (PM Catalyst) → WGS → PSA</td>
</tr>
<tr>
<td>10</td>
<td>Ethanol</td>
<td>Med. Temp. (550°C)</td>
<td>Reformer (NPM Catalyst) → Membrane Separator</td>
</tr>
<tr>
<td>13</td>
<td>Ethanol</td>
<td>Med. Temp. (550°C)</td>
<td>Integrated Reformer/WGS/Membrane Separator</td>
</tr>
</tbody>
</table>
System 06
High Temp. w/ Pre-Reformer & PSA

Capacity: 1,500 kg/day
Ethanol Efficiency: 68.1%
Overall Efficiency: 67.4%
Elec. Load: 0.461 kWe/kg H₂
Pressure: ~20 bar
H₂ Recovery: 75%
Capital Cost: $829,630
System 09
Med. Temp. w/ PSA

Capacity: 1,500 kg/day
Ethanol Efficiency: 67.3%
Overall Efficiency: 66.5%
Elec. Load: 0.607 kWe/kg H₂
Pressure: ~20 bar
H₂ Recovery: 75%
Capital Cost: $672,746
System 10
Med. Temp. w/ Membrane Separator

Capacity: 1,500 kg/day
Ethanol Efficiency: 64.5%
Overall Efficiency: 61.2%
Elec. Load: 2.209 kWe/kg H₂
Pressure: ~20 bar
H₂ Recovery: 90%
Capital Cost: $800,344

Main Components:
- Boiler
- Superheater
- Pre-Reformer
- Reformer
- Reformate-Cooler
- WGS
- Air Preheater
- Condenser
- PSA
- Membrane Separator
- Intercooled H₂ Compressor

Elec. Load: 2.209 kWe/kg H₂
H₂ Recovery: 90%
Capital Cost: $800,344
System 13a
Med. Temp. w/ Intgr. Membrane Tubes

**Capacity:** 1,500 kg/day  
**Ethanol Efficiency:** 69.8%  
**Overall Efficiency:** 67.5%  
**Elec. Load:** 2.064 kWe/kg H₂  
**Pressure:** ~20 bar  
**H₂ Recovery:** 90%  
**Capital Cost:** $711,417
Kinetics Model Used to Determine Bed Sizes

Reforming Reaction:

\[ \text{EtOH Consumption Rate} \quad = C_1 k_0 \exp \left( -\frac{E_A}{RT} \right) \left( P_{C_2H_5OH} \right)^{1.25} \left( P_{H_2O} \right)^{-0.215} \]

where

- \( k_0 = 0.013 \text{ mol/(gcat} \cdot \text{s} \cdot \text{kPa}^{1.07}) \)
- \( E_A = 39.3 \text{ kJ/mol} \)
- \( C_1 = \text{Derating Factor} = 38\%-49\% \)

Representative Data:

<table>
<thead>
<tr>
<th>Precious Metal</th>
<th>Non-Precious Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steam/Ethanol Ratio</strong></td>
<td><strong>Steam/Ethanol Ratio</strong></td>
</tr>
<tr>
<td>PNNL (King)</td>
<td>OSU (Ozkan)</td>
</tr>
<tr>
<td>8:1</td>
<td>10:1</td>
</tr>
<tr>
<td><strong>GHSV</strong></td>
<td><strong>GHSV</strong></td>
</tr>
<tr>
<td>5,786/h for long life</td>
<td>5,000/h</td>
</tr>
<tr>
<td><strong>Ethanol Conversion</strong></td>
<td><strong>Ethanol Conversion</strong></td>
</tr>
<tr>
<td>99%+</td>
<td>99%+</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td>550°C</td>
<td>550°C</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td>2wt%Rh/Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>1%Ni-1%Cu-10%Co/Ca$<em>{0.1}$Ce$</em>{0.9}$O$_{1.9}$</td>
</tr>
</tbody>
</table>

Exit Gas Composition:

- \( \text{H}_2 \) 71.12% 71.50%
- \( \text{CH}_4 \) 4.67% 3.80%
- \( \text{CO} \) 5.38% 4.10%
- \( \text{CO}_2 \) 18.83% 20.60%
- Ethylene 0% 0%
- Ethane 0% 0%


- Derating Factor selected based on PNNL (King et al) and OSU (Ozkan) data.

WGS Reaction:

\[ \text{CO Consumption Rate} \quad = C_2 \exp \left( -\frac{E_A}{RT} \right) [\text{CO}]^1 \]

where

- \( E_A = 121.8 \text{ kJ/mol} \)
DOE Tech. Targets for Dense Metallic Membranes

Based on:
- 20 psi partial pressure difference
- 15 psig permeate minimum total pressure (preferably >50 psig) (assumed to be pure H₂)
- 400°C

**Sievert’s Law**

\[ D = A \cdot \mathcal{P} \cdot (P_{\text{Reformate}}^{0.5} - P_{\text{Permeate}}^{0.5}) \]

where permeability, \[ \mathcal{P} = \frac{a}{e^{\frac{RT}{t^b}}} \]

where
- \( D \) is the hydrogen permeation rate in scfh
- \( \mathcal{P} \) is the permeability, in scfh/ft²/atm⁰.⁵
- \( A \) is the membrane effective surface area in ft²
- \( P_{\text{H}_2} \) is the hydrogen partial pressure (reformate or permeate streams) in atm
- \( t \) is the thickness of the membrane in ft
- \( T \) is the membrane temperature in °R
- \( R \) is the ideal gas constant in ft³-atm/°R/lb-mol
- \( a, b \) are the empirical constants dependent on the material of the membrane

Therefore implied Permeability Technical Targets are:

<table>
<thead>
<tr>
<th>Permeability:</th>
<th>2006 Status</th>
<th>2010 Target</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;454 scfh/ft²/atm⁰.⁵</td>
<td>567 scfh/ft²/atm⁰.⁵</td>
<td>&gt;680 scfh/ft²/atm⁰.⁵</td>
<td></td>
</tr>
</tbody>
</table>
Modeling Stand-Alone Membrane Separators

Membrane Separation Unit Sizing Model
Directed Technologies, Inc.
Jeff Kalinoski
1/2/2008

- 1-D Differential Element Separation Model Created (Excel Based)
- No reaction chemistry
- Assumed 100% selectivity (i.e. metal membrane)
- Used to determine membrane area for stand-alone Membrane Separator
- Permeance based on 2010 DOE Targets

Typical Parameters for a 1500kgH₂/day Separator

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Pressure</td>
<td>20 atm</td>
</tr>
<tr>
<td>Permate Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Inlet Molar Flow</td>
<td>83 kgmol/h</td>
</tr>
<tr>
<td>Inlet H₂ Molar Fraction</td>
<td>41%</td>
</tr>
<tr>
<td>Permeance</td>
<td>567 scfh/ft²/atm⁰.⁵</td>
</tr>
<tr>
<td>Membrane Area Required</td>
<td>48 ft²</td>
</tr>
<tr>
<td>H₂ Recovery</td>
<td>90%</td>
</tr>
<tr>
<td>Cost at $1000/ft²</td>
<td>$48,000</td>
</tr>
</tbody>
</table>
System Level Evaluation is Critical

Comparison of EtOH Efficiency vs. Recovery for a Membrane Separator System

- Steam/Ethanol Ratio has a larger effect than H₂ Recovery

Other considerations:
- Peak membrane temperature ~500-550°C (for Pd-based membranes)
- Membrane H₂ flux increases with temperature
- Membrane area increases with Recovery and H₂ Dilution
Impact of Integrated Membrane On Overall Catalyst Bed Size

Discrete Reactors (Reformer → WGS → PSA) (Sys 9)

- Near-complete EtOH conversion (99%+)
- But requires separate WGS Reactor and Gas Cleanup System

With Integrated Ref/WGS/Membrane (Sys 13a)

- Also good EtOH conversion
- Combines Reformer/WGS/Membrane into single unit
- <1/4 the total bed volume
Two Reactor Configurations Examined

Tubular Reactor

• Excellent heat transfer if small diameter tubes
• But small diam. tubes → unwieldy # of tubes
• Configuration not amenable to membrane tubes

Annular Heat Exchange Reactor (HER)

• Simpler design - fewer parts
• Amenable to membrane system integration
• ~25% lower cost than Tubular

Annular Design Selected for Design Studies

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Figure 18: Heat exchange reformer (HER) with annular concentric catalyst bed (170).

Key Assumptions and Observations

• All Systems sized for 1,500 kgH₂/day

• All catalyst systems assumed to have 5 year life
  • Precious Metal Catalysts have approx. shown multi-year life
  • Non-Precious Catalysts have shorter lifetimes

• Membranes are assumed to operate with 1atm H₂ permeate pressure
  • Cost of H₂ Compression is significant (~$200k per H₂A projection)
  • Compressor costs mostly off-sets capital cost gain of integrated reformer

• DOE 2010 Membrane Performance and Cost Targets Assumed
  • Flux: 250 scfh/ft² (at prescribed conditions)
  • Module Cost: $1,000/ft²

• H₂A Forecourt Spreadsheet Used for all $/kg projections
  • Version 26: February 2008

• Steam-to-Carbon and Steam-to-Ethanol Ratios cause confusion
  • Because ethanol is C₂H₅OH there is a 2x difference in the ratio
  • S/C=4 is the same as S/Ethanol=8
# Modeling Results

<table>
<thead>
<tr>
<th>Case #</th>
<th>Description</th>
<th>Ethanol Efficiency (H₂ LHV/Ethanol LHV)</th>
<th>Uninstalled Capital Cost $</th>
<th>Production Cost $/kg</th>
<th>Total Cost (Production/Storage/Disp.) $/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Baseline EtOH (High Temperature, Pre-Reformer) - with PSA (75% H₂ Recovery)</td>
<td>68.1%</td>
<td>$830k</td>
<td>$3.02/kg</td>
<td>$5.04</td>
</tr>
<tr>
<td>11</td>
<td>- with Membrane Separator (90% H₂ Recovery)</td>
<td>74.9%</td>
<td>$909k</td>
<td>$2.96/kg</td>
<td>$4.98/kg</td>
</tr>
<tr>
<td></td>
<td><strong>Medium Temperature EtOH</strong> (Steam/EtOH = 8 (PM) /10 (NPM) unless otherwise specified)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>- with PSA (75% H₂ Recovery)</td>
<td>67.3% (NPM) 67.5% (PM)</td>
<td>$673k $839k</td>
<td>$2.95/kg $3.04/kg</td>
<td>$4.97/kg $5.06/kg</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>64.5% (NPM) 66.8% (PM)</td>
<td>$800k $905k</td>
<td>$3.28/kg $3.25/kg</td>
<td>$5.30/kg $5.27/kg</td>
</tr>
<tr>
<td>10</td>
<td>- with Membr. Sep. (90% Recov.)</td>
<td>69.8% (NPM) 67.6% (PM)</td>
<td>$711k $929k ($10/kg catalyst) $400/kg catalyst)</td>
<td>$3.02/kg $3.23/kg</td>
<td>$5.04/kg $5.25/kg</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>79.4% (NPM) (Steam/Eth. = 6)</td>
<td>$608k</td>
<td>$2.67/kg</td>
<td>$4.69/kg</td>
</tr>
<tr>
<td>13a</td>
<td>- with Integrated Reformer/WGS/Membrane System</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13b</td>
<td>- Future Integrated Reformer/WGS/Membrane System</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PM= Precious Metal Catalyst  
NPM= Non-Precious Metal Catalyst
Summary

• Medium & High temperature EtOH reforming are efficiency competitive
• Alternative configurations to tubular designs may lower capital cost
  ➢ but must have adequate heat transfer
• Low Steam/Ethanol ratios favor high system efficiency
  ➢ but must not coke
• Methane in reformer exhaust should be minimized
  ➢ each CH$_4$ in exhaust robs 4H$_2$ from product
  ➢ Methane make is key catalyst evaluation metric
• Catalyst cost is a key cost component. Worthwhile to explore reduced/non precious metal catalysts
  ➢ but must have multi-year lifetimes
• 90% H$_2$ Recovery in a membrane separator is feasible (at 20atm/1atm)
• Membrane systems (with high recovery) can make significant efficiency improvements (up to 5%)
Summary (continued)

- Mid 70’s% LHV Ethanol efficiencies are possible
- H$_2$ Production Cost of <$3/kg is feasible
- But forecourt compression/storage/dispensing is currently very costly ($2/kgH$_2$)
  - DOE targets for compression/storage/dispensing need to be met to achieve overall H$_2$ cost target of <$3/kg
- Integrated reformers have the advantages of:
  - reduced operating temperature
  - lower capital cost
  - lower H$_2$ $/kg
  - While cost & efficiency advantage is not decisive, integrated systems are compact & simpler: important for forecourt installation
- Aqueous phase reformers using low cost feedstocks offer a potential pathway to low H$_2$ cost. Advantages include:
  - low operating temperature
  - low capital cost
  - variety of low cost feedstocks
  - Cost/Performance analysis is underway
Future Plans

• Complete System Comparisons
• Examine Aqueous Reforming System
• Write Final Report