Cost Implications of Hydrogen Quality Requirements

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Overview

Timeline
- Project start date: FY 2007
- Project end date: Open
- Percent complete: N/A

Barriers
- B. Stove-Piped/Siloed Analytical Capability
  - Segmented resources
- D. Suite of Models and Tools
  - Macro-system models

Budget
- Funding, FY 07: $200 K
- Funding, FY 08: $350 K
- Funding, FY 09: $200 K

Partners/Collaborators
- Energy Companies (BP, GTI)
- National Laboratories (NREL)
- International
  - Japan Gas Association
  - International Standards Org.
Objective

- Correlate impurity concentrations (in H₂) to the cost of hydrogen, as functions of
  - Process parameters (T, P, S/C, …)
  - Performance measures (H₂ recovery, efficiency)

Approach

- Define hydrogen production processes that can meet hydrogen quality requirements
  - SMR, NG-ATR, Coal Gas (CG) ATR
  - Reformate, syngas purification using PSA
- Model processes to determine sensitivity of process performance to
  - Design and operating parameters
    - P, T, S/C, sorbent, …
- Support data integration into H2A
<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Milestone</th>
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</thead>
<tbody>
<tr>
<td>Feb. 2009</td>
<td>With NREL, incorporate NG-SR-PSA data into H2A&lt;br&gt;<em>In progress</em></td>
</tr>
<tr>
<td>Feb. 2009</td>
<td>Define processes to be modeled and analyzed for hydrogen production via coal gasification and water electrolysis&lt;br&gt;<em>Model set up for coal gas to hydrogen pathway&lt;br&gt;(some preliminary results presented here)</em></td>
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<tr>
<td>Sep. 2009</td>
<td>Establish impurity concentration vs. efficiency correlation for coal derived hydrogen</td>
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</table>
Schematic of the SMR-PSA system (Base Case)

- **NG Compressor**: NG input at 3 atm, 25 °C.
- **Burner**: Methane (CH₄) input at 925 °C, producing Burner exhaust at 170 °C.
- **Fuel Processor**: Heat input from Burner exhaust.
- **SMR**: Water input (H₂O) at 25 °C, 3 atm, producing SMR tail-gas at 25 °C, 1.34 atm.
- **WGS**: S/C=4 input, producing PSA tail-gas at 25 °C, 1.34 atm.
- **PSA**: H₂ recovered at 25 °C, 1500 kg/day.
- **H₂ recovered**: H₂=76%, CO=2.8%, N₂=0.4%, CH₄=2.8%.
- **Qₜₜₒₜₜ**: (2.5% H₂-LHV) loss.

**Inlet Streams**:
- NG: CH₄ = 93%, N₂=1.6%.
- Air/Fuel: 275 °C.
- H₂O: (25 °C, Pₚ).

**Outlet Streams**:
- Burner exhaust: 170 °C.
- Reformate: 170 °C.
- PSA tail-gas: 25 °C, 1.34 atm.
- H₂ recovered: 25 °C.

**Additional Notes**:
- **Qₜₜₒₜₜ**: (2.5% H₂-LHV) loss.
The model tracks 9 impurities through the system

- Natural gas feed contains He, N₂, S
- Air feeds (ATR, CG) contribute Ar, N₂
- Reformate to PSA contains
  - N₂, CH₄, CO₂, CO, NH₃, H₂S, He, Ar
- The PSA is very effective for removing
  H₂S, NH₃, H₂O, CO₂, CH₄
- Helium is not removed in the PSA
- The product hydrogen from PSA contains trace concentrations of
  He, CO, N₂, Ar, CO₂, CH₄

**Diagram:**

- SR/ATR/Gasifier
- PSA
- Hydrogen (75%): Ar, He, N₂, NH₃, H₂S, CO, CO₂, CH₄, H₂O
- Hydrogen (99.97%): Ar, He, N₂, CO, CH₄

**Graph:**

- 3.8 moles H₂ / mole CH₄ from SR
- 70% H₂ Recovery in PSA
- 80% He Recovery in PSA
Base Case: A CO specification of 0.2 ppm limits the $H_2$ recovery to 74% and the efficiency to ~ 66%
**Effect of Pressure**

*The process efficiency peaks at 10-12 atm*

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**Preliminary Data**

- Higher pressures improve impurity adsorption in PSA.
- Higher pressures increase hydrogen loss during PSA bed regeneration.
- Higher pressures reduce hydrogen concentrations in reformer product gas (i.e., PSA feed)

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**Effect of Carbon / Zeolite Proportion:**
*With increasing zeolite fraction, the limiting species changes from CO to N₂*

Preliminary Data
Variations in Natural Gas Composition: Some NG contains much higher concentrations of $N_2$

<table>
<thead>
<tr>
<th>Species</th>
<th>Mean</th>
<th>10 percentile$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>93.1</td>
<td>83.9</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>3.2</td>
<td>5.7</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.6</td>
<td>6.1</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$LHV \ (kJ/mol)$ 817 785

Reformate composition to PSA (%-dry)$^*$

<table>
<thead>
<tr>
<th>Species</th>
<th>Mean</th>
<th>10$^{th}$ percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>76.4</td>
<td>75.4</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>17.5</td>
<td>17.7</td>
</tr>
<tr>
<td>CO</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^*$Feed to PSA also includes 100 ppmv H$_2$S

Variations in Natural Gas Composition:
$N_2$ concentration in product $H_2$ increases by a factor of $\sim 6$

![Graph showing variations in natural gas composition](image)

- CO still limits the hydrogen recovery from the PSA

Preliminary Data
Hydrogen cost is a weak function of CO concentration (based on NG price of $7.6 / 1000 ft³ or $7.8 / MMBTU)

Preliminary Data

Effect of S/C

Effect of inlet PSA temperature

Effect of pressure

Effect of Carbon fraction

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Schematic for a \( \text{H}_2 \) production system using natural gas ATR and PSA

Preliminary Data

- \( S/C = 3.25 \)
- \( S/C_{\text{ATR}} = 1.65 \)
- \( \text{O}_2/C = 0.55 \)
- \( P = 8 \text{ atm} \)
- \( \text{CH}_4: 1.5\% \)
- \( \text{CO}_2: 15.6\% \)
- \( \text{CO}: 1.0\% \) \( P, 25 \degree \text{C} \)
- \( \text{H}_2: 44.4\% \)
- \( \text{N}_2: 37.1\% \)
- \( \text{Ar}: 0.4\% \)

- Burner exhaust 170 \degree \text{C}
- Reformate, 170 \degree \text{C}
- 410 atm
- 1500 kg/day
- \( \text{H}_2 \), \( P, 25 \degree \text{C} \)
- \( P = 8 \text{ atm} \) PSA
- Condenser
- Preparative Data
Natural Gas ATR-PSA:
Nitrogen limits the hydrogen recovery

**Concentration, ppm**
- **$N_2$**
  - 0.024 ppm
  - 1300 ppm
- **CO**
  - 0.2 ppm

**Efficiency, %**
- 42%
- 54%

**H$_2$ Recovery, %**
- 56%
- 70%

Argon is slightly less than 10 ppm when recovery exceeds 66%.
Schematic for a $H_2$ production system using coal gasification and PSA

Coal Gasifier → Gas Cleanup & Desulfurization → CO$_2$ Recovery → CO$_2$ Sequestration → PSA → Tail-gas to turbine

Preliminary Data

*Besancon et al. – Air Liquide (2009) Journal of power sources

- $H_2$: 87.8%
- $N_2$: 5.0%
- CO$_2$: 3.9%
- CO: 2.6%
- Ar: 0.9%
- CH$_4$: 100 ppm
H₂ from Coal Gasification and PSA: Inerts (nitrogen and argon) limit the hydrogen recovery

**Argonne Model**
- 4 adiabatic beds, 2 pressure equalizations
- Adsorbent mix: 60% activated carbon (BPL), 40% Zeolite 5A
- Tail-gas pressure: 1.3 bar-a

**Air Liquide Model** (Besancon, J Power Sources, 34(2009))
- 6 Beds
- Adsorbent mix: unknown
- Tail-gas pressure: 1.3 bar-a
Summary of Technical Accomplishments

- A rigorous model of the PSA system has been set up as part of a flexible systems model (using Comsol Multiphysics and MATLAB)
  - 9 species can be tracked through the system
- The pathway for NG-SR-PSA has been studied over a broad range of design and operating parameters
  - The effect of several design and operating parameters on hydrogen quality and system efficiency has been established
  - Constraint: to meet SAE/ISO guideline values
- The system model results have been correlated with the cost of hydrogen (using H2A)
- Preliminary studies have been conducted for two additional pathways
  - NG-ATR-PSA
  - Coal Gas - PSA
Collaborations

- Presented results to stakeholders at numerous meetings
  - ISO, Conferences, Tech Team
- Participated in modeling workshop with Japan Gas Association, GTI, and BP to validate model with field data
- Working with NREL to collect field data from gas supplier
- Exploring the (confidential) sharing of model results and field data with an energy company and a hydrogen producer (electrolysis)
Conclusions

- The cost of hydrogen is only slightly affected by the impurity specification (guideline) in the NG-SR-PSA system studied.
- CO specification limits the hydrogen recovery for NG-SR for most process conditions:
  - $\text{N}_2$ may become limiting species in a few cases:
    - *When the beds are loaded with high zeolite content*
    - *When the natural gas contains high concentrations of nitrogen*
  - He passes through the NG-SR process:
    - *Emerges at a lower concentration*
- For ATR of NG with PSA purification, Ar or $\text{N}_2$ specification may limit $\text{H}_2$ recovery.
- Similarly, for coal gas reforming followed by PSA, the $\text{H}_2$ recovery may be limited by Ar or $\text{N}_2$. 
**Future work**

- Evaluate the impurity concentrations likely from other hydrogen production pathways
  - ATR, coal gasification, electrolysis
  - Coal gasification processes may be larger, central production plants
- Validate the NG-SR model results with field data
  - Incorporate more complex PSA systems if needed
- Incorporate our model results into H2A
Acknowledgements

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