Design and Demonstration of an Ethanol Fuel Processor for HT-PEM Fuel Cell Applications

AIChE Annual Meeting 2013
Fuel Processing for Hydrogen Production

07 Nov. 2013
Overview

- Introduction
- Process Simulation
- Heat Integration Analysis
- Catalyst Selection
- Component Development
- Fuel Processor Demonstration
- Outlook
Application
- Hydrogen generation for small scale fuel cell systems ($P_{el} = 200 – 500$ W)
- HT PEM fuel cell
- Off grid stationary power supply
- Backup power
- Leisure and security markets

Fuel Bioethanol ($C_2H_5OH$)
- CO$_2$ neutral
- Good portability
- High energy density
- Good storage capability

Introduction

Flow sheet of reformer fuel cell system

Source www.lacus.ch
Introduction

Requirements Fuel Processor

- $P_{H2} = 600 - 1500$ W
- HT PEM FC suitable reformate gas quality ($CO \leq 1\%$)
- Fast start up
- High robustness
- Potential of low cost manufacturing
- Low pressure drop

→ Autothermal Reforming of Bioethanol
Approach

- Parameter variation
- Reformate gas composition
- Definition heat streams and heat demand
- Carbon and side product formation
- Definition of basic operation point

**Parameter** | **Interval** | **Step** | **Basic Operation Point**
--- | --- | --- | ---
$T_{\text{ATR}}$ / °C | 500 - 800 | 25 | 700
$O_2/C$ / - | 0 – 1.5 | 0.1 | 0.4
$S/C$ / - | 0 - 5 | 0.25 | 2.75
$T_{\text{Shift}}$ / °C | 200 - 400 | 25 | 300

Flow sheet of thermodynamic process simulation
Product gas composition (example ATR out)

Equilibrium, $T_{\text{ATR}} = 700 \ ^\circ\text{C}$, $S/C = 2.75$

Equilibrium, $T_{\text{ATR}} = 700 \ ^\circ\text{C}$, $O_2/C = 0.40$
Thermodynamic Potential of Carbon Formation

Aspen settings for solid carbon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>IDEAL</td>
</tr>
<tr>
<td>Stream Class</td>
<td>Mix CISLD</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Gibbs-reactor (possible products gas phase &amp; pure solid)</td>
</tr>
<tr>
<td>Consideration of carbon formation by homogeneous gas phase reaction</td>
<td></td>
</tr>
</tbody>
</table>

Carbon formation boundaries of EtOH reforming ($O_2/C = 0.4$)
Heat Integration Analysis

**Approach**
- Basic operation point
- Simulation results (heat streams, temperatures)
- Pinch Point Analysis

**Main System Layout Targets**
**Minimization of**
- Heat exchangers
- Heat exchangers with high thermal stress (> 500 °C)
- Heat exchangers with internal evaporation (mixing of educts)

**Maximization of**
- Variance for setting of main temperatures
- Internal fulfilment of heat demand
Heat Integration Analysis

Pinch Point Analysis
for streams c1', c1, h1 and h4

Cummulative curves of heat demand and supply

<table>
<thead>
<tr>
<th>Stream</th>
<th>T_{in} / °C</th>
<th>T_{out} / °C</th>
<th>Q / W</th>
</tr>
</thead>
<tbody>
<tr>
<td>c1'</td>
<td>14</td>
<td>84</td>
<td>294</td>
</tr>
<tr>
<td>c1</td>
<td>84</td>
<td>341</td>
<td>100</td>
</tr>
<tr>
<td>h1</td>
<td>793</td>
<td>100</td>
<td>-330</td>
</tr>
<tr>
<td>h4</td>
<td>700</td>
<td>400</td>
<td>-136</td>
</tr>
</tbody>
</table>
Resulting System Flow Sheet

- Reactants (C₂H₅OH, H₂O, Air) completely premixed
- 4 heat exchangers (two coupled) for fuel processor
- T_{\text{Shift,in}} and T_{\text{Anode,in}} freely adjustable
Catalyst Selection

Screening
- Precious metal catalysts
- Ceramic monolith

EtOH conversion as function of GHSV
(S/C = 2.75, O₂/C = 0.40)

\[
X_{\text{EtOH}} = \frac{\dot{n}_{\text{EtOH, out}} - \dot{n}_{\text{EtOH, in}}}{\dot{n}_{\text{EtOH, in}}}
\]

EtOH conversion as function of O₂/C and GHSV
(S/C = 2.75)

n_{\text{EtOH, out}} calculated by means of C-atom balance
## Component Development

### ATR
- Precious metal catalyst
- GHSV = 50,000 1/h
- Ceramic monolith (600 cpsi)
- Adiabatic reactor

### Burner
- Precious metal catalyst
- GHSV = 25,000 1/h
- Ceramic monolith (600 cpsi)
- Electrical heater / glow plug (alternative)
- Evaporation zone with metal fibre structure
- Suitable for ethanol and AOG

### Shift
- Precious metal catalyst
- GHSV = 15,000 1/h
- Ceramic monolith (600 cpsi)
- Adiabatic reactor

### Evaporator Superheater Unit
- Internal cooling fins
- Counter current flow
- Flue gas as heat source
- Evaporation zone with metal foam structure
- Superheating zone
Fuel Processor Demonstration

Laboratory Fuel Processor

Fuel processor assembly equipped with thermocouples
Start up process

Start up procedure

<table>
<thead>
<tr>
<th>Pt.</th>
<th>Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Start Heater</td>
</tr>
<tr>
<td>2</td>
<td>Dosage EtOH burner</td>
</tr>
<tr>
<td>3</td>
<td>Ignition burner</td>
</tr>
<tr>
<td>4</td>
<td>Variation load burner</td>
</tr>
<tr>
<td>5</td>
<td>Start H₂O dosage</td>
</tr>
<tr>
<td>6</td>
<td>Start reforming</td>
</tr>
<tr>
<td>7</td>
<td>Switch to AOG</td>
</tr>
</tbody>
</table>

\[ x_{\text{CO}} < 2 \% \]
**Gas composition shift out**

- Variations of $O_2/C$ and $S/C$

\[ \chi_i \text{ as function of } O_2/C \text{ (S/C = 2.75), measurement vs. equilibrium, dry} \]

\[ \chi_i \text{ as function of } S/C \text{ (O}_2/C = 0.4), \text{ measurement vs. equilibrium, dry} \]
Power output / efficiency steady state

\[
\eta_H^2 = \frac{P_H^2}{P_{\text{EtOH,ATR}} + P_{\text{Burn}} + P_{\text{AOG}}}
\]

\(P^2_H\) calculated by means of \(N_2\)-atom balance

Performance data as function of \(O_2/C\) (S/C = 2.75)

Performance data as function of S/C (\(O_2/C\) = 0.4)
Gas composition shift out

- Comparison Online Gas Analyser (Rousemount Analytical NGA 2000, MLT 4) vs. Gas Chromatograph (Agilent Micro GC 3000A)

Calibrated Components for GC

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Lower limit / %</th>
<th>Upper limit / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0056</td>
<td>1.663</td>
</tr>
<tr>
<td>H2</td>
<td>0.357</td>
<td>81.363</td>
</tr>
<tr>
<td>O2</td>
<td>0.051</td>
<td>20.5</td>
</tr>
<tr>
<td>N2</td>
<td>0.524</td>
<td>89.93</td>
</tr>
<tr>
<td>CH4</td>
<td>0.3195</td>
<td>88.2</td>
</tr>
<tr>
<td>CO</td>
<td>0.1972</td>
<td>49.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0104</td>
<td>14.0</td>
</tr>
<tr>
<td>Propan</td>
<td>0.0102</td>
<td>3.01</td>
</tr>
<tr>
<td>Iso-Butan</td>
<td>0.0104</td>
<td>0.539</td>
</tr>
<tr>
<td>n-Butan</td>
<td>0.0099</td>
<td>0.803</td>
</tr>
<tr>
<td>N-pentan</td>
<td>0.0107</td>
<td>-</td>
</tr>
<tr>
<td>NH3</td>
<td>0.0487</td>
<td>1.044</td>
</tr>
<tr>
<td>N-Hexan</td>
<td>0.0107</td>
<td>-</td>
</tr>
<tr>
<td>C2H6O</td>
<td>0.0983</td>
<td>1.015</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.165</td>
<td>-</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.0103</td>
<td>0.098</td>
</tr>
</tbody>
</table>

$\chi_i$ of basic operation point ($O_2/C, S/C = 2.75$), online GA vs. GC, dry basis
## Development Status

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Basic Operation Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_{\text{EtOH}}) / g/h</td>
<td>160</td>
</tr>
<tr>
<td>(O_2/C) / -</td>
<td>0.42</td>
</tr>
<tr>
<td>(S/C) / -</td>
<td>2.75</td>
</tr>
<tr>
<td>(T_{\text{ATR}}) / °C</td>
<td>650 – 700</td>
</tr>
<tr>
<td>(T_{\text{Shift}}) / °C</td>
<td>380 – 400</td>
</tr>
<tr>
<td>(H_2) / %</td>
<td>42.0</td>
</tr>
<tr>
<td>(CO) / %</td>
<td>0.9</td>
</tr>
<tr>
<td>(CO_2) / %</td>
<td>19.0</td>
</tr>
<tr>
<td>(CH_4) / %</td>
<td>2.0</td>
</tr>
<tr>
<td>EtOH / ppm</td>
<td>54 (GC meas.)</td>
</tr>
<tr>
<td>(N_2) / %</td>
<td>36.1 (calculated)</td>
</tr>
</tbody>
</table>

### Performance Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Status</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power output (P_{H_2}) / W</td>
<td>900</td>
<td>600 - 1500</td>
</tr>
<tr>
<td>Efficiency (\eta_{H_2}) / %</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>(X_{\text{EtOH ATR}}) / % (calculated)</td>
<td>(\sim 100)</td>
<td>100</td>
</tr>
<tr>
<td>Gasquality, CO / %</td>
<td>1.0 – 1.5</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Start up time / Min</td>
<td>(\sim 30)</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>Pressure drop / mbar</td>
<td>15 - 20</td>
<td>20</td>
</tr>
</tbody>
</table>
Outlook

**Issues to be addressed**

- Long term test
- Reduction start up time
- Optimization evaporator
- Enhancing efficiency
- Optimization temperature control shift
- Coupling with HT-PEM fuel cell
Thanks!

Contact
Dr.-Ing. Ulrich Gardemann
project manager fuel processing
u.gardemann@zbt-duisburg.de / +49 (0)203/7598-1540 / www.zbt-duisburg.de

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