Sunlight Ancient & Modern: The relative energy efficiency of hydrogen from coal and current biomass

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Objectives

• Establish transparent comparisons of baseline systems to produce hydrogen from various primary energy sources.

• Establish the critical parameters & assumptions to which system is sensitive.

• Provide analyses for components of technological systems that combine hydrogen production with carbon sequestration.
Process Outline

1. **Biomass/coal** → **Pyrolysis/Gasification**
   - **Bio-oil/gases** → **Preheating**
   - **Cooling**
   - **Char Cooling**

2. **Steam Boiling/Superheating**
   - **Water**
   - **Steam**
   - **Combustion**
     - **H₂O & CO₂**
     - **O₂**
     - **Combusted Products Cooling**

3. **Reforming**
   - **Steam**

4. **PSA Separation**
   - **H₂**
   - **Off-gases**

5. **Reformed Gases Cooling**

The process outline includes steps such as pyrolysis, gasification, preheating, reforming, PSA separation, and cooling, with various inputs and outputs including biomass/coal, bio-oil/gases, steam, water, oxygen, hydrogen, and off-gases.
Pyrolysis of Biomass

Pyrolyzer (500°C)

Biomass (1kg)

Preheating: 1231.2 kJ

Energy: 1580 kJ

Bio-oil/gases (840g)

Char (160g)

Cooling: -50.91 kJ

Yield, wt% on dry feed

Reaction temperature, °C

Organics

Gas

Water

Char

450 500 550 600

50%

60%

70%

40%

30%

20%

10%

0%

70%

60%

50%

40%

30%

20%

10%

0%
Bio-oil Composition Estimation

- Contains hundreds of components
- Concentrations vary significantly
- Depends on biomass, reaction conditions, etc.
- Limited experimental results

Estimation Method

\[
\begin{align*}
\min & \quad \sum \alpha_i (W_i - W_i^T)^2 \\
\text{s.t.} & \quad Lb_i \leq W_i \leq Ub_i \\
& \quad x_{\text{ref}} / M_{W_{\text{bio}}} = \sum x_i W_i / M_i \\
& \quad y_{\text{ref}} / M_{W_{\text{bio}}} = \sum y_i W_i / M_i \\
& \quad z_{\text{ref}} / M_{W_{\text{bio}}} = \sum z_i W_i / M_i
\end{align*}
\]
Bio-oil Composition Estimation (cont.)

Other compositions

$$\min \sum (y/2 + x - z)_i W^L_i$$

s.t. $$Lb_i \leq W^L_i \leq Ub_i$$

$$x_{ref} / M_{w_{bio}} = \sum x_i W^L_i / M_{w_i}$$

$$y_{ref} / M_{w_{bio}} = \sum y_i W^L_i / M_{w_i}$$

$$z_{ref} / M_{w_{bio}} = \sum z_i W^L_i / M_{w_i}$$

$$\sum (W^L_i - W^T_i)^2 \leq \sum (W_i - W^T_i)^2$$

H2 production not sensitive to bio-oil composition

<table>
<thead>
<tr>
<th>Value of $\sum (y/2 + x - z)_i W_i^L$</th>
<th>W</th>
<th>WL</th>
<th>WU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>138.82</td>
<td>138.77</td>
<td>138.85</td>
</tr>
</tbody>
</table>

Steam Reforming (SR) reactions

$$C_x H_y O_z + (x - z) H_2 O \leftrightarrow x CO + (x + y/2 + z) H_2$$

$$CO + H_2 O \leftrightarrow CO_2 + H_2$$

$$CH_4 + H_2 O \leftrightarrow CO + 3H_2$$
Heat Integration for Biomass Conversion

- **Heat sources**
  - Steam reforming products
  - Combusted products
  - Char

- **Heat sinks**
  - Pyrolysis
  - Steam reforming
  - Biomass preheating
  - Bio-oil/gases preheating
  - Steam making

**Heat Integration by Pinch Analysis**
## Biomass Conversion Summary

<table>
<thead>
<tr>
<th>Item</th>
<th>S/C = 1</th>
<th>S/C = 3</th>
<th>S/C = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 output/mol</td>
<td>40.95</td>
<td>51.17</td>
<td>55.7</td>
</tr>
<tr>
<td>H2O input/mol</td>
<td>555.71</td>
<td>604.22</td>
<td>643.98</td>
</tr>
<tr>
<td>H2O output/mol</td>
<td>545.99</td>
<td>584.28</td>
<td>619.48</td>
</tr>
<tr>
<td>Net Usage of water/mol</td>
<td>9.72</td>
<td>19.94</td>
<td>24.50</td>
</tr>
<tr>
<td>O2 input/mol</td>
<td>30.56</td>
<td>25.45</td>
<td>23.17</td>
</tr>
<tr>
<td>CO2 output/mol</td>
<td>43.29</td>
<td>43.29</td>
<td>43.29</td>
</tr>
<tr>
<td>Total Energy Input/kJ</td>
<td>25669</td>
<td>26563</td>
<td>27913</td>
</tr>
<tr>
<td>Total Energy Waste/kJ</td>
<td>72</td>
<td>286</td>
<td>1897</td>
</tr>
<tr>
<td>Mol H2 / MJ Energy Input</td>
<td>1.60</td>
<td>1.93</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Gasification of Coal

Reactions

\[
\begin{align*}
C + \frac{1}{2}O_2 &= CO \\
CO + \frac{1}{2}O_2 &= CO_2 \\
H_2 + \frac{1}{2}O_2 &= H_2O \\
C + CO_2 &\leftrightarrow 2CO \\
C + H_2O &\leftrightarrow CO + H_2 \\
C + 2H_2 &\leftrightarrow CH_4 \\
CO + H_2O &\leftrightarrow CO_2 + H_2 \\
CH_4 + H_2O &\leftrightarrow CO_2 + 3H_2
\end{align*}
\]

Simulation results

- Hydrogen production ability changed little with increasing temperature.
- Energy requirement increased significantly with temperature.
- Oxygen is not needed if S/C ratio is above 0.6.
Heat Integration for Coal Conversion
Hydrogen production per unit energy input (Mol H2 / MJ Energy Input)

<table>
<thead>
<tr>
<th>S/C =0.2 in Gas.</th>
<th>S/C =0.3 in Gas.</th>
<th>S/C =0.4 in Gas.</th>
<th>S/C =0.5 in Gas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/C =1 in SR</td>
<td>S/C =2 in SR</td>
<td>S/C =3 in SR</td>
<td></td>
</tr>
<tr>
<td>2.46</td>
<td>2.60</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>2.43</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>2.23</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>2.10</td>
<td>2.13</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol H2 / MJ Energy Input</td>
<td>2.70</td>
</tr>
<tr>
<td>H2 output/mol</td>
<td>66.48</td>
</tr>
<tr>
<td>H2O input/mol</td>
<td>826.08</td>
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<tr>
<td>H2O output/mol</td>
<td>788.00</td>
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<tr>
<td>Net Usage of water/mol</td>
<td>38.08</td>
</tr>
<tr>
<td>O2 input/mol</td>
<td>45.94</td>
</tr>
<tr>
<td>CO2 output/mol</td>
<td>68.05</td>
</tr>
<tr>
<td>Total Energy Input/kJ</td>
<td>24622</td>
</tr>
<tr>
<td>Total Energy Waste/kJ</td>
<td>4754</td>
</tr>
</tbody>
</table>
Comparison of the Two Systems

Sunlight

Biomass

5.60 mol H₂/lb biomass

0.002445 mol H₂/MJ solar energy

Coal

Hydrogen

7.68 mol H₂/lb coal

0.000286 mol H₂/MJ solar energy
Conclusions

• Higher energy density of coal leads to greater hydrogen production efficiency (no surprise.)

• Heat integration schemes are dependent of steam/carbon ratios and specific system conditions – must be holistically optimized.

• Bio-oil composition not a key factor.

• Overall efficiency of sunlight to hydrogen is significantly better for current sunlight due to putative inefficiencies of geological coal forming processes (but it’s in the past).
Acknowledgements

• Department of Energy for funding through Clark Atlanta and Yaw Yeboah.

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