Low carbon hydrogen production via the advanced reforming of bio-oil

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5. Summary
The role of hydrogen

**Now**
- $7.2 \times 10^{18}$ joules per year\(^1\)
- (UK total energy = $8.1 \times 10^{18}$ J per year\(^2\))
- 98% from fossil fuel steam reforming\(^3\)
- **1.4% of emissions** from fossil fuels & industry\(^1,4\)

**Future**
- Population growth
- Unconventional oils
- New applications
Steam reforming

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$$

$$\Delta H_r = +165 \text{ kJ mol}_{\text{CH}_4}^{-1}$$

10 kg CO$_2$ per kg H$_2$\textsuperscript{5,6}

First patent in 1912\textsuperscript{7}
Efficiencies over 80%\textsuperscript{8}
Lowest cost route to H$_2$\textsuperscript{9}
Bio-oil steam reforming

Pyrolysis → Reforming → $\text{H}_2$

Biomass
Waste plastics
MSW

Acids
Ketones
Aldehydes
Phenolics

Energy
Bio-oil refining
Fischer-Tropsch
Research question

How does bio-oil perform in a steam reforming process?

How do advanced steam reforming techniques enhance this performance?

Key performance indicators are:
• Hydrogen yield
• CO$_2$ emissions
• Thermal efficiency
• Cost
2. Conventional SR of bio-oil

Process modelling
- Bio-oil modelled as surrogate mixture
- Industrial pressure (30 bar) & scale (10-100,000 Nm³/h)
Process performance at 30 bar

Yield (wt%, moisture free) vs. Reformer temperature (°C)

- **S/C = 3**
- **S/C = 5**
- **Max theoretical yield**

*S/C = steam to carbon ratio*
**Process performance at 30 bar**

Without heat export:

$$\eta_{\text{thermal}} = \frac{\dot{Q}_{H2}}{\dot{Q}_{\text{bio-oil}} + \dot{Q}_{\text{methane}} + P_{\text{electrical}}^+}$$

With heat export:

$$\eta_{\text{thermal}} = \frac{\dot{Q}_{H2} + \dot{Q}_{\text{heat}}^-}{\dot{Q}_{\text{bio-oil}} + \dot{Q}_{\text{methane}} + P_{\text{electrical}}^+}$$

where ‘+’ and ‘-’ signify import or export of utilities.
CO₂ emissions

\[ C_nH_mO_k + (2n - k)H_2O \leftrightarrow nCO_2 + (2n + \frac{m}{2} - k)H_2 \]

CO₂ emissions (kg CO₂/kg H₂) = \[ \frac{n}{2n + \frac{m}{2} - k} \] + CO₂ from furnace
3. CCS in bio-oil reforming

Preliminary study
CCS in steam reforming

Hydrogen generation in the IEA 2°C high H2 scenario

From IEA, 2015 [1]
Diagram adapted from Soltani et al. [10]
Technology selections based on Im et al. [11]
CCS: impact of location

Capacity: 50,000 Nm$^3$ h$^{-1}$
Bio-oil feed: 34500 kg h$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>Base case</th>
<th>1 and 2</th>
<th>3</th>
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<tbody>
<tr>
<td>CCS location</td>
<td>-</td>
<td>Syngas or off-gas</td>
<td>Flue</td>
</tr>
<tr>
<td>% of total CO$_2$</td>
<td>-</td>
<td>81%</td>
<td>100%</td>
</tr>
<tr>
<td>CO$_2$ capture rate</td>
<td>From stream</td>
<td>0%</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>Process total</td>
<td>0%</td>
<td>77%</td>
</tr>
<tr>
<td>Emissions (kg CO$_2$/kg H$_2$)</td>
<td>Captured</td>
<td>0.0</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Biogenic</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Fossil</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Emitted</td>
<td>13.4</td>
<td>3.1</td>
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</tbody>
</table>
**CCS: process net emissions**

*Process net emissions*

= fossil emissions released - biogenic emissions captured

<table>
<thead>
<tr>
<th></th>
<th>Bio-oil no CCS</th>
<th>Bio-oil with CCS (1 or 2)</th>
<th>Bio-oil with CCS (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process net emissions</td>
<td>3.1</td>
<td>-9.6</td>
<td>-11.7</td>
</tr>
<tr>
<td>kg CO₂/kg H₂</td>
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<td></td>
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**Simplified analysis** - direct emissions from the process.

It does not represent a full LCA, but provides a benchmark:

**Bio-oil SR with CCS has net negative emissions if:**

- Total other life cycle emissions < 9.6 kg CO₂/kg H₂
- Bio-oil production << 1.2 kg CO₂/kg bio-oil
CCS: modelling Rectisol™

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<thead>
<tr>
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<th>Theoretical</th>
<th>Actual</th>
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<tbody>
<tr>
<td><strong>CO₂ capture rate</strong></td>
<td></td>
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<td>From stream</td>
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<td>95%</td>
</tr>
<tr>
<td>Process total</td>
<td>77%</td>
<td>79%</td>
</tr>
<tr>
<td><strong>Emissions (kg CO₂/kg H₂)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process net</td>
<td>-9.6</td>
<td>-10.0</td>
</tr>
</tbody>
</table>

Assumes PSA recovery = 80%

Thermal efficiency (with heat export):
No CCS: 78%
With CCS: 64%
4. Advanced reforming

Improving H$_2$ production from bio-oil
Sorption-enhanced chemical looping

**STAGE 1**
Reduction, reforming, sorption

Fuel + H₂O

- CaO→CaCO₃
- NiO→Ni

H₂, CH₄, CO, H₂O, CO₂

**STAGE 2**
Regeneration, oxidation

- CaCO₃→CaO
- Ni→NiO

Air

N₂, CO₂
Thermodynamic analysis

Autothermal operation at industrial pressures

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Temp (K)</th>
<th>Yield (wt% m.f.)</th>
<th>H₂ purity (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.013</td>
<td>723</td>
<td>13.6</td>
<td>99.5</td>
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<tr>
<td>30</td>
<td>973</td>
<td>11.8</td>
<td>96.9</td>
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</table>

(S/C ratio = 2)

Carbon deposition
(S/C ratio = 1)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>NiO/C = 0, CaO/C = 1</th>
<th>NiO/C = 0.1, CaO/C = 1</th>
<th>NiO/C = 0.3, CaO/C = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>Solid carbon yield (mol/mol carbon feed)</td>
<td>Solid carbon yield (mol/mol carbon feed)</td>
<td>Solid carbon yield (mol/mol carbon feed)</td>
</tr>
<tr>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
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<tr>
<td>800</td>
<td>0</td>
<td>0</td>
<td>0</td>
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Next steps

Modelling of sorption-enhanced chemical looping:
- kinetic data
- rigorous reactor modelling
- whole process modelling

Economic assessment

Techno-economic comparison of processes
The challenge:
New methods to produce low carbon H\textsubscript{2} on a large scale.

A solution?

- **Bio-oil reforming**
  - is a route to low carbon H\textsubscript{2}

- **CCS**
  - captures biogenic emissions

- **Advanced steam reforming**
  - improves yield, purity and thermal efficiency
References
