Chemical Looping Combustion - power generation and H$_2$ production with CO$_2$ capture

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What is CLC?

<table>
<thead>
<tr>
<th>Fuel Reactor</th>
<th>Air Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_nH_{2m}$</td>
<td>Air</td>
</tr>
<tr>
<td>Me</td>
<td>MeO</td>
</tr>
<tr>
<td>$CO_2 + H_2O$</td>
<td>Reduced Air</td>
</tr>
<tr>
<td>Heat</td>
<td></td>
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</tbody>
</table>
What are the advantages?

- No sorbent required
- No ASU required
- High fuel conversions ($\approx 100\%$) achievable
- Applicable for range of fuel types
A typical CLC plant

Fuel Gas

Air

Reduced Air

Cyclone

Oxygen

Carrier

Fuel

Reactor

Oxidation

Reactor

Cyclone

Circulation of oxygen carrier

Fuel Gas

Dual Circulating Fluidised Bed

Packed Bed

Fuel Gas

Air

Reduced Air

CO₂, H₂O

CO₂, H₂O

Reduced Air

Oxygen Carrier
CLC with H₂ production and Power Generation

Fuel Reactor

CO₂ + H₂O → FeO/Fe

Steam Oxidation Reactor

H₂O → H₂/H₂O

Air Oxidation Reactor

CₙH₂m → Fe₂O₃

Air

Heat

Reduced Air
Flowsheeting of a CLC Process with H₂ Production and Power Generation
Solving of Flowsheet

• Modelled in MATLAB
  – Thermodynamic data from NASA-Glenn database
  – Reactions solved by Gibbs Energy minimisation

• Two key system variables
  – Iron oxide circulation rate $n_{Fe}$
  – Steam flowrate into OX1 $n_{st}$
Heat Integration

$n_{Fe} = 390 \text{ mol/s}$

$n_{st} = 150 \text{ mol/s}$
Suitable Operating Regime

0 = Unsuitable
1 = Suitable, external heat required
2 = Suitable, fully heat-integrated

Operating Criteria
- $\text{H}_2$ stream $\geq 95\%$ pure.
- Conversion of fuel to CO$_2$ and H$_2$O $\geq 95\%$.
- CO in the produced H$_2$ stream $< 50$ ppm.
Exergetic Efficiency \( (\eta_{ex}) \)

\[
\eta_{ex} = \frac{E_{H2} + W_{net}}{E_{fuel}} = \frac{E_{H2} + W_{net}}{E_{fuel,G} + E_{fuel,util}}
\]
Enhancing oxygen carrier performance with Al$_2$O$_3$ support
Al₂O₃ as a support material

![Graph showing the yield (actual/theoretical) of H₂ at different pH values and Fe₂O₃ concentrations.]

- 90 wt % Fe₂O₃, 10 wt % Al₂O₃
- 100 wt % Fe₂O₃
Fe-Al-O phase diagram

\[ \xi = \frac{n_{Fe}}{n_{Fe} + n_{Al}} \]

Direction of decreasing \( \log(p_{O2}) \)

 wt % Fe = 0 0.2 0.4 0.6 0.8 1 wt % Al = 0

0 50 wt % Fe\textsubscript{2}O\textsubscript{3} 75 wt % Fe\textsubscript{2}O\textsubscript{3}

0.4 Fe\textsubscript{3}O\textsubscript{4}(ss) + Fe\textsubscript{2}O\textsubscript{3}(ss)

0.6 Fe\textsubscript{3}O\textsubscript{4}(ss) + Fe\textsubscript{2}O\textsubscript{3}(ss)

0.8 Fe\textsubscript{3}O\textsubscript{4}(ss) + Fe\textsubscript{2}O\textsubscript{3}(ss)

1 Fe\textsubscript{3}O\textsubscript{4}(ss) + Fe\textsubscript{2}O\textsubscript{3}(ss)
Effect of Fe-Al-O phase equilibrium on H$_2$ production

![Graph showing the effect of Fe-Al-O phase equilibrium on H$_2$ production. The x-axis represents the CO$_2$/CO ratio, and the y-axis represents the yield of H$_2$ (Measured/Theoretical). The graph includes data points for 90 wt% Fe$_2$O$_3$, 10 wt% Al$_2$O$_3$, with cycle order numbers indicated.]
Oxygen carrier particle after cycling

75 wt% Fe₂O₃, 25 wt% Al₂O₃ after 20 cycles, sectioned

EDXS map
(red = Fe
yellow = Al)
Conclusions

- CLC has high potential for highly efficient CO$_2$ capture with both power generation and H$_2$ production
- Can be optimised towards producing electrical power/H$_2$
- Oxygen carrier support material (such as Al$_2$O$_3$) essential for long-term performance
  - Interaction between reactive and support material must be fully understood.
Related Publications

Thank you
Any questions?
Phase diagram

\[ K_p = \frac{P_{CO_2}}{P_{CO}} \]

1.202Fe\textsubscript{3}O\textsubscript{4} + CO $\leftrightarrow$ 3.808Fe\textsubscript{0.947}O + CO\textsubscript{2}

0.25Fe\textsubscript{3}O\textsubscript{4} + CO $\leftrightarrow$ 0.75Fe + CO\textsubscript{2}

3Fe\textsubscript{2}O\textsubscript{3} + CO $\leftrightarrow$ 2Fe\textsubscript{3}O\textsubscript{4} + CO\textsubscript{2}

Fe\textsubscript{0.947}O + CO $\leftrightarrow$ 0.947Fe + CO\textsubscript{2}

Fe\textsubscript{2}O\textsubscript{3} 

Fe\textsubscript{3}O\textsubscript{4}

Fe\textsubscript{0.947}O

Fe

Temperature (K)
Hydrogen Production

Units denote mol H₂/s/kg fuel