Progress on CLC processes

Tobias Mattisson

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Department of Energy and Environment
Division of Energy Technology
Outline

• CLC with gaseous, liquid and solid fuels
  - Operational experience
  - Oxygen carrier development

• Processes for hydrogen production

• Fuel processing using CLR

• Costs of CO₂ capture using CLC

• Outlook
Oxygen carrier testing

- A vast number of oxygen carriers based on Fe, Mn, Ni, Cu and Co have been tested (>1000 materials)
- Actual operation has been carried out in units up to 3 MW_th
- Operational experience exceeds a total of 7000 h
- For gaseous and liquid fuels complete gas conversion can be obtained with 100% CO₂ capture
- For solid fuels, gas conversion is typically between 80-95%, with CO₂ capture efficiencies up to 99%
## Overview of operational experience

<table>
<thead>
<tr>
<th>Location</th>
<th>Unit</th>
<th>Oxides tested</th>
<th>Time</th>
<th>Fuel</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers</td>
<td>10 kW</td>
<td>NiO, Fe$_2$O$_3$, ilmenite, CaMnO$_3$</td>
<td>1618</td>
<td>nat. gas, fuel oil</td>
<td>2004</td>
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<tr>
<td>KIER</td>
<td>50 kW</td>
<td>NiO, CoO</td>
<td>31</td>
<td>nat. gas</td>
<td>2004</td>
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<tr>
<td>CSIC</td>
<td>10 kW</td>
<td>CuO, NiO</td>
<td>120</td>
<td>nat. gas</td>
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<tr>
<td>Chalmers</td>
<td>0.3 kW</td>
<td>NiO, Mn$_3$O$_4$, Fe$_2$O$_3$, ilmenite, CaMnO$_3$, Mn-Si, Mn-Si-Ti, Mn-Fe-Si, Mn ore,</td>
<td>1040</td>
<td>nat. gas, syngas</td>
<td>2006</td>
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<tr>
<td>Chalmers</td>
<td>10 kW-SF</td>
<td>ilmenite, manganese ore, CaMnO$_3$</td>
<td>253</td>
<td>coal, petcoke</td>
<td>2008</td>
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<tr>
<td>CSIC</td>
<td>0.5 kW</td>
<td>CuO, NiO, Fe$_2$O$_3$, CaMnO$_3$</td>
<td>949</td>
<td>nat. gas</td>
<td>2009</td>
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<tr>
<td>KAIST</td>
<td>1 kW</td>
<td>NiO + Fe$_2$O$_3$</td>
<td>?</td>
<td>CH$_4$</td>
<td>2009</td>
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<tr>
<td>Vienna UT</td>
<td>140 kW</td>
<td>ilmenite, NiO, Fe$_2$O$_3$, CuO, CaMnO$_3$</td>
<td>519</td>
<td>nat. gas, CO, H$_2$</td>
<td>2009</td>
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<tr>
<td>Alstom</td>
<td>15 kW</td>
<td>NiO</td>
<td>100</td>
<td>nat. gas</td>
<td>2009</td>
</tr>
<tr>
<td>Nanjing</td>
<td>10 kW-SF</td>
<td>NiO, Fe$_2$O$_3$</td>
<td>260</td>
<td>coal, biom.</td>
<td>2009</td>
</tr>
<tr>
<td>KIER</td>
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<td>NiO, CoO</td>
<td>450</td>
<td>nat. gas, syngas</td>
<td>2010</td>
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<tr>
<td>Nanjing</td>
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<td>NiO, iron ore</td>
<td>260</td>
<td>coal, biomass</td>
<td>2010</td>
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<tr>
<td>IFP-Lyon</td>
<td>10 kW</td>
<td>NiO, Mn ore</td>
<td>90</td>
<td>CH4</td>
<td>2010</td>
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<td>Stuttgart</td>
<td>10 kW</td>
<td>ilmenite</td>
<td>?</td>
<td>syngas</td>
<td>2010</td>
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<td>Xi’an</td>
<td>10 kW-Pr</td>
<td>CuO/Fe$_2$O$_3$</td>
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<td>2010</td>
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<td>Jiaotong</td>
<td>0.5 kW-SF</td>
<td>ilmenite, CuO, Fe2O3, iron ore</td>
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<td>Chalmers</td>
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<td>NiO, Mn3O4, CuO</td>
<td>199</td>
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<td>2011</td>
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<tr>
<td>Chalmers</td>
<td>100 kW-SF</td>
<td>ilmenite, Mn ore, iron ore</td>
<td>116</td>
<td>coal, biochar</td>
<td>2012</td>
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<tr>
<td>Hamburg</td>
<td>25 kW-SF</td>
<td>ilmenite</td>
<td>60</td>
<td>coal</td>
<td>2012</td>
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<tr>
<td>Ohio</td>
<td>2.5 kW-SF</td>
<td>Fe$_2$O$_3$</td>
<td>300</td>
<td>coal</td>
<td>2012</td>
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<tr>
<td>Ohio</td>
<td>25 kW-SF</td>
<td>Fe$_2$O$_3$</td>
<td>530</td>
<td>coal, CH$_4$, syngas</td>
<td>2012</td>
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<tr>
<td>Darmstadt</td>
<td>1 MW-SF</td>
<td>ilmenite</td>
<td>?</td>
<td>coal</td>
<td>2012</td>
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<tr>
<td>Alstom, Windsor</td>
<td>3 MW-SF</td>
<td>CaSO$_4$/CaS</td>
<td>75</td>
<td>coal</td>
<td>2012</td>
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<tr>
<td>Huazhong</td>
<td>5 kW-SF</td>
<td>iron ore</td>
<td>6</td>
<td>coal</td>
<td>2014</td>
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<tr>
<td>Zaragoza</td>
<td>50 kW-SF</td>
<td>ilmenite</td>
<td>?</td>
<td>coal</td>
<td>2014</td>
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</tbody>
</table>
CLC with gaseous fuels: Recent European projects

Innovative Oxygen Carriers Uplifting Chemical-Looping Combustion (INNOCUOUS)
- Natural gas/refinery gas
- Find viable alternatives to Ni
- Over 70 novel compositions examined

Industrial steam generation with 100% carbon capture and insignificant efficiency penalty - Scale-Up of oxygen Carrier for Chemical-looping combustion using Environmentally SuStainable materials (SUCCESS)
- Scale-up of particle production to tonnage scale
- Operation in different units up to 1 MW with natural gas
- Focus on spray-dried CaMn$_{0.775}$Ti$_{0.125}$Mg$_{0.1}$O$_3$ and impregnated Fe- and Cu-based materials
**CLC with gaseous fuels: Reactions in the fuel reactor**

Main overall reaction

\[ \text{CH}_4 + 4\text{Me}_x\text{O}_y \leftrightarrow 4\text{Me}_x\text{O}_{y-1} + \text{CO}_2 + 2\text{H}_2\text{O} \]

Possible reactions

\[ \text{CH}_4 + \text{Me}_x\text{O}_y \leftrightarrow \text{Me}_x\text{O}_{y-1} + \text{CO} + 2\text{H}_2 \]

\[ \text{CO} + \text{Me}_x\text{O}_y \leftrightarrow \text{Me}_x\text{O}_{y-1} + \text{CO}_2 \]

\[ \text{H}_2 + \text{Me}_x\text{O}_y \leftrightarrow \text{Me}_x\text{O}_{y-1} + \text{H}_2\text{O} \]

\[ \text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \]

\[ 2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \]

\[ \text{H}_2\text{O} + \text{C} \leftrightarrow \text{CO} + \text{H}_2 \]

\[ \text{H}_2\text{O} + \text{CO} \leftrightarrow \text{CO}_2 + \text{H}_2 \]
### Monometallic oxygen carriers

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$</th>
<th>Mn$_3$O$_7$/MnO</th>
<th>CuO/Cu</th>
<th>NiO/Ni</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_0$</td>
<td>0.03</td>
<td>0.07</td>
<td>0.20</td>
<td>0.21</td>
<td>Oxygen ratio</td>
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<tr>
<td>Reactivity towards methane</td>
<td>☹</td>
<td>← decreasing</td>
<td>increasing →</td>
<td>☻</td>
<td></td>
</tr>
<tr>
<td>Cost</td>
<td>☻</td>
<td>← decreasing</td>
<td>increasing →</td>
<td>☹</td>
<td></td>
</tr>
<tr>
<td>Health, safety &amp; environm. risks</td>
<td>☻</td>
<td>☻</td>
<td>← decreasing risk</td>
<td>☹</td>
<td></td>
</tr>
<tr>
<td>Thermodynamics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;99.5% conv. for NiO</td>
</tr>
<tr>
<td>Reaction enthalpy w. CH$_4$</td>
<td>☻</td>
<td></td>
<td></td>
<td>CuO exothermic w. CH$_4$</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1085°C for Cu</td>
</tr>
<tr>
<td>CLOU</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CuO/Cu$_2$O</td>
</tr>
</tbody>
</table>
Oxygen carrier development: Performance of impregnated oxygen carriers (CSIC) developed in SUCCESS

**Fe-based OCs**

- Lifetime = 1100 h
- Solid inventory = 890 kg/MW
- $T_{FR} = 900^\circ$C
- $T_{AR} = 950^\circ$C

**Cu-based OCs**

- Lifetime = 2500 h
- Solid inventory = 390 kg/MW
- $T_{FR} = 800^\circ$C
- $T_{AR} = 800^\circ$C

**Fe20Al OCs**

- Lifetime = 5000 h
- Solid inventory = 590 kg/MW
- $T_{FR} = 800^\circ$C
- $T_{AR} = 800^\circ$C

**INNOCOUS benchmark**

- SUCCESS development

**Lifetime**

- Fe-based OCs: 2500 h
- Cu-based OCs: 1100 h
- Fe20Al: 1100 h
- Cu14Al: 5000 h

**Solid inventory**

- Fe-based OCs: 500 kg/MW
- Cu-based OCs: 390 kg/MW
- Fe20Al: 890 kg/MW
- Cu14Al: 590 kg/MW

**Performance of impregnated oxygen carriers (CSIC)** developed in SUCCESS
**CLOU: The case for combined Mn-oxides**

Combined oxides of manganese and certain metal cations can have advantageous thermodynamic and kinetic effects with respect to CLOU.

Some examples:

a) $6(Mn,Fe)_2O_3 \leftrightarrow 4(Mn,Fe)_3O_4 + O_2(g)$

b) $CaMnO_{3-\delta_{ar}} \leftrightarrow CaMnO_{3-\delta_{fr}} + \frac{1}{2}(\delta_{fr}-\delta_{ar}) O_2(g)$

c) $(^{2/3})Mn_7SiO_{12} + 4SiO_2 \leftrightarrow (^{14/3})MnSiO_3 + O_2(g)$

Other cations of interest are Cu, Ni, Mg, which all affect the performance of manganese oxide.
\((Mn_yFe_{1-y})O_x\)

- \(6(Mn,Fe)_2O_3 \leftrightarrow 4(Mn,Fe)_3O_4 + O_2(g)\)
- \(p_{O_2,eq} = 0.05\) atm at \(\approx 800^\circ C\) for \(Mn_2O_3\) (too low?)
- \(p_{O_2,eq} = 0.05\) atm at \(\approx 1330^\circ C\) for \(Fe_2O_3\) (too high?)

![Phase diagram showing the compositions and temperatures for different phases.]
## Oxygen carrier development II: Indicative numbers of performance of spray-dried oxygen carriers without Ni

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Specific solids inventory</th>
<th>Average gas yield, $\gamma_{CO2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO (VITO-A) (ref)</td>
<td>6 kg/MW 57 kg/MW</td>
<td>80-90% 99%</td>
</tr>
<tr>
<td>CaMn$<em>{y}$M$</em>{1-y}$O$_{3-\delta}$</td>
<td>57 kg/MW</td>
<td>86-99%</td>
</tr>
<tr>
<td>Mn$_{3-y}$Mg$_y$O$_4$</td>
<td>57 kg/MW</td>
<td>46-84%</td>
</tr>
<tr>
<td>CuO + support material</td>
<td>57 kg/MW</td>
<td>83-100%</td>
</tr>
<tr>
<td>(Mn$<em>y$Si$</em>{1-y}$)O$_x$</td>
<td>57 kg/MW</td>
<td>73-98%</td>
</tr>
<tr>
<td>Fe$<em>y$Mn$</em>{1-y}$Ti$_x$O$_z$</td>
<td>57 kg/MW</td>
<td>4-76%</td>
</tr>
<tr>
<td>(Fe$<em>y$Mn$</em>{1-y}$)Si$_x$O$_z$</td>
<td>57 kg/MW</td>
<td>45-71%</td>
</tr>
</tbody>
</table>
Testing at industrial conditions: $\text{CaMn}_x\text{Mg}_{1-x}\text{Ti}_y\text{O}_{3-\delta}$ oxygen carrier materials in Vienna’s 120 kW reactor
CLC with kerosene: Some results
10 kW reactor with HVR

Injection principle (diesel)  New injection nozzle (HVR)
10 kW reactor with HVR
**CLC with solid fuels: Main projects**

Novel combustion principle with inherent capture of CO₂ using combined manganese oxides that release oxygen (NoCO2)
- Investigation of natural and synthetic Mn-materials
- Reactor design and modelling

Advanced Coal Chemical-Looping combustion, AIMing at highest performance (ACCLAIM)
- Investigation of coal combustion up to 1MW scale
- Reactor design and modelling
- Technological assessment
CLC with solid fuels: Reactions in the fuel reactor

Char gasification:
C + H\textsubscript{2}O $\leftrightarrow$ CO + H\textsubscript{2}
C + CO\textsubscript{2} $\leftrightarrow$ 2CO

Oxygen carrier reactions
Volatile + Me\textsubscript{x}O\textsubscript{y} $\leftrightarrow$ Me\textsubscript{x}O\textsubscript{y-1} + CO\textsubscript{2} + H\textsubscript{2}O

CO + Me\textsubscript{x}O\textsubscript{y} $\leftrightarrow$ Me\textsubscript{x}O\textsubscript{y-1} + CO\textsubscript{2}
H\textsubscript{2} + Me\textsubscript{x}O\textsubscript{y} $\leftrightarrow$ Me\textsubscript{x}O\textsubscript{y-1} + H\textsubscript{2}O
**CLOU with solid fuels: Reactions in the fuel reactor**

No char gasification!

Oxygen carrier reactions

\[ 2\text{Me}_x\text{O}_y \leftrightarrow 2\text{Me}_x\text{O}_{y-1} + \text{O}_2 (g) \]

\[ \text{C} + \text{O}_2 \leftrightarrow \text{CO}_2 \]

Volatile oxidation

\[ \text{Volatile} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \]
Ores, Minerals, Waste Products

There are many low-cost materials available that could be possibly be used as oxygen carrier for chemical-looping combustion:

1) Ores containing high concentrations of iron oxide or manganese oxide or a mix of both

2) Other ores and minerals which can act as oxygen carrier for example ilmenite
   \[(\text{Fe}_2\text{TiO}_5 + \text{TiO}_2 \leftrightarrow 2\text{FeTiO}_3 + \frac{1}{2}\text{O}_2)\]

3) Industrial waste materials such as iron oxide scales, iron oxide powders etc
Chalmers 100kW unit for solid fuels

$100\,\text{kW}_{th}$
## Operation overview, 100 kW unit

<table>
<thead>
<tr>
<th>Year</th>
<th>Oxygen carrier</th>
<th>Fuel</th>
<th>Duration of operation (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011-2012</td>
<td>IIm</td>
<td>Coal</td>
<td>35</td>
</tr>
<tr>
<td>2013</td>
<td>IIm</td>
<td>Wood char, pet coke</td>
<td>35</td>
</tr>
<tr>
<td>2013</td>
<td>IIm + Mn</td>
<td>Coal, wood char</td>
<td>18</td>
</tr>
<tr>
<td>2013-2014</td>
<td>Tierga iron ore</td>
<td>Coal, wood char</td>
<td>26</td>
</tr>
<tr>
<td>2015</td>
<td>Manganese material</td>
<td>Coal, ...</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Fate of fuel-N
Bituminous coal as fuel

Composition of outbound gaseous fuel-N from FR

- Tierga iron ore
- Ilmenite
- Ilmenite + Mn ore

Composition details:
- NO
- NH3
- N2
Fate of sulfur
Bituminous coal as fuel

Composition of outbound gaseous sulfur from FR

- Tierga iron ore
- Ilmenite + Mn ore
- Ilmenite

SO2  H2S
Operation with OC mixture: Ilmenite (90%) + Mn ore (10%)

Red and blue markers: Cerrejon coal.
Green markers: Polish coal.
Black markers: reference tests, Day 1 only ilmenite as OC
Hydrogen production from gaseous and liquid fuels
– CLR(a) and CLR(s)

Example: CLC and CLR\(\text{(a)}\) with a NiO-based oxygen carrier

CLC in Chalmers 300W reactor, 950\(^\circ\)C, 300 g NiO/Mg-ZrO\(_2\), 0.50 L\(_n\)/min natural gas, 8.40 L\(_n\)/min air, combustion efficiency 99.3%

CLR in Chalmers 300W reactor, 950\(^\circ\)C, 300 g NiO/Mg-ZrO\(_2\), 1.40 L\(_n\)/min natural gas, 0.60 L\(_n\)/min steam, 4.30 L\(_n\)/min air, air factor 30%
Chemical Looping Reforming of tars from biogas

• Process scheme:

• Objectives of our current research:
  - Determination of conversion pathways
    • Resolution of tar conversion behaviour as a function of degree of oxidation/reduction of bed material
  - Rapid screening of bed materials for their tar surrogate conversion capacity
    • Testing of a bed material within a day
    • Tar surrogates used: C$_2$H$_4$, C$_6$H$_6$, C$_7$H$_8$
Screening study with \( C_2H_4 \) as tar surrogate
CLC and CFB

- CLC uses circulating bed material (sand/limestone/ash/other)
- Very common technology for combustion of coal and biomass
- Largest plant: 600 MW_e
- *Today’s state-of-the art CFB design is the natural starting point for a future CLC boiler.*
Oxygen carrier cost

\[
CC_{OC} = \frac{C_{OC} \cdot SI}{SE \cdot \eta_{CO_2} \cdot \tau}
\]

- \(CC_{OC}\) = cost of oxygen carrier, €/tonne CO\(_2\)
- \(C_{OC}\) = cost of oxygen carrier, €/tonne
- \(SI\) = solids inventory, tonne oxygen carrier/MW\(_{th}\)
- \(SE\) = specific emission, tonne CO\(_2\)/MWh\(_{th}\)
- \(\tau\) = estimated life of oxygen carrier, h

<table>
<thead>
<tr>
<th></th>
<th>ilmenite</th>
<th>manganese ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE, tonne/MWh(_{th})</td>
<td>0.334</td>
<td>0.334</td>
</tr>
<tr>
<td>SI, tonne/MW(_{th})</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>(\eta_{CO_2})</td>
<td>98%</td>
<td>98%</td>
</tr>
<tr>
<td>(\tau), h</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>(C_{OC}), €/tonne oxygen carrier</td>
<td>175</td>
<td>225</td>
</tr>
<tr>
<td>(CCC_{OC}), €/tonne CO(_2)</td>
<td>2.0</td>
<td>5</td>
</tr>
</tbody>
</table>

Ilmenite 100-300 h lifetime (estimated to 700 h in 100 kW unit)
Resulting cost: 1.3-4 €/tonne CO\(_2\)
# Cost of carbon capture

<table>
<thead>
<tr>
<th>Type of cost</th>
<th>estimation, €/tonne CO₂</th>
<th>range, €/tonne CO₂</th>
<th>Efficiency penalty, %</th>
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<tbody>
<tr>
<td>CO₂ compression</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Oxy-polishing</td>
<td>6.5</td>
<td>4-9</td>
<td>0.5</td>
</tr>
<tr>
<td>Boiler cost</td>
<td>1</td>
<td>0.1-2.3</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen carrier</td>
<td>2</td>
<td>1.3-4</td>
<td>-</td>
</tr>
<tr>
<td>Steam and hot CO₂ fluidization</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Coal grinding</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Lower air ratio</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Total</td>
<td>20</td>
<td>15.9-25.8</td>
<td>3.9</td>
</tr>
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**Outlook**

- For gas, a larger demo-plant could be viable. CLC may be a suitable process in niche markets. However, non-Ni based materials need to be developed. Preferably with CLOU effect.

- For liquid fuels, the process needs to be demonstrated with heavier oil fractions for longer time periods.

- For solid fuels, CLC is a potential breakthrough technology, with low costs and high capture rates. Focus should be on developing cheap materials with some CLOU properties.

- For hydrogen production, CLR(s) seems highly promising, but limited experimental work on the process.

- Use of CLR for reforming of tars from biomass gasification could have a potential as a fuel processing technology.