Chemical Looping Technology

by

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ICEST
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Number of Publications with “Chemical Looping” in the Titles on Google Scholars
Combustion System

Schematic Diagram of a PCC-based Power Plant

Steam Out

Super heater

Preheater

Lime slurry

Economizer

Bag House or ESP

ID Fan

Stack

Coal Hopper

Coal Receiving

Ash Hopper

Water Injection

Ash/FGD Disposal

The Ohio State University
Gasification System

IGCC Efficiency: 33% with CO₂ control

Steigel and Ramezan, 2006
Chemical Looping Systems with CO₂ Generation or Separation

Two typical types of looping reaction systems

<table>
<thead>
<tr>
<th>Oxygen Carrier (Type I)</th>
<th>CO₂ Carrier (Type II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me/MeO, MeS/MeSO₄</td>
<td>MeO/MeCO₃</td>
</tr>
</tbody>
</table>

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Reduction → Oxidization 

- **Reduction**: CO₂/H₂O → Me/MeS → MeO/MeSO₄ → Fuel
- **Oxidization**: H₂/Flue Gas → MeO/MeSO₄ → Steam/Air

Carbonation → Calcination 

- **Carbonation**: CO₂ Lean → MeCO₃ → CO₂ Rich
- **Calcination**: MeO → Heat → CO₂

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Chemical Looping Systems with Non-CO$_2$ Generation

Syngas CO + H$_2$

chemical looping

CH$_4$ or other Carbonaceous Fuels

Chemicals

CH$_4$ or other Carbonaceous Fuels

Solar Energy/ Nuclear Energy

H$_2$O $\rightarrow$ H$_2$ + O$_2$

chemical looping
CO₂ Capture from Fossil Energy – Technological Solutions

CO₂ Capture Targets:
- 90% CO₂ Capture
- <10% increase in COE (IGCC)
- <35% increase in COE (PC)

Source: José D. Figueroa, National Energy Technology Laboratory (NETL), USDOE
Comparison of OSU SYNGAS and Coal Direct Chemical Looping (CDCL) Processes with Traditional Coal to Hydrogen/Electricity Processes

Assumptions used are similar to those adopted by the USDOE baseline studies.
Exergy Analysis on Hydrogen Production

I. Contional Process
Exergetic Efficiency
\[
\frac{322.9}{407.7} = 79.2\%
\]

II. Chemical Looping Process
Exergetic Efficiency
\[
\frac{396.9}{(407.7 + 12.41)} = 94.5\%
\]
Economics of Chemical Looping Process

- Retrofit to conventional coal combustion process
- CDCL replaces existing PC boiler
  - Additional equipment for CO₂ compression and transportation required
- Techno-Economic analysis performed comparing CDCL to Base Plant with no CO₂ capture and 90% CO₂ capture via post-combustion MEA process


The CDCL process can be also used for high efficient hydrogen production
Oxygen Carrier Particle Development

Ellingham Diagram: Selection of Primary Metal
Recyclability of Pure Fe$_2$O$_3$

Recyclability of Composite Fe$_2$O$_3$

100 Cycle Pellet Reactivity

100 Cycle Pellet Strength
Structures of Iron Oxide

\[ \text{FeO} \]

\[ \text{Fe}_3\text{O}_4 \]

**NaCl Type**
- oxygen close-packed cubic pattern
- iron occupy all octahedral interstices

**inverse Spinel Type**
- octahedral interstices
- 1/2 occupation rate
- tetrahedral interstices
- 1/8 occupation rate
Core-Shell Particle Formation through Cyclic Gas-Solid Reactions

\[
4\text{Fe}_{(s)} + 3\text{O}_2_{(g)} \rightarrow 2\text{Fe}_2\text{O}_3_{(s)} \tag{1}
\]

\[
\text{Fe}_2\text{O}_3_{(s)} + 3\text{H}_2_{(g)} \rightarrow 2\text{Fe}_{(s)} + 3\text{H}_2\text{O}_{(g)} \tag{2}
\]

If the cyclic reactions proceed through Fe cation diffusion, core-shell structure forms, e.g. Fe2O3 + Al2O3.

If the cyclic reactions proceed through O anion diffusion, core-shell structure does not form, e.g. Fe2O3 + TiO2.

*Al2O3* is only a physical support, while TiO2 alters the solid-phase ionic diffusion mechanism.
Fe$_2$O$_3$+Al$_2$O$_3$ VS Fe$_2$O$_3$+TiO$_2$

after 50 redox cycles

Raw TiO$_2$-Supported Particle

after 50 redox cycles

TiO$_2$-Supported Particle after 50 Redox Cycles
Evolution in Cyclic Binary Metal/Metal Oxide Systems

I. FeTi

Original cross section

Oxidation: cross section

Oxidation: surface with platelets and whiskers

EDS mapping of oxidized FeTi

Fe Ka1

Ti Ka1

O Ka1
Role of Support – Oxidation of Fe and Fe/TiO$_2$

DFT Calculation

Energy barrier for O$^{2-}$ can be reduced after support addition

Oxygen anion transfer in Wüstite and Ilemnite
Modes of CFB Chemical Looping Reactor Systems

**Mode 1** - reducer: fluidized bed or co-current gas-solid (OC) flows

**Mode 2** - reducer: gas-solid (OC) counter-current dense phase/moving bed flows

Chalmers University CLC System

OSU CLC System

Chemical Looping Reactor Design

$\text{FeO}_x \rightarrow \text{CO}_2/\text{H}_2\text{O}$

$\text{FeO}_y \rightarrow \text{CO}/\text{H}_2$

$x > y$

Fluidized Bed vs. Moving Bed

- Maximum Solid Conversion
  - Fluidized Bed: 11.11%
  - Moving Bed: 50.00%

- Gas Velocity
  - Fluidized Bed: $U_{mfv}$
  - Moving Bed: $< U_{mfv}$

- Particle Size
  - Fluidized Bed: Small
  - Moving Bed: Large

Graph showing PCO2/PCO vs. Temperature (C) for FeO, FeO, FeO, FeO.
<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Data</td>
<td>Lab</td>
<td>CFB 120</td>
<td>Lab</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CFB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300W</td>
<td>25 kW</td>
<td>Moving bed + H₂</td>
</tr>
<tr>
<td>NiO/MgAl₂O₄</td>
<td>MgAl₂O₄</td>
<td>11784</td>
<td>CuO/Al₂O₃</td>
</tr>
<tr>
<td>NiO/MgAl₂O₄</td>
<td>MgAl₂O₄</td>
<td>1309</td>
<td>CuO/Al₂O₃</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>Fe₂O₃</td>
<td>MgAl₂O₄</td>
<td>Composite Fe₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃/Al₂O₃</td>
<td>MgAl₂O₄</td>
<td>300W</td>
<td>Moving bed + H₂</td>
</tr>
</tbody>
</table>

| Air Flow Rate @1000 MWth and 10% Excess (mol/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Volumetric Air Flow Rate at 1 atm and 900 ºC (m³/s) | < 3,000 ton/hour |

| Particle Circulation Rate @ 1000 MWth (kg/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Reducer Solids Inventory (tonne) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Oxidizer Solids Inventory (tonne) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Medium Particle Size (μm) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Particle Density (g/cm³) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Ut (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Uc (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Use (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Typical Riser Superficial Gas Velocity (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Bed Area Turbulent Section (if Required) at 1 atm (m²) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Bed Area Required for Riser Section at 1 atm (m²) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Corresponding Riser Diameter (m) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |

| Solids Flux at 1 atm (kg/m²s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Number of Beds Needed given 8 m ID Riser | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Number of Beds Needed given 1.5 m ID Riser | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Ug for a Single 1.5 m ID Riser at 1 atm (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Ug for a Single 8 m ID riser at 1 atm (m/s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Required Pressure for a Single 1.5m ID Riser (atm) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Solids Flux for a Single 1.5 m ID Riser (kg/m²s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Required Pressure for a Single 8 m ID Riser (atm) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
| Solids Flux for a Single 8 m ID Riser (kg/m²s) | 4000 – 10000 kg/s or 14,000 – 36,000 ton/hour |
OSU Chemical Looping Process Development

Scale

Time

Particle

Fixed Bed Tests

Bench Scale Tests

Sub-Pilot SCL Integrated Tests
25 kW<sub>th</sub> OSU Sub-Pilot CDCL Demonstration for Coal Combustion

- Fully assembled and operational
- 500+ hours of operational experience
- 200+ hours continuous successful operation
- Smooth solid circulation
- Confirmed non-mechanical gas sealing under reactive conditions
- 13 test campaigns completed
200+ Hour Sub-Pilot Continuous Run - Sample Results

Once-Through Reducer Carbon Conversion Profile

- Continuous steady >90% carbon conversion from reducer throughout all solid fuel loading (5-25 kWth)
- <0.25% CO and CH₄ in reducer outlet = full fuel conversion to CO₂/H₂O
- <0.1% CO, CO₂, and CH₄ in combustor = negligible carbon carry over, nearly 100% carbon capture

Reducer Gas Concentration Profile

Reducer NOₓ/SOₓ Analysis

<table>
<thead>
<tr>
<th></th>
<th>Reducer</th>
<th>Combustor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOₓ (ppm)</td>
<td>190-1170</td>
<td>0 - 70</td>
</tr>
<tr>
<td>NOₓ (lb/MMBTU)</td>
<td>0.100 – 0.200*</td>
<td>~ 0</td>
</tr>
</tbody>
</table>

*Conventional PC Boiler NOₓ Generation = 0.2 – 0.5 lb/MMBTU

Combustor Gas Concentration Profile
Recent Unit Demonstration

- Over 300+ hours operation
- Average CO₂ purity generated throughout run > 99%
- >99.99% hydrogen purity at steady state
- Steady Pressure Profile throughout Test run

Differential Pressure Profile
Concluding Remarks

• Chemical Looping embodies all elements of particle science and technology - particle synthesis, reactivity and mechanical properties, flow stability and contact mechanics, gas-solid reaction engineering...

• OSU processes characterized by the moving bed reducer configuration are compact in design and high efficiency in operation. Success achieved in the operation of 200+ hour continuous sub-pilot CDCL run using coal and progress made in the on-going SYNGAS Chemical Looping pilot demonstration reflect the likelihood of commercialization of these technologies in the near future.
My Graduate Students and Research Associates

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