Coal Direct Chemical Looping (CDCL) Retrofit to Pulverized Coal Power Plants for In-Situ CO₂ Capture

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The Ohio State University

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Clean Coal Research Laboratory at The Ohio State University

**Coal-Direct Chemical Looping**
- Cold Flow Model
- Sub-Pilot Scale Unit

**Syngas Chemical Looping**
- Sub-Pilot Scale Unit
- 250kW\textsubscript{th} Pilot Unit (Wilsonville, Alabama)

**Calcium Looping Process**
- Sub-Pilot Unit

**CCR Process**
- 120kW\textsubscript{th} Demonstration Unit

**F-T Process**
- HPHT Slurry Bubble Column
Coal Direct Chemical Looping Retrofit to Pulverized Coal Power Plants for In-Situ CO₂ Capture

Period of Performance: 2009-2013

Total Funding ($3.98 million):

- U.S. Department of Energy, National Energy Technology Laboratory ($2.86 million)
- Ohio Coal Development Office ($300,000)
- The Ohio State University ($487,000)
- Industrial Partners ($639,000)

Major Tasks:

- Phase I: Selection of iron-based oxygen carrier particle - COMPLETE
- Phase II: Demonstration of fuel reactor (coal char and volatile conversion) at 2.5 kWₜ scale and cold flow model study - COMPLETE
- Phase III: Demonstration of integrated CDCL system at 25 kWₜ scale and techno-economic analysis of CDCL process – IN PROGRESS

This material is based upon work supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-NT0005289 and the Ohio Coal Development Office of the Ohio Air Quality Development Authority under Contract Number CDO-D-08-02.
Coal-Direct Chemical Looping Process Development
Chemical Looping Process Concept

Reducer: $\text{MeO}_x + \text{Fuel} \rightarrow \text{MeO}_y + \text{CO}_2 + \text{H}_2\text{O}$

Combustor: $\text{MeO}_y + \text{Air} \rightarrow \text{MeO}_x + \text{Heat}$

Overall: Coal + Air $\rightarrow$ CO$_2$ + H$_2$O + Heat

$y < x$
Coal-Direct Chemical Looping Process for Retrofit/Repower


The CDCL process can be also used for high efficient hydrogen production.
**OSU CDCL Process Development**

**Phase I**
More than 300 types of particle tested. A low cost, robust, highly reactive, and O2-conductive composite particle is obtained.

**Phase II**
300+ hours operation with >99% volatile conversion, >95% char conversion

**Phase III**
640+ hours operation with >99% solid fuel conversion, smooth solid circulation, gas sealing and in-situ ash removal

- TGA
- Fixed Bed Tests
- Bench Scale Tests
- Cold Model Tests
- Sub-Pilot Integrated Tests

Fuel Tested:
- Syngas
- Natural gas
- Biomass
- Met coke
- Lignite char
Phase III Results
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

<table>
<thead>
<tr>
<th>Reducer</th>
<th>Mode 1</th>
<th>Mode 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation Regime</td>
<td>Bubbling, turbulent, fast fluidized, or spouted bed</td>
<td>Moving packed, or multistage fluidized bed</td>
</tr>
<tr>
<td>Gas Solid Contacting Pattern</td>
<td>Mixed/Cocurrent</td>
<td>Countercurrent</td>
</tr>
<tr>
<td>Controllability on Fuel and OC Conversions</td>
<td>Poor, due to back mixing and gas channeling</td>
<td>High</td>
</tr>
<tr>
<td>Maximum Iron oxide Conversion</td>
<td>11.1% (to Fe₃O₄)</td>
<td>&gt;50% (to Fe &amp; FeO)</td>
</tr>
<tr>
<td>Solids circulation rate</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Ash Separation Technique</td>
<td>Separate Step</td>
<td>In-Situ</td>
</tr>
<tr>
<td>Subsequent Hydrogen Production</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Particle size, µm</td>
<td>100-600</td>
<td>1000-3000</td>
</tr>
<tr>
<td>Reducer gas velocity*, m/s</td>
<td>&lt;0.4</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>Reactor size for the same fuel processing capacity</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Hydrodynamics effects on scaling up</td>
<td>Large</td>
<td>Small</td>
</tr>
</tbody>
</table>

*Reducer gas velocity calculated at 900 °C, 1 atm

Reducer Reactor Design

- **Stage 1** for gaseous volatiles
- **Stage II** for coal char

**Enhancer Gas**

- $4 \text{CO} + 4 \text{FeO}_x \rightarrow 4 \text{FeO}_{x-1} + 4 \text{CO}_2$
- $2 \text{CO}_2 + 2\text{C} \rightarrow 4 \text{CO}$
- $2 \text{CO} + 2 \text{FeO}_x \rightarrow 2 \text{FeO}_{x-1} + 2 \text{CO}_2$
- $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$
- $\text{H}_2 + \text{FeO} \rightarrow \text{Fe} + \text{H}_2\text{O}$
- $\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$

**Particle reduction:**

- $\text{CH}_4 + \text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{FeO}$

**Coal devolatilisation:**

- Coal $\rightarrow$ C + $\text{C}_x\text{H}_y$

**Char gasification and particle reduction:**

- $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$
- $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
- $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$

**Reaction Initiation:**

- $\text{H}_2 + \text{FeO} \rightarrow \text{Fe} + \text{H}_2\text{O}$
- $\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$

Phase III: Integrated CDCL System Testing

- Fuel Design Input: 25 kW\textsubscript{th}
- Fully assembled and operational
- 640+ hours of operational experience
- 200+ hours continuous successful operation
- Smooth solid circulation
- Confirmed non-mechanical gas sealing under reactive conditions
## Phase III: Integrated CDCL System Testing

### Fuel Feedstock Studied

<table>
<thead>
<tr>
<th>Fuel Feedstock</th>
<th>Type</th>
<th>Fuel Flow (lb/hr)</th>
<th>Enhancer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syngas</td>
<td>CO/H₂</td>
<td>0.1-1.71</td>
<td>N/A</td>
</tr>
<tr>
<td>Coal volatile/ Natural Gas</td>
<td>CH₄</td>
<td>0.1-0.4</td>
<td>N/A</td>
</tr>
<tr>
<td>Coal char</td>
<td>Lignite</td>
<td>0.7-2.0</td>
<td>CO₂/H₂O</td>
</tr>
<tr>
<td></td>
<td>Metallurgical Coke</td>
<td>0.05-3</td>
<td>CO₂/H₂O</td>
</tr>
<tr>
<td>Coal</td>
<td>Sub-Bituminous</td>
<td>0.05-7.38 (25 kWₜₜ)</td>
<td>CO₂/H₂O</td>
</tr>
<tr>
<td></td>
<td>Bituminous</td>
<td>0.05-3</td>
<td>CO₂/H₂O</td>
</tr>
<tr>
<td></td>
<td>Anthracite</td>
<td>0.2-0.7</td>
<td>CO₂/H₂O</td>
</tr>
<tr>
<td></td>
<td>Lignite</td>
<td>2.84-6.15 (20 kWₜₜ)</td>
<td>CO₂</td>
</tr>
<tr>
<td>Biomass</td>
<td>Wood pellets</td>
<td>0.1</td>
<td>CO₂</td>
</tr>
<tr>
<td>Coke</td>
<td>Petroleum Coke</td>
<td>1.98-5.95</td>
<td>CO₂/H₂O</td>
</tr>
</tbody>
</table>

- Combined >940 hours of sub-pilot operational experience
- Achieved high conversion on all fuel feedstock
- Successful results for all coal/coal derived feedstock tested
Phase III: Integrated CDCL System Testing

200+ Sub-Pilot Continuous Run Results
Once-Through Reducer Carbon Conversion Profile

- Continuous steady carbon conversion from reducer throughout all solid fuel loading (5-25 kW<sub>th</sub>)
- <0.25% CO and CH<sub>4</sub> in reducer outlet = full fuel conversion to CO<sub>2</sub>/H<sub>2</sub>O
- <0.1% CO, CO<sub>2</sub>, and CH<sub>4</sub> in combustor = negligible carbon carry over, nearly 100% carbon capture
## Phase III: Integrated CDCL System Testing

Parametric Studies Performed

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Fuel Flow (g/min)</th>
<th>Enhancing Gas Flow (L_n/min)</th>
<th>CO₂ Purity (%)</th>
<th>Reducer Carbon Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subbituminous</td>
<td>23</td>
<td>5.0, CO₂</td>
<td>99.7%</td>
<td>96.9%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>23</td>
<td>3.0, CO₂</td>
<td>99.6%</td>
<td>96.5%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>22</td>
<td>1.0, CO₂</td>
<td>99.0%</td>
<td>88.0%</td>
</tr>
<tr>
<td>Subbituminous, lower port</td>
<td>22</td>
<td>1.0, CO₂</td>
<td>98.0%</td>
<td>~100%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>32</td>
<td>5.0, CO₂</td>
<td>99.7%</td>
<td>96.9%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>46</td>
<td>5.0, CO₂</td>
<td>99.7%</td>
<td>96.9%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>56</td>
<td>5.0, CO₂</td>
<td>99.5%</td>
<td>96.9%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>68</td>
<td>5.0, CO₂</td>
<td>98.5%</td>
<td>99.9%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>15</td>
<td>5.0, H₂O</td>
<td>98.9%</td>
<td>97.8%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>22</td>
<td>5.0, H₂O</td>
<td>94.0%</td>
<td>99.8%</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>38</td>
<td>5.0, H₂O</td>
<td>99.3%</td>
<td>96.3%</td>
</tr>
<tr>
<td>Lignite</td>
<td>22</td>
<td>5.0, CO₂</td>
<td>99.6%</td>
<td>97.7%</td>
</tr>
<tr>
<td>Lignite</td>
<td>46</td>
<td>5.0, CO₂</td>
<td>99.6%</td>
<td>96.3%</td>
</tr>
</tbody>
</table>

Parameters studied include:
- Fuel flow rate
- Fuel type
- Enhancer gas type (CO₂, H₂O)
- Enhancer gas flow rate
- Injection location

Phase III: Integrated CDCL System Testing

Unsteady State Studies Performed

Effect of enhancing gas on approach to steady state

Effect of coal injection on system temperatures and pressures

Bayham et al., *Energy Fuels* (2013) 27, 1347–1356
Supporting Work: Phases I, II
### Phase I: Oxygen Carrier Particle Development

#### Primary Metal Properties

<table>
<thead>
<tr>
<th>Redox Pair</th>
<th>Fe₂O₃-Fe₃O₄</th>
<th>Fe₂O₃-Fe</th>
<th>CuO-Cu₂O</th>
<th>CuO-Cu</th>
<th>CaSO₄-CaS</th>
<th>Mn₃O₄-MnO</th>
<th>NiO-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducer Mode</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>1566-1538</td>
<td>1566-1535</td>
<td>1326-1235</td>
<td>1326-1085</td>
<td>1460-2525</td>
<td>1567-1650</td>
<td>1955-1455</td>
</tr>
<tr>
<td>Cost, $/ton¹</td>
<td>319</td>
<td>319</td>
<td>7679</td>
<td></td>
<td>27</td>
<td>1000</td>
<td>21804</td>
</tr>
<tr>
<td>Recyclability Test, cycles</td>
<td>&gt;100</td>
<td>&gt;100³</td>
<td>&gt;33⁴</td>
<td></td>
<td>&lt;5</td>
<td>5⁵</td>
<td>5⁵</td>
</tr>
<tr>
<td>Theoretical OCC, kg O₂/kg</td>
<td>0.033</td>
<td>0.3</td>
<td>0.1</td>
<td>X</td>
<td></td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Conversions²</td>
<td>50-60%</td>
<td>60%</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Support, %</td>
<td>X</td>
<td>40-60</td>
<td>60-80</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual OCC, kg O₂/kg</td>
<td>0.06-0.11</td>
<td>0.012-0.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushing Strength, N</td>
<td>&gt;60</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Primary material cost, dollars in 2010 from US Geological Survey;
2. The actual conversion limited by both thermodynamics and kinetics;
Phase I: Oxygen Carrier Particle Development

Ellingham Diagram: Selection of Primary Metal

\[ \Delta G, \text{kcal/mol } O_2 \]

- \( \text{Mn}_2\text{O}_3 \)
- \( \text{CuO} \)
- \( \text{Cu}_2\text{O} \)
- \( \text{Fe}_2\text{O}_3 \)
- \( \text{NiO} \)
- \( \text{CaSO}_4 \)
- \( \text{Fe}_3\text{O}_4 \)
- \( \text{H}_2\text{O} \)
- \( \text{FeO} \)
- \( \text{CO} \)
- \( \text{FeTiO}_3 \)

\[ \text{P}_{\text{O}_2} = 0.21 \text{ atm, Ambient Air} \]
\[ \text{P}_{\text{O}_2} = 0.01 \text{ atm} \]

\[ \frac{\text{P}_{\text{CO}}}{\text{P}_{\text{CO}_2}} = 5/995 \]

Mode 1 Range

Mode 2 Range

Full Air Conversion

Full Fuel Conversion

Hydrogen Production
Phase I: Oxygen Carrier Particle Development

OSU Particle (over 300 particles) Performance

High Reactivity

High Carbon Deposition Tolerance

High Recyclability

High Pellet Strength
Phase II: Reducer Reactor Design and Testing

Phase Diagram – Thermodynamic Restrictions

Shaded area is not reducer operation zone

Operating Equation for Moving Bed Reducer

Countercurrent moving bed: straight operation line with negative slope

Similarly, Concurrent fluidized bed: straight operation with positive slope

Phase II: Reducer Reactor Design and Testing

Operation Diagram

The operating line is straight when feeding ratio is fixed: solid line represents countercurrent moving bed operation, dash line represents co-current fluidized bed operation.

**Phase II: Reducer Reactor Design and Testing**

**Stage I – Volatile Conversion**

**Stage II – Char Conversion**

---

**Summary of Bench Scale Unit Testing Results**

<table>
<thead>
<tr>
<th>Type of Fuel</th>
<th>Stage I - Coal Volatile</th>
<th>Stage II - Coal Char</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂, H₂, CH₄</td>
<td>Lignite char</td>
<td>Bituminous</td>
</tr>
<tr>
<td>Fuel Conversion, %</td>
<td>99.9</td>
<td>99.8</td>
<td>94.9</td>
</tr>
<tr>
<td>CO₂ purity, %</td>
<td>99.9</td>
<td>98.8</td>
<td>99.23</td>
</tr>
</tbody>
</table>

- Conducted in co-current mode, no gas analyzer was used to monitor the CO₂ purity.

300+ hours operation with >95% conversions of various types of fuel.
Techno-Economic Analysis
Systems Analysis Methodology

- Performance of CDCL plant modeled using Aspen Plus® software
- Results compared with performance of conventional pulverized coal (PC) power plants with and without CO₂ capture
  - U.S. Department of Energy, National Energy Technology Laboratory; *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity* (November 2010)
    - Case 11 – Supercritical PC plant without CO₂ capture ("Base Plant")
    - Case 12 – Supercritical PC plant with MEA scrubbing system for post-combustion CO₂ capture ("MEA Plant")
- All plants evaluated using a common design basis
  - 550 MWₑ net electric output
  - Illinois No. 6 coal: 27,113 kJ/kg (11,666 Btu/lb) HHV, 2.5% sulfur, 11.1% moisture as received
  - Supercritical steam cycle: 242 bar/593°C/593°C (3,500 psig/1,100°F/1,100°F)
  - ≥ 90% CO₂ capture efficiency (MEA and CDCL Plants)
  - CO₂ compressed to 153 bar (2,215 psia)
- Results are preliminary, will be used to guide further design improvements
Process Simulation and Analysis

### Aspen Plus® Modeling Results

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>MEA Plant</th>
<th>CDCL Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coal Feed, kg/h</strong></td>
<td>185,759</td>
<td>256,652</td>
<td>207,072</td>
</tr>
<tr>
<td><strong>CO₂ Emissions, kg/MWh(_{\text{net}})</strong></td>
<td>802</td>
<td>111</td>
<td>28</td>
</tr>
<tr>
<td><strong>CO₂ Capture Efficiency, %</strong></td>
<td>0</td>
<td>90.2</td>
<td>97.0</td>
</tr>
<tr>
<td><strong>Solid Waste,(^a) kg/MWh(_{\text{net}})</strong></td>
<td>33</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
<td><strong>Net Power Output, MW(_{e})</strong></td>
<td>550</td>
<td>550</td>
<td>548</td>
</tr>
<tr>
<td><strong>Net Plant HHV Heat Rate, kJ/kWh (Btu/kWh)</strong></td>
<td>9,165 (8,687)</td>
<td>12,663 (12,002)</td>
<td>10,248 (9,713)</td>
</tr>
<tr>
<td><strong>Net Plant HHV Efficiency, %</strong></td>
<td>39.3</td>
<td>28.5</td>
<td>35.2</td>
</tr>
<tr>
<td><strong>Energy Penalty,(^b) %</strong></td>
<td>-</td>
<td>27.6</td>
<td>10.6</td>
</tr>
</tbody>
</table>

\(^a\)Excludes gypsum from wet FGD. \(^b\)Relative to Base Plant; includes energy for CO₂ compression.
## First-Year Cost of Electricity

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>MEA Plant</th>
<th>CDCL Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-Year Capital ($/MWh)</td>
<td>31.7</td>
<td>59.6</td>
<td>44.2</td>
</tr>
<tr>
<td>Fixed O&amp;M ($/MWh)</td>
<td>8.0</td>
<td>13.0</td>
<td>9.6</td>
</tr>
<tr>
<td>Coal ($/MWh)</td>
<td>14.2</td>
<td>19.6</td>
<td>15.9</td>
</tr>
<tr>
<td>Variable O&amp;M ($/MWh)</td>
<td>5.0</td>
<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
<td><strong>TOTAL FIRST-YEAR COE ($/MWh)</strong></td>
<td><strong>58.9</strong></td>
<td><strong>100.9</strong></td>
<td><strong>78.4</strong></td>
</tr>
</tbody>
</table>

$\Delta = +71\%$

$\Delta = +33\%$

Techno-Economic Analysis of a Coal Direct Chemical Looping Power Plant with Carbon Dioxide Capture.
Accomplishments

Completed

• >640 hrs of integrated 25 kW\textsubscript{t} sub-pilot scale operations achieving 90-99+% coal conversion

• The longest demonstration to date is >200 hours continuous with smooth operations and high fuel conversions.

• The CDCL process has the potential to meet DOE’s goal of \(\geq 90\%\) CO\textsubscript{2} capture at no more than a 35% increase in cost of electricity

Future work

• Test other fuels such as woody biomass and corn stover

• Work closely with B&W to scale-up to pilot plant (3 MW\textsubscript{th})
Partners

Government Agencies

• DOE/NETL: Bruce Lani, Timothy Fout, David Lang
• OCDO/ODSA: Chad Smith, Greg Payne

Industrial Collaborators

• Babcock & Wilcox (B&W): Tom Flynn, Luis Vargas, Doug Devault, Bartev Sakadjian and Hamid Sarv
• Clear Skies Consulting LLC: Bob Statnick
• CONSOL Energy: Dan Connell, Richard Winschel, and Steve Winberg
• Air Products: Robert Broekhuis, Bernard Toseland
• Shell/CRI
Thanks