Application of Chemical Looping with Spouting Fluidized Bed for Hydrogen-Rich Syngas Production from Catalytic Coal Gasification

Award # DE-FE0024000

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Traditional Coal Gasification

Limitations

- ASU & external water gas shift reaction
- Narrowed temperature range, and limited availability of sensible heat
- Extensive CH₄ and tar formation for low temperature gasification
- Low H₂ / CO ratio, and complicated process for slag discharge and waste water treatment

Characteristics of different gasification process

<table>
<thead>
<tr>
<th>Process</th>
<th>Outlet Gas Temperature (°C)</th>
<th>Oxidant Demand</th>
<th>Steam Demand</th>
<th>Carbon Conversion</th>
<th>CH₄ concentration/tar</th>
<th>H₂/CO (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moving/fixed bed</td>
<td>425-650</td>
<td>low</td>
<td>high</td>
<td>low</td>
<td>&gt;4% / high</td>
<td>2</td>
</tr>
<tr>
<td>Fluidized bed</td>
<td>900-1050</td>
<td>moderate</td>
<td>moderate</td>
<td>moderate</td>
<td>&gt;2%/ low</td>
<td>0.6~0.7</td>
</tr>
<tr>
<td>Entrained flow</td>
<td>1250-1600</td>
<td>high</td>
<td>low</td>
<td>High&gt;95%</td>
<td>&lt;1000ppm/No</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Project Objectives

- **Develop an transformative catalytic coal gasification technology**
  - Avoid of ASU and external WGS
  - High temperature gasification to improve cold gas efficiency
  - Improve H₂/CO and eliminate CH₄ formation

- **Multi-function oxygen carrier development**
  - Oxygen & heat carrier
  - Catalyst to improve gasification and WGS reaction

- **Demonstration of novel spouted bed reactor**
  - Combination of gasification and WGS reaction
  - Avoid of ash melting
  - Ash separation
Why Red Mud – The Properties

Physical Characteristics

- Particle size: **80% particles <10μm**
- Concentration: **50-65%**
- pH: 12-13.5 (need neutralization)

Chemical Composition (Dry)

- **Fe₂O₃**: 30%-60%
- **Al₂O₃**: 10%-20%
- **SiO₂**: 3%-50%
- **TiO₂**: 2%-25%
- **Na₂O**: 2%-10%
- **CaO**: 2%-8%

Active composition

Support

Bonding

Direct Granulation (spray dry method)

Calcination

Cost-effective OC

Cost-effective OC (1100°C)

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No mechanical grinding & slurry preparation needed

No additive needed
Catalytic Function for In-situ WGS

Gas residence time: 6s (973 K)
Inlet gas: 10% CO + 30% Steam

\[ \log J_{eq} = -2.4198 + 0.0003855T + \frac{2180.6}{T} \]
**OC/Fuel Ratio**

### Gas Composition

- Volume Fraction, \( Y_i, \% \)
- OC/fuel Ratio
- Syngas Yield L/g Fuel

Number in brackets: \( H_2/CO \) ratio

### Fuel Conversion Rate

- Instantaneous rate of conversion (g/g/s)
- Degree of Carbon conversion (Xc)

- RM 100 g, Char 0.8-3.2 g
- 950 °C, 50 vol.% WV
Large Quantity Production

- Raw Material
- Fire in Kiln
- Clinker
- Crush Sieve
- OC Product

Strength: 3.10 N
Cost: $87-113/ton

OC Conversion vs. Time Graph:
- RM Kiln 1250
- RM Kiln 1300
- RM FG 1150

Conditions: 950°C, 20% CO
The Leachability

- Water Leaching (ASTM D-3987)

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Received</td>
<td>237.3</td>
<td>0.9</td>
<td>0.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Calcined</td>
<td>36.4</td>
<td>3.8</td>
<td>3.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

pH(calcined)=11 < EPA limit 12.5

- Acid Leaching (TCLP - Toxicity Characteristic Leaching Procedure)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>As</th>
<th>Se</th>
<th>Ag</th>
<th>Cd</th>
<th>Ba</th>
<th>Hg</th>
<th>Pb</th>
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</thead>
<tbody>
<tr>
<td>Received</td>
<td>0.17</td>
<td>0.01</td>
<td>0.05</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.01</td>
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<tr>
<td>Calcined</td>
<td>0.38</td>
<td>0.02</td>
<td>0.05</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>&lt;0.01</td>
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<tr>
<td>EPA Limits</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>100</td>
<td>0.2</td>
<td>5</td>
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</table>
## Grindability Comparison

### OPC

<table>
<thead>
<tr>
<th>Grind Time (min)</th>
<th>&lt;125 um (g)</th>
<th>125-500 um (g)</th>
<th>&gt;500 um (g)</th>
<th>Total Before Sieve (g)</th>
<th>Total After Sieve (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>500</td>
<td>500</td>
<td>500</td>
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<tr>
<td>15</td>
<td>253</td>
<td>246</td>
<td>1</td>
<td>500</td>
<td>500</td>
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<tr>
<td>30</td>
<td>341</td>
<td>159</td>
<td>0</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>45</td>
<td>399</td>
<td>101</td>
<td>0</td>
<td>500</td>
<td>500</td>
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<tr>
<td>60</td>
<td>443</td>
<td>56</td>
<td>0</td>
<td>499</td>
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<tr>
<td>75</td>
<td>470</td>
<td>29</td>
<td>0</td>
<td>499</td>
<td>499</td>
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<tr>
<td>90</td>
<td>488</td>
<td>11</td>
<td>0</td>
<td>499</td>
<td>499</td>
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<tr>
<td>105</td>
<td>496</td>
<td>3</td>
<td>0</td>
<td>499</td>
<td>499</td>
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<tr>
<td>120</td>
<td>497</td>
<td>1</td>
<td>0</td>
<td>498</td>
<td>498</td>
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</tbody>
</table>

### RM

<table>
<thead>
<tr>
<th>Grind Time (min)</th>
<th>&lt;125 um (g)</th>
<th>125-500 um (g)</th>
<th>&gt;500 um (g)</th>
<th>Total Before Sieve (g)</th>
<th>Total After Sieve (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>500</td>
<td>500</td>
<td>500</td>
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<td>101</td>
<td>344</td>
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<td>495</td>
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<tr>
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<td>0</td>
<td>494</td>
<td>494</td>
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<tr>
<td>120</td>
<td>493</td>
<td>1</td>
<td>0</td>
<td>494</td>
<td>494</td>
</tr>
</tbody>
</table>
The Fate of Sulfur and Nitrogen

Pollutants: SOₓ, NOₓ

Atmosphere emissions

Heat

Air reactor

Air

Fuel reactor

Coal

Ash

H₂O, CO₂

MeₓOᵧ

N₂, O₂

with SOₓ, NOₓ
H₂S, COS, NH₃

H₂O, CO₂

MeₓOᵧ₋₁
# Composition of Coal and OCs

<table>
<thead>
<tr>
<th></th>
<th>Proximate Analysis (wt.%)</th>
<th>Ultimate Analysis (wt.%)</th>
<th>LHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed Carbon</td>
<td>Volatile Matter</td>
<td>Moisture</td>
</tr>
<tr>
<td>PRB</td>
<td>52.43</td>
<td>34.59</td>
<td>4.96</td>
</tr>
<tr>
<td>WKY</td>
<td>52.43</td>
<td>36.55</td>
<td>2.47</td>
</tr>
<tr>
<td>EKY</td>
<td>52.56</td>
<td>34.44</td>
<td>0.96</td>
</tr>
</tbody>
</table>

**Red Mud Oxygen Carrier**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>43.74</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>23.37</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>11.78</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>7.74</td>
</tr>
<tr>
<td>CaO</td>
<td>5.54</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>6.43</td>
</tr>
</tbody>
</table>
Operation to Ensure 100% Carbon Conversion

Fluidized bed reactor 950 °C
OC: 75g red mud + 75 g quartz sands coal 1g
50 vol% steam balanced by N₂
Sulfur and Nitrogen Balance

- Most S presented at the FR as SO$_2$
- In FR, more than 70% of total sulfur in coal

- N in coal exits as NO in FR and AR
No S- and N- Compounds in OCs

- No new phase generated, no sulfides or sulfates formed with red mud
Conclusions

- Red mud is proven to be an effective oxygen carrier and catalyst for the CLG process. Stable reactivity is observed within 20 cycles. It also shows a good fuel selectivity.

- Gasification rate of char can be enhanced approximately by 1.5-3 times in the bed of red mud.

- The effect of OC/fuel ratio on the produced syngas composition was studied. Syngas fraction increases when OC/fuel decreases due to oxygen lean condition.

- RM produced by rotary kiln displays a similar reactivity to RM synthesized by traditional freezing granulation method.

- The cost of RM produced by rotary kiln is estimated to be approximately $113/ton.
Acknowledgements

- **DOE/NETL**
  - David Lyons
  - Steven Markovich
  - Heather Quedenfeld
  - Jenny Tennant

- **CAER**
  - Jinhua Bao
  - Jacob Blake
  - Zhen Fan
  - Liang Kong
  - Heather Nikolic
  - Lisa Richburg
  - Steve Summers
  - Amanda Warriner
  - Jimin Zeng

- **CMRG**
  - Duke
  - EPRI
  - LGE and KU