Development of promoted ilmenite for high-Temp CLC and Cu based oxygen carrier for low-Temp CLC and continuous tests in dual fluidized beds

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- Ilmenite for high temp. CLC
- Cu-based OC for low temp. CLC
- Continuous tests
- Conclusions
Introduction: Direct solid fuel CLC

Key requirements for oxygen carrier:
1. High reducing reactivity
2. Low-cost (restraints from ash)

Syngas Conversion
Gasifying rate + Reducing rate

Syngas out of fuel reactor
1. Position where syngas is released
2. Reaction equilibrium

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## Study of ilmenite

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<thead>
<tr>
<th>Location</th>
<th>Apparatus</th>
<th>Fuel</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lab scale test facility</td>
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<tr>
<td>CSIC</td>
<td>TGA</td>
<td>$\text{H}_2,\text{CO,CH}_4$</td>
<td>2010</td>
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<tr>
<td>Chalmers</td>
<td>FB</td>
<td>coal</td>
<td>2008</td>
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<tr>
<td>Siegen</td>
<td>FB</td>
<td>CO</td>
<td>2012</td>
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<tr>
<td></td>
<td><strong>Interconnected fluidized bed reactors</strong></td>
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</tr>
<tr>
<td>CSIC</td>
<td>500 W</td>
<td>coal</td>
<td>2011</td>
</tr>
<tr>
<td>Chalmers</td>
<td>10 kW</td>
<td>coal</td>
<td>2008</td>
</tr>
<tr>
<td>Stuttgart</td>
<td>10 kW</td>
<td>syngas</td>
<td>2011</td>
</tr>
<tr>
<td>Hamburg</td>
<td>25 kW</td>
<td>coal</td>
<td>2012</td>
</tr>
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<td></td>
<td><strong>Pilot dual fluidized beds plant</strong></td>
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<tr>
<td>Chalmers</td>
<td>100 kW</td>
<td>coal</td>
<td>2012</td>
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<tr>
<td>Vienna</td>
<td>120 kW</td>
<td>$\text{H}_2,\text{CO,CH}_4$</td>
<td>2010</td>
</tr>
<tr>
<td>Darmstadt</td>
<td>1 MW</td>
<td>coal</td>
<td>2011</td>
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</table>
Main issue with Ilmenite

- Low reactivity
- Incomplete gas conversion
- Large bed inventory

How to improve the reactivity?

Redox cycles in fluidized bed activation
Foreign ion modified Ilmenite

How we prepare:
Wet impregnation

Raw ilmenite \(\xrightarrow{\text{Impregnation}}\) Solution:
- \(K_2CO_3\)
- \(Na_2CO_3\)
- \(Ca(NO_3)_2\cdot4H_2O\)

\(\xrightarrow{\text{Impregnation Dry@120^\circ C}}\) Calcine \(\xrightarrow{\text{Calcine @900^\circ C 30min}}\) Sieve to 125-300 µm

Metal/ilmenite=5, 10, 15 wt.%

How we test this OC:
- Single fluidized bed
- TGA for dynamic parameters
- SEM for microscopic structure
- Dual fluidized bed Continuous test
Results in TGA

- Reactivity of some modified Ilmenite (10%Na, 10%K, 15%K) increases after 40 cycles; this increase is far greater than the raw Ilmenite;
- 15%K is the best option for improving reactivity;
- 40-cycled K15-ilmenite has a 7 times faster reactivity than the activated raw Ilmenite.
Results – Change of microstructure

The modified ilmenite produce more pores or cracks than the activated raw ilmenite.

- The surface area and pore volume of the modified ilmenite increase as the $K^+$ increases
- K15-ilmenite: BET (1.27 m$^2$/g), pore volume ($4.63 \times 10^{-6}$ m$^3$/kg)
During 100-cycle test, K15-ilmenite keeps its stability, almost no attrition and agglomeration happens. Almost all CO can be burned during the 100 cycles.
Results – K loss issue

15% K-ilmenite after 70 cycles

15% K-ilmenite after 100 cycles

EDS results of K distribution

<table>
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<tr>
<th></th>
<th>Fresh</th>
<th>40cycle</th>
<th>70cycle</th>
<th>100cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outside surface</td>
<td>8.46</td>
<td>1.34</td>
<td>1.18</td>
<td>1.88</td>
</tr>
<tr>
<td>Middle</td>
<td>0.94</td>
<td>4.27</td>
<td>3.77</td>
<td>2.73</td>
</tr>
<tr>
<td>Center</td>
<td>0.28</td>
<td>3.46</td>
<td>3.33</td>
<td>3.38</td>
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</table>
Results – Effect of ilmenite reactivity on bed inventory

Because the reducing rate of promoted ilmenite is 8~10 times faster than the raw ilmenite, the bed inventory in fuel reactor will decrease as 8~10 times. The promoted natural ilmenite behaves like synthetic materials.
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Two-Stage CLC process

Particles in gas after cyclone; bag filter – temp decrease; to involve low temp. CLC
The dust-free gas do not contaminate carriers; to involve high reactivity OCs
Cu-based OC: high reactivity, no agglomeration at low temp.

Removing unburnt gaseous components
Cement supported CuO OC

How we prepare OC: Mechanical mixing

How we design this low temp. CLC and test the OC:

- TGA for dynamic parameters
- TGA for stability
- Bench fluidized bed experiments
- Interconnected fluidized bed experiments
Results in TGA

- The increase of reduction conversion rate is not obvious within 300-700°C.
- Conversion within 150s: 100% at 700°C, 90% at 300°C.

- The increase of oxidation conversion rate is obvious from 400 °C to 500 °C, but not from 500 °C to 600 °C.
- 500 °C for air reactor.
The cement supported carrier shows good reactivity stability over 20 cycles.
Results in the fluidized bed

- Complete CO conversion: 30g 25%Cu, CO 2.5L/min 160s,
- No agglomeration
- Attrition: mass loss after 100 cycle 11.2% of the initial mass.
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1 kW three fluidized bed reactor

1 kW: focus on testing OC
50 kW: focus on reactor design

Three bubbling FB, cyclones, loopseals
Diameter: 50mm
Bed inventory: ~6 kg
Raw Ilmenite

- The stable CO conversion ~60%
- No agglomeration
- Mass loss caused by attrition and fragmentation is 0.87%
10% K promoted Ilmenite

After 100 h running, 24% (1500 g) raw Ilmenite was extracted and impregnated with 10% K.

- The CO conversion >79%;
- Gradual increase of CO: the particle elutriation along with K volatilization;
- No agglomeration;
- Mass loss caused by attrition and fragmentation is 0.79%.
Effect of FR temp. on CO conversion is less than the raw Ilmenite.
Cement supported CuO

18h continuous running with 5%CO

- Complete CO conversion;
- No agglomeration;
- Low temperature CLC for converting the unburnt fuel is feasible.
Conclusions

Achieved:
- Raw ilmenite improved by introducing foreign ion
- A method to eliminate the combustible gas from the outlet of the fuel reactor
- Continuous operations shows the effect of introducing foreign ion to OCs; No agglomeration happens, low attrition rate; proves the feasibility of low temp. CLC

Next step:
- Scale up the reactor to 50 kW;
- >500 h Continuous test of biomass and lignite with the developed oxygen carriers in the 50 kW unit.
Thank you!

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Reference


