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

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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/OO (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>

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Project Objectives

✓ Develop a transformative catalytic coal gasification technology
  - Avoidance of ASU and external WGS
  - High temperature gasification to improve cold gas efficiency
  - Improve H2/CO ratio 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
  - Avoidance of ash melting
  - Ash separation
Diagram of Proposed CLG Process

Avoiding the external ASU and WGS and their auxiliary power through cost effective chemical looping.

1. Temp = 950-1000 °C
2. Temp = 800-950 °C
3. Temp = 600-800 °C
Challenges

- Catalyst-Oxygen Carrier: reactivity, cost, sintering or attrition
- Heat balance
- Fuel reactor configuration
CLG in Bench Scale Fluidized Bed

Test condition:
1. Fuel: WKY Char 2.4 g
2. Temperature: 950 °C
3. Gasification agent: 50 vol% steam
4. Oxygen carrier: Red Mud OC 100 g

Oxygen loss from OC

Fuel Combustion
Catalytic Gasification

Time (s)
Rate of oxygen loss from OC (g/s)
Gas composition (%)
Feasibility and Iron State of Red Mud Catalyst-OC During Reaction

Fe$_2$O$_3$ → Combustion → Fe$_3$O$_4$ → Gasification → Fe$_3$O$_4$ → WGS → Fe$_3$O$_4$

Iron Phase Diagram

Fe$_2$O$_3$ → Fe$_3$O$_4$ → Fe$_{0.945}$O

CO/(CO+CO$_2$) (%) vs. T (°C)

H$_2$/(H$_2$+H$_2$O) (%) vs. H$_2$O/(H$_2$+H$_2$O) (%)
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

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Why Red Mud – Abundant

Global Production Rate

Year
1920 1940 1960 1980 2000 2020
Cumulative residue/Mt
0 500 1000 1500 2000 2500 3000

Global Inventory

Year
1920 1940 1960 1980 2000 2020

Global Production Rate

Production Rate (Mtpa)
0 30 60 90 120 150

Global Production Rate

OC/8Mt
4,000~5,000h
Capture
> 2Gt CO₂
>30% of total CO₂ emission of USA

Availability

Caribbean 6%
Africa 1%
Asia 22%
N. America 14%
S. America 8%
Europe 19%
Australasia 30%

Lifetime
50%

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Catalytic Function for WGS Reaction

T = 973 K
Identical gas space velocity:
- residence time = 6s
Inlet gas composition:
- 10% CO + 30% Steam + 60% N₂

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Gas Composition of CLG

- At different oxygen carrier/fuel ratios

Test Conditions:
1. Bed material: SRM100g
2. Solid fuel: WKY coal char (700°C)
3. Temperature: 950°C
4. Fluidizing agent: 50 vol% Water Vapor
Predicting Real Application

Test condition:
1) Fuel: Char 2.4 g
2) Temperature: 950 °C
3) Gasification agent: 50 vol% steam
4) Red Mud OC 100 g

Syngas product

<table>
<thead>
<tr>
<th></th>
<th>1 bar</th>
<th>4 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>42.9</td>
<td>43.0</td>
</tr>
<tr>
<td>CO</td>
<td>11.4</td>
<td>8.3</td>
</tr>
<tr>
<td>H2</td>
<td>45.6</td>
<td>48.7</td>
</tr>
<tr>
<td>CH4</td>
<td>0.14</td>
<td>0</td>
</tr>
</tbody>
</table>

Promotion of gasification rate at elevated pressure
Cyclic Performance Evaluation

Gas concentration profile

Conditions:
1. Bed material: SRM 100g
2. Solid fuel: 2.4 g WKY700
3. Temperature: 950°C
4. Fluidizing agent: 50 vol% Water Vapor

Carbon conversion rate

Conditions:
1. Bed material: SRM 100g
2. Solid fuel: 2.4 WKY(700)
3. Temperature: 950°C
4. Fluidizing agent: 50 vol% Water Vapor

Particle size distribution

SRM-Fresh [d(0.5)=310 μm]
SRM-after 20 cycle of CLG [d(0.5)=292 μm]

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Regeneration at high excess temperature: >35 °C

Test conditions:
(1) Fuel: WKY Coal Char 2.4 g
(2) Temperature: 950 °C
(3) Gasification agent: 50 vol% steam
(4) Oxygen carrier: A Red Mud OC 100 g

Gas composition (%)

Time (s)

CO2
CO
CH4
H2

After 15 cycles

Fresh OC
Agglomerate
Sintering Surface
Ash-induced Agglomerate

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Strategy to Avoid Agglomeration (2)

Low steam concentration < 30%

Fresh OC

Soft Agglomeration

Sintering bridge

Molten surface (×5 k & ×100 k)

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Future Plans

- **Cyclic performance of catalyst-OC with CuO additives**
  - Better heat balance between two reactors

- **Modification of existing spouted bed facility**
  - On going

- **Demonstration of spouted bed reactor and performance evaluation of gasifier**

- **Process modeling and performance evaluation**
  - Sensitivity study (operation pressure, OC/fuel/steam ratio and catalyst-OC type)
Available Instruments & Equipment

- TGA/DSC/DTA/MS with WV Furnace
- Hitachi S-4800
- Philips X’pert

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Available Facilities

Bench Scale Fluidized Bed Facility

Spouted Bed Reactor

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