Hydrogen Production by CFB Ca Looping Coal Gasification
(Used for exergy regeneration FC system (A-IGFC))

Shiyong LIN

Japan Coal Energy Center (JCOAL)
Research and Development Department
Recycle the exhaust heat of gas turbine or fuel cell to the endothermic reactions of gasification or reforming to produce hydrogen. By Exergy Regeneration, high power efficiency can be made.

The exergy regeneration power generation system needs a low temperature coal gasification (700~850°C).
Exergy regeneration power system
Ca looping coal gasification /FC power system flow

Points
- Ca Looping coal gasification
- CH₄ content in product gas: 10～20%
- Below 750°C gasification (catalyst, if needed)
- 30%-40% FC exhaust heat used for CH₄ reforming

Ca looping coal gasification /FC power system flow

Coal Catalyst
Limestone make-up

Gasifier 700～800°C
Gas clean up
H₂ 80%, CH₄ 20%
η_C > 75%

H₂ separation
η_C > 85%

H₂ reforming separation
H₂ Off gas
(FCQ:0.3-0.4)

FC Power system η_e > 60%

Char
CaCO₃

CaO
CaSO₄
Ash

CO₂

O₂

Combustor (Calciner) 950～1100°C
Heat changer
Tar reforming

Steam

Water

Q₁

Q₂
Ca Looping low temperature coal gasification

**Gasifier type**

**Circulating Fluidized Bed**
- Unreacted char in low temperature gasifier can be burned in combustor to calcine CaCO$_3$ and heat bed materials.
- Can separated the exhaust gases of combustor and gasifier, to obtain high concentration CO$_2$ and H$_2$/CH$_4$

**Gasification improvement**

**Ca looping + Catalyst (if needed)**
- Using CaO as heating material can largely reduced the amount of heating material like SiO$_2$
- Using Ca looping and catalyst can obtain enough gasification rate and purity of H$_2$/CH$_4$ at low temperature.
- CaO absorb CO$_2$ can improve steam gasification

\[
\text{Ca Looping gasification: } C + 2H_2O + CaO \leftrightarrow CaCO_3 + 2H_2
\]

\[
\text{Steam gasification: } C + H_2O \leftrightarrow CO + H_2
\]

**Reaction equilibrium constant, KC for Ca Looping and steam gasification**

![Graph showing reaction equilibrium constants for Ca Looping and steam gasification with reaction temperatures and equilibrium constants labeled.]
Ca Looping coal gasification concept and main results until now

**Gasifier**

1. Gasification: \( \text{C(coal)} + \text{H}_2\text{O(steam)} + \text{Heat} \rightarrow \text{H}_2 + \text{CO}_2 + \text{C} \)
2. CaO absorb CO\(_2\): \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{Heat} \)
3. CaO absorb H\(_2\)S: \( \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} \)

**Combustor (Calciner)**

1. CaCO\(_3\) decompositi: \( \text{CaCO}_3 + \text{Heat} \rightarrow \text{CaO} + \text{CO}_2 \)
2. Char combustion: \( \text{C(Char)} + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{Heat} \)
3. CaS combustion: \( \text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4 \)

**Main results until now**

1. Gas products: mainly H\(_2\) 80%; CH\(_4\) 20%
2. CaO had enough strength during cycle.
3. Ash and Sulfur compounds can be separated by cyclone.
4. CaO also improve tar steam reforming.
5. Under pressure condition, CaCO\(_3\) can be calcined at 1000 °C.

**Feature**

- High efficiency
- CO\(_2\) remove
- Sulfur remove in gasifier
- Can use low rank coal
- Cheap material

**Concept of Ca Looping coal gasification**

- Combustor (Calciner) at 1000 °C
- Gasifier at 750 °C
- Coal input
- Steam input
- CaO/Ash/\(\text{CaSO}_4\)
- \(\text{H}_2/\text{CH}_4\)
- CaO output
- Ash/\(\text{CaSO}_4\)
- \(\text{CO}_2\) output
- \(\text{O}_2\) or Air input
- CaCO\(_3\)/\(\text{CaS}/\text{Char}\) output
- Coal output
- Steam output
It was found that the decomposition temperature of natural limestone is lower than the theoretical decomposition temperature of CaCO$_3$.

- Increases impurity content in material, decrease the decomposition temperature of material.
Ca Looping gasification/FC power generation process analysis
-Aspen Plus model-

Analysis conditions:
- Coal supply: 42t/h，S/Coal=1/1；
- Limestone making up: 4.2t/h
- Pressure: ~20 atm；Gasifire T: 500-850°C
- Material circulating: enough heat transfer for gasification

Studies:
- Gasification product gas
- Cold gas efficiency
- Hydrogen cold gas efficiency
- FC Power generation efficiency
- Material circulating amount

Diagram:
- Gasification Part
  - Coal supply
  - Coal Heating value
  - CH₄ reforming
  - Steam generation
- Gas Reforming Part
  - H₂ Separation 1
  - CH₄ reforming
- FC Heat Recycle Part
  - CO Shift
  - H₂ Separation 2
- TGFC power Generation
- IGFC Exhaust Heat recycle
- Product gas Heating value
- Gasification Steam generation
- Gasifier and cyclone
- Gasification Residue heating
- Calciner and Cyclone
Analysis result—1

Variation of gasification gases under various T and P

- Under 1 atm and 500°C～650°C temperature area can obtained about 10% CH₄. Over 650°C, CH₄ and H₂ were decreased.
- Under 10 atm, 500°C～750°C temperature area can obtained about 20% CH₄. Over 750°C, CH₄ and H₂ were decreased.
Exergy regeneration effect

Hydrogen cold gas efficiency can be raised 10% by FC exhaust heat exergy regeneration.

By FC exhaust heat exergy regeneration, hydrogen cold gas efficiency can be raised 10%.

Analysis result—2

- Hydrogen cold gas efficiency
- Gasification cold gas efficiency
- IGFC power generation efficiency

**Effect of CH₄ reforming by used FC exhaust heat on exergy regeneration**

- Used a part of FC exhaust heat to generate steam, and heat supply materials, gasification cold gas efficiency can be obtained as 85%.
- Used a part of FC exhaust heat to reform CH₄, hydrogen cold gas efficiency can be obtained as high as 95%.
- However, over 750℃, the area which CaO cannot absorb CO₂, hydrogen cold gas efficiency.

### Analysis result-2

<table>
<thead>
<tr>
<th>Gasification temperature [℃]</th>
<th>Hydrogen cold gas efficiency [%]</th>
<th>Exergy regeneration effect</th>
<th>Gasification cold gas efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>750 (P: 10 atm)</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Analysis result—3

Material circulation ratio for gasification heat supply

\[
\text{Material circulation ratio} = \frac{\text{Amount of material circulation}}{\text{Amount of coal supply}}
\]

- At CaO absorbs CO₂ area (<750°C), the ratio is about 1.7
- At the area which is difficult for CaO absorbing CO₂ (>750°C), the material circulation ratio quickly increased, at 900°C, is about 36.

Heat capacity /kg:

\[
\begin{align*}
\text{SiO}_2 (950°C - 750°C) : & 270 \text{ kJ} \\
\text{CaO} (950°C - 750°C) : & 187 \text{ kJ} \\
\text{CaO} (950°C) \rightarrow \text{CaCO}_3 (750°C) : & 3,186 \text{ kJ}
\end{align*}
\]
Ca looping coal gasification/FC power system with exergy regeneration was analyzed by using Aspen model. The results are shown as follows.

(1) Under 10 atm, 500°C ~ 750°C temperature area, Ca looping coal gasification can obtained product gases about 20% CH₄ with 80% H₂.

(2) A part of FC exhaust heat can be used for CH₄ reforming. The hydrogen cold gas efficiency was obtained as 95%, is 10% higher than gasification cold gas efficiency.

(3) At the temperature area with CaO absorb CO₂, since the absorption heat can be supply to coal gasification, the material circulating ratio was low as 1.7. However, at the temperature area with CaO can not absorb CO₂, the material circulation ratio become higher as 36.