Synthesis Gas Production from Catalytic Coal Gasification Suitable for Power generation/Liquid Fuel Production

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Presented at 6th Intl. Freiberg Conf. 19th May 2014, Dresden, Germany
### Energy Security as a Driver: Past, Present & Future

<table>
<thead>
<tr>
<th>Country</th>
<th>Driver</th>
<th>Targets/company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>2nd World War/ Fuel Supply</td>
<td></td>
</tr>
<tr>
<td>South Africa</td>
<td>International sanctions</td>
<td>Coal-to-Gasoline/ Sasol</td>
</tr>
<tr>
<td>USA</td>
<td>Oil crisis</td>
<td>Coal-to-CH4/ Catalytic gasification/ Exxon Mobil</td>
</tr>
<tr>
<td>China</td>
<td>Significant Increase in demand for Gasoline/Supply security</td>
<td>Coal-to-Liquid/ Shenhua others</td>
</tr>
<tr>
<td></td>
<td>Coal Fields &amp; Major hubs are far separated (Coal fields in west, Beijing, Dalian, Shanghai on East)</td>
<td>Coal-to-CH₄/Great Point·China Wanxiang Holdings ($1.25 billion, 2012)</td>
</tr>
<tr>
<td>Japan</td>
<td>Environment &amp; Efficient Energy System</td>
<td>Electricity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IGCC (MHI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eagle (J-Power)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brown Coal to H₂-Liquified H₂-Fuel Cell/Kawasaki Heavy (Feasibility study)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene as H₂ carrier (SPERA HYDROGEN™, Chiyoda)/ Demonstration plant</td>
</tr>
</tbody>
</table>
‘Coal-to-H₂’ **NOT** ‘H₂-from-Coal’
Gasification is a BRIDGE TECHNOLOGY

Japan’s New Coal Policy
C3 Initiative towards the establishment of the Clean Coal Cycle
Demonstration of diversified CCT models, with coal gasification as the core technology

- **Gasification**
- **Chemical**
- **Syn gas (H₂, CO)**
- **Co-production of chemicals**
- **Co-production of Steel iron**
- **Iron ore**
- **Reduced ore**
- **Electric power**
- **IGCC／IGFC**
- **DME, GTL**
- **Hydrogen Station**
- **Stationary FC**
- **H₂ Production**
- **CO₂ sequestration**
- **H₂ from Brown Coal - LH₂-Fuel Cell application (Kawasaki Heavy) (Feasibility Study)**
- **Chiyoda, SPERA**
- **H₂/Liquid Fuel from Brown Coal**
- **METI**

- EAGLE project (150 ton/day)
- IGCC Nakoso (250 MWe)
- 2 new IGCC Power Plants (Fukushima)
- H₂ from Brown Coal - LH₂-Fuel Cell application (Kawasaki Heavy) (Feasibility Study)
- Chiyoda, SPERA

**AIST/ETRI**

**H₂/Liquid Fuel from Brown Coal**
OUR research group
# Coal Gasification

<table>
<thead>
<tr>
<th></th>
<th>High Temp. Oxygen Gasification</th>
<th>Catalytic Gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification T &amp; P</td>
<td>$&gt;1200 , ^\circ C, 30 , \text{atm}$</td>
<td>$&lt; 700 , ^\circ C, 35 , \text{atm}$</td>
</tr>
<tr>
<td>Oxygen Plant</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Thermal Efficiency</td>
<td>61.9 %</td>
<td>71.4 %</td>
</tr>
<tr>
<td>Methanator</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Capital Investment $/$ per MSCF per day</td>
<td>$6250$</td>
<td>$4688$</td>
</tr>
<tr>
<td>Catalyst requirement</td>
<td>No</td>
<td>Yes (20% of coal, $500/\text{ton}$)</td>
</tr>
<tr>
<td>Production cost $/$ per MSCF methane</td>
<td>6.10</td>
<td>5.12</td>
</tr>
<tr>
<td>End use</td>
<td>Multi–End use (Syn Gas, Methane, Power)</td>
<td>Methane production only</td>
</tr>
</tbody>
</table>

*HCEI-1-05-1*
Low temperature coal catalytic gasification

Coal + Catalyst (K₂CO₃) → 650 °C

Steam → H₂+CO₂ → H₂ → CO₂ → 650 °C

Problems:
1. Catalyst deactivation and loss
2. Gas composition control is difficult (H₂/CO)

Catalytic gasification
- Exxon Mobile process
- New process

High Pressure

CH₄ (SNG)

Normal Pressure

Synthesis Gas (H₂, CO)

DME

Methanol
Catalyst deactivation

Ash content in HyperCoal: <0.1%

Ash content in Brown coal: 0.5~1.0%

Single step process to produce and control Syngas Composition

<table>
<thead>
<tr>
<th>Target</th>
<th>SynGas Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td></td>
</tr>
<tr>
<td>3CO + 3H₂ ⇌ CH₃OCH₃ + CO₂</td>
<td>H₂/CO= 1</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>CO + 2H₂ ⇌ CH₃OH</td>
<td>H₂/CO= 2</td>
</tr>
<tr>
<td>Methane</td>
<td></td>
</tr>
<tr>
<td>CO + 3H₂ ⇌ CH₄ + H₂O</td>
<td>H₂/CO= 3</td>
</tr>
</tbody>
</table>
Effect of gasifying agent: Steam+CO₂ gasification

Steam  →  Steam + CO₂

![Conversion graph](Image)

- Steam = 100%
- CO₂ = 0%
- T = 700 °C

- Steam = 50%
- CO₂ = 50%

Gas yield (mmol/g)

- CO
- H₂

Selective H₂ production by catalytic gasification

Synthesis gas production by catalytic gasification
H$_2$O gasification

C + H$_2$O $\rightarrow$ CO + H$_2$ \[1\] gasification

CO + H$_2$O $\rightleftharpoons$ H$_2$ + CO$_2$ \[2\] Shift reaction

CO$_2$ gasification

C + CO$_2$ $\rightleftharpoons$ 2CO \[3\] Boudard

H$_2$O/CO$_2$ co-gasification

C + H$_2$O $\rightarrow$ CO + H$_2$ \[1\] Gasification

CO + H$_2$O $\rightleftharpoons$ H$_2$ + CO$_2$ \[2\] Shift reaction

C + CO$_2$ $\rightleftharpoons$ 2CO \[3\] Boudard

Addition of CO$_2$ to H$_2$O

H$_2$ decrease $\rightarrow$ Contribution of R[1] ↓; Equilibrium of R[2]←

CO increase $\rightarrow$ Contribution of R[3]↑; Equilibrium of R[2]←
Calculated (Thermodynamic equilibrium)

Experimental

Trend of change in $\text{H}_2/\text{CO}$ fraction with $\text{CO}_2$ is similar to predicted trend

Big difference in quantitative fractions values

Steam/Coal ratio uncertain in case of TGA
Continuous gasifier: Experimental conditions

<table>
<thead>
<tr>
<th>Gasifier:</th>
<th>Fluidized bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal:</td>
<td>Adaro (IND)</td>
</tr>
<tr>
<td>Size:</td>
<td>0.5 ~1.0 mm</td>
</tr>
<tr>
<td>Catalyst:</td>
<td>K$_2$CO$_3$</td>
</tr>
<tr>
<td>Coal amount:</td>
<td>30 g</td>
</tr>
<tr>
<td>Catalyst amount:</td>
<td>30 g</td>
</tr>
<tr>
<td>Temperature:</td>
<td>700 °C</td>
</tr>
<tr>
<td>Gasifying agent:</td>
<td>H$_2$O, H$_2$O+CO$_2$</td>
</tr>
<tr>
<td>Run time:</td>
<td>4~5 h (300 min)</td>
</tr>
<tr>
<td>Feeding rate:</td>
<td>0.1~0.3 g/min</td>
</tr>
</tbody>
</table>
Continuous catalytic gasifier

- Coal
- $\text{K}_2\text{CO}_3$
- $\text{K}_2\text{CO}_3 + \text{Ash}$

Coal + K2CO3
0.1~1g/min

Steam + CO2

Gasifier

Tar Cracker (K2CO3)

Synthesis gas

Catalyst + Ash recovery

Graph showing gas rate (%): H2 - blue, CO - red, CO2 - purple, CH4 - black

Time, min:
0 - 300
Catalytic Gasification Results: 1

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Expt. (%)</th>
<th>Calc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>62</td>
<td>64.4</td>
</tr>
<tr>
<td>CO</td>
<td>7</td>
<td>7.15</td>
</tr>
<tr>
<td>CO2</td>
<td>30</td>
<td>28.3</td>
</tr>
<tr>
<td>CH4</td>
<td>0.8</td>
<td>0.01</td>
</tr>
</tbody>
</table>

H2 production

T=700°C
Steam/CO₂=100/0
H₂/CO=10

Methanol production

T=700°C
Steam/CO₂=70/30
H₂/CO=2.5

DME production

T=700°C
Steam/CO₂=50/50
H₂/CO=1.0
Water gas shift equilibrium


Catalyzed reaction: >655 C WGS achieves Equilibrium

Our results also confirm that WGS equilibrium achieved at 700 C

* Carbon 1983, 21, 1-12
Wigmans et al.
[WGS equilibrium is doubtful]
Catalytic Gasification Results 2

Graph showing the ratio of Cin/Cout over gasification time. The graph indicates a significant increase in the ratio with an increase in gasification time.

Residence time

Cold Tar Trap residue

Without Tar Cracker

With Tar Cracker

Temperatures ranging from 0°C to 800°C are shown on the y-axis, with corresponding gasification times on the x-axis. The ratio of Cin/Cout is plotted against these axes, showing a notable increase in the ratio as the gasification time progresses.

The images depict samples with and without the use of a tar cracker, highlighting the differences in the resulting residues.
Application of the results: H$_2$/CO, Gasification time and Temperature

<table>
<thead>
<tr>
<th>H$_2$/CO</th>
<th>Temp.</th>
<th>Time</th>
<th>Steam/CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>= 2.5~1.0</td>
<td>= 700 C</td>
<td>= 10~20 min</td>
<td>= 50/50~30/70</td>
</tr>
</tbody>
</table>
Comparison of syngas process with new process

Current process

AIST process

1\textsuperscript{st} Stage
T > 1200 \degree C

2\textsuperscript{nd} Stage
T \sim 400 \degree C

\textbf{ASU}

\begin{align*}
\text{N}_2 & \quad \text{Coal} \\
\text{O}_2 & \quad \text{Ash}
\end{align*}

\begin{align*}
\text{H}_2/\text{CO} & \quad 0.5 \sim 0.7 \\
\text{Gasifier} & \\
\text{Gas Cleaning} & \\
\text{Shift Converter} & \\
\text{Steam} & \\
\eta & = 42 \%
\end{align*}

\begin{align*}
\text{H}_2/\text{CO} & \quad 1.0 \sim 3.0 \\
\text{To FT synthesis process} & \\
\eta & = 55 \sim 70 \%
\end{align*}

\begin{align*}
\text{H}_2/\text{CO} & \quad 1.0 \sim 3.0 \\
\text{Gasifier} & \\
\text{Gas Cleaning} & \\
\text{Coal+K} & \\
\text{CO}_2+\text{Steam} & \\
\text{Ash} & \\
\text{Single Stage} & \\
T \sim 700 \degree C
\end{align*}

\textbf{Coal+K}
Business Model:
Production of clean transportable fuel/H₂ from Lignite

- **High ash coal**
  - US$10~15/ton
  - On-site consumption (High moisture, High ash)
  - HyperCoal

- **Low ash coal**
  - US$100~150/ton
  - 49 % Bit + Sub Bit.
  - 51 % Lignite

- **Catalytic gasification**

- **H₂, Methanol, DME, Methane**
  - Clean fuel
  - Chemical Feedstock

- **Exportable fuel**
  - Local clean application

- **Energy security**
  - Environment

- **Contribution to regional economic/social development**

- **Australia, Indonesia**
  - Coal producing country

- **Japan**
  - Business Model:
    - Production of clean transportable fuel/H₂ from Lignite

- **Contact:** Advanced Fuel Group
1. H2/CO of syngas can be controlled by adjusting Steam/CO2 ratio.

2. Atmospheric pressure continuous catalytic coal gasification system.

3. Synthesis gas with H2/CO suitable for methanol, DME and methane production by FT synthesis was produced in a single step.

4. Comparison of experimentally observed gas composition with the calculated values confirmed that synthesis gas produced by catalytic gasification of coal is in thermodynamic equilibrium state.

5. Tar cracking by K2CO3 was effective and very little tar was observed.