Progress of HyPr-RING Process Development for Hydrogen Production from Fossil Fuels

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Abstract

Hydrogen generates no pollutants and, through the use of fuel cells, is a potential source of energy for power and transportation. In 1999, we proposed a method for production of hydrogen from water by using the hydrocarbons: the reaction-integrated novel gasification (HyPr-RING) method. The process involves four main reactions that are integrated in a gasifier.

CaO first reacts with high pressure steam to form reactive Ca(OH)\textsubscript{2} and to release heat, hydrocarbon reacts with steam to CO\textsubscript{2} and H\textsubscript{2}, then CO\textsubscript{2} is absorbed by Ca(OH)\textsubscript{2} and CaO to fixed into CaCO\textsubscript{3}. We have performed theoretical and experimental studies to understand what happens in the gasifier when these reactions are integrated, and to find suitable conditions for producing higher concentrations of hydrogen by one reactor. We have built a 50kg-coal/d continuous reactor system that contained feed mechanism, fluidized bed reactor, and equipments for supplying heat and pressure and for separating gases and solids. Coal/CaO mixtures were continuously supplied into reactor, to react with high-temperature, and high-pressure steam. Product gases were separated from solid residues, and were continuously analyzed. We found that H\textsubscript{2} was the main product gas (>80%) and that a small amount of CH\textsubscript{4} was also produced.

Thermodynamic calculations were also used to analyze the material and energy balances in the HyPr-RING process for H\textsubscript{2} production. A fuel gas comprising an equilibrium mixture of 91% H\textsubscript{2} and 9% CH\textsubscript{4} can be obtained by gasification of coal at 923 K and 3.0 MPa. The amount of the fuel gas produced was calculated to be equivalent to 1.4 Nm\textsuperscript{3}/kg\_coal, giving a high cold-gas efficiency of 0.77.

Keywords: Hydrogen, Energy, CO\textsubscript{2}, Gasification, Hydrocarbon
1. Introduction

Hydrogen generates no pollutants and, through the use of fuel cells, is a potential source of energy for power and transportation\(^1\). It is expected to be one of the primary energy resources of the 21st century. Hydrogen is mainly produced from water (H\(_2\)O) by splitting the molecule into H\(_2\) and O. The key aspects of hydrogen production are supplying sufficient energy to split the water molecule, and fixing the oxygen produced. One method for hydrogen production from water is an oxidation-reduction reaction by using a reductant, M.

\[
\text{H}_2\text{O} + M \xrightarrow{\text{energy}} H_2 + MO
\]  

M may be a metal or carbon, C. Fortunately carbon is readily available from abundant hydrocarbon materials (CH\(_m\)) like coal, oil, natural gas, and biomass.

\[
2\text{H}_2\text{O} + CH_m \xrightarrow{\text{energy}} (2 + m/2)H_2 + CO_2
\]

This offers a large-scale method for production of hydrogen from water and carbon, both of which can be readily and inexpensively obtained, to meet energy needs worldwide, if emissions of CO\(_2\) can be controlled.

In 1999, we proposed for the production of hydrogen from water by using the hydrocarbons: the reaction-integrated novel gasification (HyPr-RING) method.\(^2,3\) This method integrates gas production and separation, and the associated endothermic and the exothermic reactions, in one reactor, to produce H\(_2\) in one step. In addition to the hydration reaction for recovering CaO reactivity, Lin et al.\(^2\) suggested that the following four main reactions take place in the gasifier.

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 ; \quad \Delta H_{298}^\circ = -109 \text{kJ/mol}
\]

\[
C + \text{H}_2\text{O} \rightarrow CO + H_2 ; \quad \Delta H_{298}^\circ = 132 \text{kJ/mol}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow CO_2 + H_2 ; \quad \Delta H_{298}^\circ = -41.5 \text{kJ/mol}
\]

\[
\text{Ca(OH)}_2 + CO \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} ; \quad \Delta H_{298}^\circ = -69 \text{kJ/mol}
\]

Integrating of reactions (3)-(6) in a single reactor is the key point in the HyPr-RING method.

Process development was started at year 2000 by CCUJ (Center for coal utilization, Japan; from 2005.4, CCUJ was merged with JCOAL, Japan coal energy center). Members contained five companies, two universities and national institute (AIST). During the passed years, efforts were made at process design, feasibility studies and experimental confirmations which are most important for obtaining data of reactor design, gas product, material reactivity and operating conditions. Early studies\(^2,3\) demonstrated that when coal or organic material, water and CaO were allowed to react in an autoclave at 873-973 K, the produced gas consisted of mostly H\(_2\) with only a very small portion of CH\(_4\). Recently, on the basis of these findings, we built a high-pressure flow-type reactor in which coal/CaO and high pressure steam can be continuously introduced and the gas and solid reaction products continuously removed. We investigated the effects of coal/CaO-steam contact, fluidization, solid residence time, and temperature and pressure on the production of H\(_2\). In this present, progress of the HyPr-RING project will be introduced.
2. HyPr-RING method

HyPr-RING method integrates gas production and separation, and the associated endothermic and the exothermic reactions, in one reactor, to produce H₂ in one step. CaO (lime) sorbent is used to remove CO₂ and thereby CO completely, during coal gasification. The heat of absorption of CO₂ is available for gasification of the coal. Four main reactions take place in the gasifier: CaO hydration (3); Carbon gasification (4); Gas shift reaction (5); Ca(OH)₂ carbonation (6);

The overall reaction is written as follows:

\[ C + CaO + 2H₂O \rightarrow CaCO₃ + 2H₂ \quad \Delta H_{298}^{\circ} = -88kJ / mol \ (7) \]

*Product gases with CaO addition*

Integration of these reactions (3)-(6) is exothermic, no combustion of coal is needed for gasification. Overall reaction equilibrium is suitable for a gas composition of high concentrations of hydrogen. Equilibrium compositions from C-H₂O-CaO and C-H₂O-CaO reaction systems were calculated using HSC Chemistry 4.0 software. Gas compositions for the C-H₂O and C-H₂O-CaO reaction system are shown in Fig. 1.

![Equilibrium composition for C-H₂O and C-H₂O-CaO reaction system](image)

It can be seen that, with CaO addition, as in C-H₂O-CaO reaction system, CO and CO₂ decreased with increasing pressure, and reached below 1 % at pressures above 3 MPa. CO₂ fixation by CaO is a significant factor in the reduction of CO and CH₄ and the increase of H₂. Without CO and CO₂, H₂ was the primary resultant gas, together with a small amount of CH₄. The ratio of H₂/CH₄ was about 6.7/1 at 3 MPa.

*Process components*

HyPr-RING process contains two main reactors, gasifier and regenerator. Coal and sorbents inject into
gasifier with steam together, producing H$_2$ and CaCO$_3$. CaCO$_3$ then be regenerated in regenerator to CaO for reusing. Fig. 2 shows process components and mass/energy flows for a 1000t/d coal process. Since CO$_2$ separation energy can be recycled as CaO chemical energy to be released in gasifier for coal gasification, process can obtained cold gas efficiency as high as 77%.

The operating temperature of gasifier is 873-973K, as determined from experimental results. A comparatively lower gasification temperature is used to prevent eutectic melting of calcium compounds and to improve CO$_2$ absorption and the water-gas shift reaction. A high pressure over 2.0 MPa (steam pressure) is used for hydration of CaO in the gasifier to restore sorbent reactivity. Accordingly, CO$_2$ in the gasifier is absorbed mainly by Ca(OH)$_2$. Regenerator is operated at 1373 K and 0.1 MPa (Fig. 2) based on the conditions of traditional calcination process.

A method for separating coal ash from the CaO sorbent has not yet been tested experimentally. In the calculation, we considered the disposal of a part of CaO/ash mixture and the injection of fresh CaCO$_3$ into the process system to maintain a certain CaO/ash ratio in the process.

In the solid residue from HyPr-RING process, CaO is main material (larger than 80%) with coal ash of SiO$_2$, Al$_2$O$_3$ and CaSO$_4$. Some CaO absorb H$_2$S to form CaS in gasifier, and then be oxidized in regenerator to CaSO$_4$. In case of a Taiheiyo coal (ash content 7.6 wt%), when Coal/CaCO$_3$ supply ratio is 1/0.5 wt/wt into the process, contents of SiO$_2$, Al$_2$O$_3$ and CaSO$_4$ in solid residue are expected as 13.3, 6.7 and < 1 wt%. Solid residue is good source material for cement industry.
Energy contained in coal supply should be distributed to the gasifier and the regenerator rationally, too. It is designed that a part of carbon (about 40-50%) after gasification is sent to regenerator as a fuel for CaCO$_3$ regeneration. Since most of the energy used in the regenerator can be return to the gasifier by CaO reaction heat, energy distributed to the gasifier, in fact, is larger than 85% for producing H$_2$.

3. Process development

Process development was started at year 2000 by CCUJ (Center for coal utilization, Japan; CCUJ have changed to JCOAL, Japan coal energy center from 2005.4). Members contained five companies, two universities and national institute (AIST). Table 1 shows the project schedule. During the passed years, efforts were made towards process design, feasibility studies and experimental confirmations which are most important for obtaining data of gas product, material reactivity and operating conditions. Recently, we built a continuously running reactor system, including feeding, solid-gas contacting, and gas-solid separating. In the following, some recent results will be reported.

3.1 Obtain reactor design data

HyPr-RING process contains two main reactors, gasifier and regenerator. Coal and sorbent inject into gasifier with steam together, producing H$_2$ and CaCO$_3$. CaCO$_3$ then be regenerated in regenerator to CaO for reusing. However, most challenges in the process development are focused on the gasifier which is required to:

1) completely fix CO$_2$ in gasifier ;
2) completely shift CO in gasifier;
3) maximize H$_2$, minimize other hydrocarbon products;
4) use CaO reaction heat for coal gasification;
5) minimize sorbent/coal supply ratio; and
6) restore CaO reactivity

Correct choices of sorbent and operation conditions are the keys for requirement terms.

Coal reactivity confirmation

Used a high pressure flow type fixed bed (Fig.3) to test the solid-gas reaction rates, in order to find control reaction step in the integration of reactions. It was reported that the CaO hydration and the Ca(OH)$_2$ carbonation rates were faster than char gasification. The char gasification rates were on levels of 0.145 [1/min] and 0.486 [1/min] at 923 K and 973 K, respectively, and were about twice those produced by char-only gasification. Fig.3 also shows results of hydrogen product from various rank of coal. It can be seen that yang rank coal can produce more hydrogen than old rank coals.
Various reaction rate data high pressure fixed bed reactor

Fig. 3 Coal reactivity and reaction rate measurement

Reactivity of CO₂ sorbent

CaO hydration is an exothermic reaction that can be used to supply heat. The amount of heat released by the reaction depends on the operating steam pressure. In this work, the rate of CaO hydration was measured with a high-pressure thermogravimetric apparatus (Fig.4) under steam pressures ranging from 0.67 to

CaO hydration rate High-pressure TG apparatus

Fig. 4 CaO hydration rate results and TG apparatus.
3.8 MPa. At these pressures, CaO hydration occurred at high temperatures up to 1023 K. The CaO hydration rate varied as the 2 power with respect to the difference between the reactant steam pressure and the equilibrium steam pressure, \((P_{\text{H}_2\text{O}} - P^*_{\text{H}_2\text{O}})\). The apparent activation energy for reaction constant \(k\) was determined to be 8.4 kJ/mol. The particle size \((dp)\) slightly affected the CaO hydration rate.

### 3.2 Results of 50kg-coal/d facility

A 50kg-coal/d continuous run facility was build two years ago, to confirm reactor form (fluidized bed), operating condition, feeding method, product gas composition, sorbent recycle et. al..

![Fig.5](image)

<table>
<thead>
<tr>
<th>Terms</th>
<th>conditions</th>
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</thead>
<tbody>
<tr>
<td>Coal and CaO</td>
<td>Lignite-Bituminous</td>
</tr>
<tr>
<td></td>
<td>Coal/CaO=1/2.5 wt/wt</td>
</tr>
<tr>
<td>Pressure</td>
<td>~3.0 MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>600-700 °C</td>
</tr>
<tr>
<td>Steam temperature</td>
<td>600 °C</td>
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<tr>
<td>Feed speed</td>
<td>~3.5 kg/h</td>
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The continuous running reactor system contained feeding, fluidized bed reactor, and gas-solid separating. Coal/CaO powder mixture was continuously supplied into a fluidized bed reactor to react with high temperature and high pressure steam. Product gases were separated with solid residue and then continuously analyzed. Fig. 5 shows the continuously running reactor system and operating conditions. Fig. 6 shows results of gas product and carbon conversion during the continuous run test. Without H\textsubscript{2}O and N\textsubscript{2}, hydrogen is the primary product, is about 80-90% contained in gas. In a stable run range as shown in Fig. 6 (b), it can be seen that, carbon in coal converted about 60% into gas phase, and H\textsubscript{2}/CH\textsubscript{4} ratio in product gas is about 6.6, is similar as the result of equilibrium calculation in Fig. 1. CO was completely shifted to H\textsubscript{2} and CO\textsubscript{2}, and CO\textsubscript{2} was completely fixed. H\textsubscript{2}S can be fixed by CaO(Ca(OH)\textsubscript{2}) sorbent, too. For example, as a result from other run, H\textsubscript{2}S composition was below 2.2 ppm and HCN was 3.2 ppm. NH\textsubscript{3} was decomposed by CaO(Ca(OH)\textsubscript{2}) catalysis to be about zero.

**Conclusion**

Process development of H\textsubscript{2} production from coal by using method of HyPr-RING has been started 6 years ago. Continuous run test (fluidized bed) experiments have confirmed that, high concentration H\textsubscript{2} as >80 % with few CH\textsubscript{4} can be made from coal by using one reactor. Feasibility study shown that, this process has potential high H\textsubscript{2} production efficiency as 77 %.

**Reference**

2 Lin, S. Y., Suzuki Y. and Hatano H., Japan patent, No. 2979149, 1999