Enhancement of H₂ Production by Combination with CO₂ Absorption in Steam Methane Reforming in Bench Scale

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Received April 9, 2007; Accepted May 30, 2007

Abstract: Zero emission coal technology (ZECT) has recently been as a solution for reducing CO₂ levels in developed country. This will involve the development of a highly efficient pre-combustion process for fossil fuels. The objective of this study is to maximize hydrogen yield by a combination with carbonation and calcinations steps, which are core components of zero emission coal techniques. Hydrogen production by steam reforming without heat loss using steam and methane produced mainly during coal gasification is enhanced by a shift in the reaction equilibrium as the result of removing carbon dioxide, a byproduct produced during steam methane reforming, using dry sorbents. As a result of studies, the composition of methane that has not reacted, carbon monoxide and carbon dioxide as byproducts in the reforming process decreased at 750 °C and the optimum reaction conditions were a ratio of steam/methane = 3 and a GHSV (Gas Hourly Space Velocity) = 3000 hr⁻¹. The addition of calcium based-carbon dioxide sorbents to the catalyst used in steam methane reforming increases the production of hydrogen to 92+% in a combined process with carbonation and calcination.

Keywords: absorption, CaCO₃, energy, catalysis, hydrogen production, carbonation

Introduction

Concerns about climate change and the environmental consequences of increased levels of atmospheric CO₂ will require the power generation industry to reduce CO₂ emissions from their current levels. The problem of continuously increasing the CO₂ content of the Earth’s atmosphere requires a solution, which will allow the generation of sustainable power at increased levels.

Pre-combustion, a technology for reducing carbon dioxide, is a highly economical and efficient process that involves the exhausted heat and the use of micro equipment in combination with several technologies. For example, catalytic incineration, oxyfuel incineration and hydrogen power plants using fossil fuel combined with zero emission technology are potential pre-combustion technologies.

This concept, zero emission coal technology (ZECT), in the combining reaction and separation in hydrogen production is not new. Rostrup-Nielson reported that the first description of the conversion of hydrocarbons in the presence of steam and a CO₂ sorbent using a different reactor was published in 1868 [1]. Many researchers have been granted patents for combining the steam methane reforming reaction (SMR) and a CO₂ sorbent and reactor types such as a fluidized bed process using a reforming catalyst and a CO₂ sorbent [2-7]. The combination of ZECT and fuel cell technology has been studied in developed countries such as the USA, Japan and Germany in the late 1990s. Balasubramanian reported hydrogen production from methane in a single-step process at temperatures above 550 °C and a 95+% yield of hydrogen using a NiO/Al₂O₃ catalyst and a CaO sorbent in a lab scale reactor [8]. In Korea, many researchers have reported similar studies such as hydrogen production using SMR in a fluidized reactor, SMR reactions and water gas shift reactions in a fixed bed reactor [9-10].

The sorption enhanced reaction process (SERP) is similar to ZECT using a CO₂ sorbent. However, the SERP technology involves the use of an adsorbent such as K₂CO₃/hydrotalcite at a lower temperature, 450 °C, in-
stead of sorbent for removing CO\(_2\) from the SMR reaction [11,12].

This paper reports on experimental obtained for a fixed bed reactor packed with two layers of a commercial reforming catalyst and a sorbent based on calcium, which has several advantages such as a similar reaction temperature zone between the SMR and CO\(_2\) removal reactions and the cost of raw materials, which are cheaper than the K\(_2\)CO\(_3\)/hydrotalcite used in SERP. The main differences between this study and other researches are that a process with ZECT at 750 ∼ 800 °C in continuous SMR and CO\(_2\) removal conditions has not been reported beyond laboratory scale and the results of the multicycle test. Experiments were executed at conditions of a gas hourly space velocity (GHSV) = 10,000 hr\(^{-1}\), beyond lab scale and were repeated for 10 cycles.

SMR, the main reaction of carbonation, and the CO\(_2\) removal reaction were optimized for characterizing these hybrid reactions and Le Chatelier’s principle was used to acquire a higher purity of hydrogen in the hybrid reaction.

**Theoretical View**

Figure 1 shows the ZECT process, combined with technology using hydrogen such as fuel cell (SOFC), which consists of gasification, carbonation, calcination and a power generation process using hydrogen. Figure 2 shows the flow diagram for energy and the chemical species in the process.

Reaction (1) using coal as the carbon source and hydrogen for the gasifying agent proceeds as follows. This exothermic reaction controlled by water or recycled steam results in no heat supply in the gasification step. Heat of reaction from reaction (1) to reaction (5) is at T = 298 K and P = 1 atm.

The carbonation step is the SMR process using methane from step one and a water feed. The reactions are summarized as follows. The carbonation step consists of the water gas production reaction (2) and the water gas shift reaction (3). Reaction (4) is the overall reaction by combining (2) and (3) and the endothermic reaction.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad \text{(exothermic)} \quad (1) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad 41.15 \text{ kJ/mol} \quad \text{(exothermic)} \quad (2) \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + 4\text{H}_2 \quad \text{165.0 kJ/mol} \quad \text{(endothermic)} \quad (4)
\end{align*}
\]

The exothermic reaction (5) plays the role of removing CO\(_2\) as a byproduct. If the endothermic reaction (4) and exothermic reaction (5) are considered simultaneously, heat supplied from the outside, can be reduced because of the heat exchange between reactions (4) and (5). Heat value supplied from is about 13.8 kJ/mol which is subtracted 165.0 from 178.8 kJ/mol.

\[
\begin{align*}
\text{CaO} + \text{CO}_2 & \rightarrow \text{CaCO}_3 + 178.8 \text{ kJ/mol (exothermic)} \quad (5)
\end{align*}
\]

The calcination step is to regenerate sorbents by desorbing carbon dioxide at a high temperature. For a organizing continuous process, the exhausted heat of the fuel cell system can supply a high temperature to the calcination, permitting calcium carbonate to be regenerated [13]. Hydrogen, in a high degree of purity, can be acquired in the carbonation step. The process using hydrogen is the step that is applied to a fuel cell using hydrogen such as a solid oxide fuel cell (SOFC). Electricity can be acquired as a final product and exhausted heat can be supplied to the calcination reactor.
Table 1. Properties of Catalyst and Sorbent

<table>
<thead>
<tr>
<th></th>
<th>Formulation</th>
<th>Shape</th>
<th>Bulk density (g/cm(^3))</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst (KATALCO 57-7)</td>
<td>Ni/Ca/Al</td>
<td>Cylinder</td>
<td>1.26</td>
<td>Reforming Gas</td>
</tr>
<tr>
<td>Sorbent (based on CaCO(_3))</td>
<td>CaCO(_3) 80 (wt%) + (\alpha)-Al(_2)O(_3) 15 (wt%) + activated carbon 5 (wt%)</td>
<td>Sphere</td>
<td>0.779</td>
<td>Absorption of CO(_2)</td>
</tr>
</tbody>
</table>

Figure 3. Picture of prepared spherical sorbent based on Ca (D = 3 mm).

Figure 4. The chemical phase change of catalyst before and after reduction.

**Experimental**

**Catalyst and Sorbent**

The composition of the reforming catalyst and sorbent used in this study is listed in Table 1. The reforming catalyst, from the Synetix company, KATALCO 57-7, consisted of NiO and CaO supported on Al\(_2\)O\(_3\). The shape of the catalyst is a cylinder having diameter \(\times\) length, 0.032 \(\times\) 0.032 m. A spherical sorbent based on calcium, prepared using a granulator, is used at the optimum composition for removing CO\(_2\), as in the previous study and shown in Figure 3 [14]. Figure 4 shows that the chemical phase of catalyst is changed before and after reduction from NiO/Al\(_2\)O\(_3\) to Ni/Al\(_2\)O\(_3\) by XRD analysis. And Ni/Al\(_2\)O\(_3\) form is maintained mainly throughout SMR reaction.

**Experimental Apparatus and Procedure**

Figure 5 shows the experimental apparatus for testing the SMR reaction and the hybrid reaction combined with a CO\(_2\) removal reaction. The system consists of an injector for the mixed gases, a reactor for the SMR and an analyzer. CH\(_4\), H\(_2\), and N\(_2\) are controlled by a mass flow controller (Brooks, Co. Ltd) in the injector section and water is supplied and controlled continuously by means of a HPLC pump (AlITech, Co. Ltd) to the SMR reactor. The SMR reactor is composed of a preheater and stainless steel tube 2.54 cm in diameter for the reforming reaction. The preheater, a coil, located in the tubular furnace, plays an important part in supplying steam in a stoichiometric ratio.

As shown in Figure 6, there is a spherical \(\alpha\)-alumina, 0.3 cm in diameter, for the uniform diffusion of feed in the upper layer and the catalyst for SMR and the sorbent to remove CO\(_2\) in the next layer. In addition, \(\alpha\)-alumina is packed to keep the position of catalyst and sorbent in the lower layer.

A line filter is installed to remove impurities and a cold...
trap to dehydrate after the SMR process. Gas chromatography (HP agilent 6890, a TCD detector, and Column: Porapak N for CO$_2$ and Molecular sieve 5A for H$_2$, CH$_4$ and CO) was used for a quantitative analysis of products. A fixed bed reactor was used for testing the capacity of the catalyst and the sorbent based on calcium in the temperature range from 650 to 850 °C with a single layer. Before the hybrid reaction and the single SMR reaction, catalyst reduction was carried out first to activate catalyst at 800 °C, 1 atm for 12 h using a mixed gas composed of H$_2$ 10 % and He 90 %. The gas flow rate for the reduction reaction was 100 mL/min. The fixed bed reactor was then purged with nitrogen to set the SMR reaction temperature after the reduction. When the temperature of the reactor was maintained isothermally at the desired conditions, methane and steam were supplied with the reactor for 2 h. Average concentration data acquired during the SMR reaction was used to indicate the capacity of the system at each reaction condition. After checking the uniform concentration pattern of each species from the output, a regeneration reaction was carried out for 2 h at 950 °C and 1 atm using nitrogen gas. Cyclic tests were executed through these procedures.

**Results and Discussion**

Generally, space velocity is used for a catalytic reaction process as a variable and GHSV (Gas Hourly Space Velocity) is one aspect of space velocity for gaseous feeds. GHSV is defined as follows;

\[
\text{GHSV} = \frac{\text{Volumetric flow velocity of gas}}{\text{Volume of catalyst}} = \frac{v_o}{V} \quad (6)
\]

The S/C ratio was also used in this study, meaning the moles of injected steam divided by methane. If value of GHSV is 3,000 hr$^{-1}$, volumetric flow of gas is 598.5 cm$^3$/min (9.5 g · 1.26 g/cm$^3$ · 3,000/60 min$^{-1}$).

**Steam Methane Reforming Reaction**

The SMR reaction was carried out with a GHSV of 6,000 hr$^{-1}$, owing to the optimum value from the pretests among GHSV values of 2,000 ~ 12,000 hr$^{-1}$, to test the performance of the commercial catalyst using α-alumina instead of a CO$_2$ sorbent in the fixed bed reactor at atmospheric pressure. Figure 7 shows the composition of products as a function of reaction temperature and a ratio of S/C = 2, 2.5, 3, and 3.5. The composition of H$_2$ in the products increased as reaction temperature increased from 600 to 850 °C, but CH$_4$ decreased and CO$_2$ levels were maintained uniformly. The overall reaction involves the reaction (1) of SMR production and the reaction (3) of water gas shift reaction. When the temperature is high and the pressure is low, the SMR reaction occurs readily because it is an endothermic reaction. On the other hand, water gas shift reaction occurs readily at low temperature because it is an exothermic reaction.

If total heats of reaction between reaction (2) and reaction (3) are concerned, the overall reaction is an endothermic reaction similar to the forward reaction. As a result, the production of H$_2$ increases as the reaction temperature increases, the pressure is lower and the ratio of S/C is larger. A characteristic of the SMR reaction can be seen in the equation (4).

The composition of the produced H$_2$ was maintained at 78 % at temperature over 700 °C and the byproduct, unreacted CH$_4$, was below 3 % at temperature over 800 °C. If the ZECT process proceeds continuously, SOFC (solid oxide fuel cell) as a fuel cell which uses hydrogen at the final stage, can be selected because cell bodies made of
ceramic anticorrosive material are not affected by unreacted CH$_4$ or a reducing gas such as CO. At this point, the maximum composition of H$_2$ and the minimum composition of byproduct could be acquired in an S/C ratio of 3 \sim 3.5, and 700 \sim 800 \degree C in the case of this commercial catalyst, KATALCO 57-7. It is reported that the commercial catalyst, KATALCO 57-7, is deactivated mainly by sulfur compounds.

Figure 8 shows the isopleths for H$_2$ and CH$_4$ composition as a function of reaction temperature versus the ratio of S/C. As the temperature and ratio of S/C increases, the composition of H$_2$ in the product gases increases, but the composition of CH$_4$ decreases. We know that the reaction conditions for acquiring H$_2$ above 76 \% should be maintained above S/C = 2.7 at 700 \degree C and S/C = 2.6 at 750 \degree C and S/C = 1.5 at 800 \degree C. There is a correlation between the temperature and the S/C ratio in the feed. Therefore, the optimum operation conditions for increasing the production of H$_2$ and decreasing unreacted CH$_4$ could be selected from intersection between the temperature of x-axis and the S/C ratio of y-axis in the isopleths.

Removal of CO$_2$ by Sorbent
Conversion of the CO$_2$ removal reaction was carried out at variable temperatures to analyze the performance of the fresh sorbent and the data are shown in the Figure 9. The smooth line after 20 min is caused by the saturation of carbonation at each temperature. As a result, conversion as a function of temperature varies in the decreasing order 750 \degree C (0.84) > 700 \degree C (0.79) > 800 \degree C (0.78) and the maximum yield can be acquired at 750 \degree C. We consider that the CO$_2$ removal reaction rate is slower than the SMR reaction rate from long time into reaching that a steady state is needed. Lower capacity at 800 and 850 than 750 \degree C is caused by a competitive reaction between CO$_2$ absorption (carbonation) and decomposition reactions (calcination). The conversion of sorbent did not reach 100 \% because of the addition of alumina and activated carbon in consideration of the maintenance of reactivity in spite of the cycle tests.

Figure 10 shows 10 cycles test results for a carbonation reaction at 750 \degree C for 2 h and calcination at 950 \degree C for 1 h. The grams of CO$_2$ absorbed is maintained at 0.16 during the 10 cycles in spite of the deactivation of sorbent involving a decrease in surface area owing to sintering and incomplete calcination (Ryu and coworkers, 2003). We conclude the optimum temperature is 750 \degree C for a hybrid reaction between a high composition of H$_2$ in SMR and high CO$_2$ removal reaction from these results.
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Figure 10. 10 Cyclic test of sorbent at 750 °C for carbonation and 950 °C for calcinations.

Figure 11. The composition of gases produced by hybrid reaction according to GHSV.

Hybrid Reaction

The optimum carbonation temperature and the ratio of steam/methane were selected in sections 4.1 and 4.2. Although GHSV and the ratio of sorbent/catalyst were selected as a variable in the hybrid reaction, we selected GHSV as a variable instead of the ratio of sorbent/catalyst because it is certain that \( \text{CO}_2 \) removal increases according to an increase in the sorbent/catalyst ratio. The fixed ratio of sorbent/catalyst is 10 and catalyst weighs 9.5 gram.

Figure 11 shows the result of the hybrid reaction with variation in GHSV. As GHSV increases, the composition of \( \text{H}_2 \) decreases. However, the composition of \( \text{H}_2 \) in the hybrid reaction improves more than that for a single SMR reaction. The composition of product gas in the single SMR is about 72 % \( \text{H}_2 \), 12 % \( \text{CO} \), 6 % \( \text{CH}_4 \), and 10 % \( \text{CO}_2 \) at GHSV = 3,000 hr\(^{-1}\), 750 °C, 1 atm during 100 min, but that of hybrid reaction is about 94 % \( \text{H}_2 \), 3.5 % \( \text{CO} \), 2.0 % \( \text{CH}_4 \), and 0.5 % \( \text{CO}_2 \) at same conditions.

These results in the simultaneous removal of \( \text{CO}_2 \), one of products of reaction (4), by the sorbent located in the lower layer and hydrogen production reaction is accelerated by Le Chaterlier’s theory. As the one of the products in the reaction (4), \( \text{CO}_2 \), is removed by the sorbent, the overall reaction is shifted to forward direction by Le Chaterlier’s theory and the production of \( \text{H}_2 \) increases. Despite being enhanced by the sorbent, the amount of \( \text{H}_2 \) produced decreased and the other increased above GHSV = 5,000 hr\(^{-1}\) because of short contact time by the large GHSV and lowering the capacity of the sorbent to remove \( \text{CO}_2 \) by the large GHSV. Although it is possible to acquire the maximum concentration of \( \text{H}_2 \) at 1,000 hr\(^{-1}\), the speed of \( \text{H}_2 \) generation at 1,000 hr\(^{-1}\) is relatively low. The optimum GHSV is chosen to be 3,000 hr\(^{-1}\) from these results. A decrease in the optimum GHSV from 6,000 hr\(^{-1}\) in the single SMR reaction to 3,000 hr\(^{-1}\) in the hybrid reaction is caused by the obstruction of flow and diffusion by the height of the packed particles though the height of the sorbent. Two reactions, SMR and \( \text{CO}_2 \) removal, occur subsequently in the hybrid reaction and the relatively slow reaction determines the overall reaction rate. The reaction rate of \( \text{CO}_2 \) removal by the dry sorbent is relatively slower than the SMR catalytic reaction rate [15].

Figure 12 shows the change in composition of the product gases for 120 min. The conditions for the reaction are temperature = 750 °C, ratio of sorbent/catalyst = 10, steam/methane = 3 and GHSV = 3,000 hr\(^{-1}\), which are the operating conditions, as evidenced by the data shown in Figure 10. The average composition of \( \text{H}_2 \) in the product gases maintained a continuous value, 96 %, in the initiation step for 60 min. However, as time elapsed, the decrease in the \( \text{H}_2 \) production capacity of the hybrid reaction was caused by the problem in the reaction (2). \( \text{CO}_2 \) and \( \text{CO} \) composition in the product gases increased
Figure 13. 10 Cyclic test of hybrid reaction at 750 °C, S/C = 3 and GHSV = 3,000 hr\(^{-1}\).

because the water gas shift reaction and CO\(_2\) removal reaction did not progress smoothly according to reaction time because of different temperature zone for water gas shift reaction and saturation of sorbent for CO\(_2\). Sorbent for removing CO\(_2\) is deactivated faster than catalyst with time because of consumption reaction itself. Reaction (2) will be deactivated gradually by deactivated sorbent in the hybrid reaction and then unreacted CO and CO\(_2\) flow out. If experiment is executed for a long time, the composition in the hybrid reaction is equal to that of the single SMR reaction because of the sorbent which captures CO\(_2\) fully.

Therefore, we considered that the CO\(_2\) removal step by the sorbent was the reaction rate determining step in the hybrid reaction and the continuous purity of H\(_2\) was depended on the capacity of the sorbent.

The average composition of each component in the product gases for a 120 min was used as a representative data point at each count as shown in Figure 13. Figure 13 shows the results for a 10 cycles test for conditions of 750 °C for carbonation, 950 °C for calcination, steam/methane = 3, sorbent/catalyst = 10, 1 atm and GHSV = 3,000 hr\(^{-1}\). The composition of H\(_2\) was 92+% during the 10 cycles test. However, as the number of cycles progresses, the activities of the sorbent and catalyst show a tendency to decrease. Deactivation is always accompanied by a significant decrease in pore volume and surface area and an increase in the average crystallite size of the CaO components of the sorbent. These effects are currently being investigated.

A hybrid system using a sorbent and catalyst without heat loss can be a positive process for ZECT from these results in comparison with the SERP process, which involves heat loss. If we combined this hybrid system for producing high purity H\(_2\) and an application stage using H\(_2\), many economic advantages can result, such as a higher composition of H\(_2\) in the product gases, an economical process that will conserve energy as a single process and the sequestration or recovery of CO\(_2\) by recycling, from the calcination process to the sorbent.

Conclusion

Various experiments were carried out to improve the yield of H\(_2\). A high concentration (about 92+%) of H\(_2\) in the product gas streams can be produced using the hybrid process using KATALCO 57-7 as a commercial reforming catalyst and a sorbent as a dry absorber of CO\(_2\), composed of CaCO\(_3\) 80 wt%, \(\alpha\)-Al\(_2\)O\(_3\) 15 % and activated carbon 5 wt%.

1) Performance tests of reforming catalyst were carried out at atmospheric pressure, 600 ~ 850 °C and a ratio of S/C = 2 ~ 3.5. Under these conditions, the maximum composition of H\(_2\) from the products was 78 %, above S/C = 2.7 at 700 °C and S/C = 2.6 at 750 °C and S/C = 1.5 at 800 °C.

2) As a result of the performance test of the dry sorbent for removing CO\(_2\) in the temperature of 650 to 850 °C, the optimum temperature was determined to be 750 °C and the capacity for removing CO\(_2\) was maintained uniformly during a 10 cycles test.

3) For the hybrid reaction, the sorbent and catalyst are packed in the fixed bed reactor at a ratio of 10 (sorbent/catalyst = 10) and the reaction executed at 750 °C and 3,000 hr\(^{-1}\). The composition of H\(_2\) was 92+% and the capacity was continuously maintained during a 10 cycles test. Increase in H\(_2\) composition is caused by a shift in the overall reaction with the removal of CO\(_2\), a by-product of the SMR reaction, based on Le Chaterlier’s theory.

Acknowledgment

This research was supported by a grant (DE2-101) from the Carbon Dioxide Reduction and Sequestration Research Center, one of the 21\(^{st}\) Century Frontier Programs funded by the Ministry of Science and Technology of Korean government.

Reference