Effect of Hydrogen Separation on Coal Char Gasification with Subcritical Steam Using a Calcium-Based CO2 Sorbent

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ABSTRACT: Coal char was gasified using subcritical steam with/without a CO2 sorbent (CaO) and/or a hydrogen separation membrane (palladium-23% silver) in a batch/semibatch autoclave reactor to investigate the kinetics in terms of the effect of hydrogen separation at 590−650 °C and 1.9−2.4 MPa in order to support a hydrogen production process of the HyPr-RING method. CO2 sorption by CaO affects the production rate of H2 but scarcely affected the carbon conversion to gas. Hydrogen separation promotes the hydrogen production in spite of the absence of CO2 sorption. The effect of hydrogen separation on hydrogen yield and carbon conversion was higher than that of CO2 sorption. A higher gasification temperature increased the hydrogen yield and carbon conversion. Using a first-order reaction form in parallel, the gasification reaction mechanism was explained for the components of the volatile matter and char in coal char. A higher reaction temperature results in an increase of the values of any kinetic constant for subcritical steam gasification of Adaro coal char with/without CaO and/or a hydrogen separation membrane. CO2 sorption promoted hydrogen production due to the tar from volatiles with the catalytic effects of CaO, whereas hydrogen separation promoted hydrogen production due to char.

INTRODUCTION

The clean use of carbonous resources such as low-rank coal, biomass, and organic wastes is desired due to fossil fuel depletion and global environment problems. Careful consideration to minimize CO2 emissions is required in energy generated from organic matters; however, a stable supply of hydrogen is critical to construct a clean and efficient energy system such as fuel cells. The gasification of carbonous resources with steam is a key technology currently applied in the development of hydrogen generation.

The HyPr-RING process is one of new hydrogen production methods from organic matters using steam under high pressure, without CO2 emissions using a Ca-based sorbent.1−26 Figure 1, shown in our previous work,27−30 is a diagrammatic representation of this concept. By the reaction of organic matters using steam and Ca-based sorbents, hydrogen and calcium carbonate are mainly produced. By calcining CaCO3, it can be regenerated to CaO with a high concentration of CO2.

The following reactions are those occurring within a reactor in the HyPr-RING process.

Steam gasification

\[
\text{C(s) + H}_2\text{O(g)} \rightarrow \text{CO(g) + H}_2\text{(g)}, \quad \Delta H_{923} = 136 \text{ kJ/mol} (1)
\]

Water−gas shift reaction

\[
\text{CO(g) + H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g) + H}_2\text{(g)}, \quad \Delta H_{923} = -36 \text{ kJ/mol} (2)
\]

CaO hydration

\[
\text{CaO(s) + H}_2\text{O(g)} \rightarrow \text{Ca(OH)}_2\text{(s)}, \quad \Delta H_{923} = -97 \text{ kJ/mol} (3)
\]

Ca(OH)2 carbonation

\[
\text{Ca(OH)}_2\text{(s) + CO}_2\text{(g) \rightarrow CaCO}_3\text{(s) + H}_2\text{O(g)},} \quad \Delta H_{923} = -74 \text{ kJ/mol} (4)
\]

Here, in eqs 1−4, “(s)” and “(g)” denote solid and gas phases, respectively.

The enthalpy required for steam gasification is compensated by the enthalpies of CaO hydration and Ca(OH)2 carbonation. CO is converted to CO2 and H2 via eq 2 with Ca(OH)2 carbonation by eq 4. The overall stoichiometric reaction can be written by combining eqs 1−4, as follows:

\[
\text{C(s) + 2H}_2\text{O(g) \rightarrow CO}_2\text{(g) + 3H}_2\text{(g)},} \quad \Delta H_{923} = 54 \text{ kJ/mol} (5)
\]

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Figure 1. Concept of the proposed hydrogen production (HyPr-RING) method.27−30
C(s) + CaO(s) + 2H₂O(g) → 2H₂(g) + CaCO₃(s),
ΔH°₂₃ = −70 kJ/mol

The steam gasification of the organic material with CO₂ sorption by Ca(OH)₂ requires high-pressure conditions, according to thermodynamic analysis. The kinetics of the gasification of organic materials such as Taiheiyo coal (Japanese sub-bituminous coal), Adaro coal (Indonesian sub-bituminous coal), and dried sewage sludge with steam and calcium hydrate at 600–727 °C and 3–20 MPa were investigated in our previous work.²⁷

By the use of membranes, particularly palladium (Pd)-based metallic membranes, high purity hydrogen can be separated from gas mixtures.³¹–³⁴ However, the impurities, particularly H₂S, in the gas stream affect the surface of Pd membranes.³⁵–³⁷ The alloying of Pd membranes can improve the hydrogen flux and resistance to surface poisoning.³⁸ In addition, temperatures more than 350 °C and large differential pressures across the membrane surface can efficiently operate Pd-based membranes.⁴¹

In this report, Adaro coal char gasification with subcritical steam was carried out with/without CaO with/without a hydrogen separation membrane [Pd-23% silver (Ag)] in a batch/semibatch autoclave reactor to consider the kinetics in terms of the effect of hydrogen separation at 590–650 °C and 1.9–2.4 MPa in the application of the HyPr-RING method, as shown in Figure 2.

RESULTS AND DISCUSSION

Effect of CO₂ Sorption on the H₂ Production Rate and Carbon Conversion to Gas. Figures 3 and 4 show the changes in the H₂ production rate and carbon conversion to gas, respectively, with/without CaO and with/without the hydrogen separation membrane with reaction time for subcritical steam gasification at 650 °C and 1.9–2.4 MPa.

The H₂ production rates for subcritical steam gasification without and with CaO in the absence of the hydrogen separation membrane were maximum at a reaction time of approximately 90 min. The total H₂ production amounts without and with CaO were 71 and 120 mL, respectively, whereas the carbon conversion to gas without and with CaO after the reaction time of 1000 min was 13 and 20%, respectively. These results suggest that CO₂ sorption by CaO affected the production rate of H₂ but scarcely affected the carbon conversion to gas because more than 80% of the pressure in the reactor was due to steam.²⁸ In addition, CO and CO₂ were produced without CaO, whereas they were not produced with CaO, according to eqs 2 and 4.

The H₂ production rates for subcritical steam gasification without and with CaO in the presence of the hydrogen separation membrane were a maximum at a reaction time of 80–90 min. The total H₂ production amounts without and with CaO were 530 and 760 mL, respectively, whereas the carbon conversion to gas without and with CaO after the reaction times of 1360 and 1600 min was 59 and 84%, respectively. This suggests that CO₂ produced without CaO inhibited the chemical reactions represented by eqs 1 and 2 despite hydrogen separation, whereas the CO₂ sorption with CaO promoted the reactions represented by eqs 1 and 2 with hydrogen separation.¹–¹⁴,¹⁶–³⁰

Effect of Hydrogen Separation on the H₂ Production Rate and Carbon Conversion to Gas. The H₂ production rate and carbon conversion to gas with a hydrogen separation membrane were higher than those without the membrane. The total H₂ production amounts without and with the hydrogen separation membrane in the absence of CaO were 71 and 530 mL, respectively, whereas those in the presence of CaO were 120 and 760 mL, respectively. The final carbon conversion to gas without and with the hydrogen separation membrane in the absence of CaO was 13 and 59%, respectively, whereas those in the presence of CaO were 20 and 84%, respectively. This suggests that the H₂ that remained in the reactor without...
the hydrogen separation membrane inhibited the reactions represented by eqs 1 and 2 in spite of CO₂ sorption, whereas hydrogen separation promoted the reactions associated with these equations in spite of the absence of CO₂ sorption.34,36 Thus, the effect of hydrogen separation on the hydrogen production and carbon conversion to gas was higher than that of CO₂ sorption.

Effect of Reaction Temperature on the H₂ Production Rate and Carbon Conversion to Gas. The changes in the H₂ production rate and carbon conversion to gas with CaO as a function of reaction time for subcritical steam gasification without and with the hydrogen separation membrane at 590–650 °C and 1.9–2.4 MPa are shown in Figures 5 and 6, respectively.

![Figure 5](image)

**Figure 5.** Changes in the H₂ production rate (solid line) and carbon conversion to gas (dotted line) with CaO as a function of reaction time for subcritical steam gasification without the hydrogen separation membrane at 590 °C (blue line), 620 °C (yellow line), and 650 °C (red line).

![Figure 6](image)

**Figure 6.** Changes in the H₂ production rate (solid line) and carbon conversion to gas (dotted line) with CaO as a function of reaction time for subcritical steam gasification with the hydrogen separation membrane at 590 °C (blue line), 620 °C (yellow line), and 650 °C (red line).

In Figures 5 and 6, the H₂ production rate and carbon conversion to gas with/without the hydrogen separation membrane increased with the reaction temperature. This result is similar to that of our previous study.27 In addition, H₂ production without the hydrogen separation membrane seemed to be completed after the reaction time of 1000 min at 590–650 °C, whereas the H₂ production time with the membrane was longer as the reaction temperature increased. These results suggest that the amount of reactive carbon increased with the reaction temperature and hydrogen separation.27,29,30

Effect of CO₂ Sorption and Hydrogen Separation on Kinetics of Adaro Coal Char Gasiﬁcation with Subcritical Steam. The reaction mechanism of coal gasification in the HyPr-RING process, as considered in our previous studies28–30 is shown in Figure 7.30

![Figure 7](image)

**Figure 7.** Reaction mechanism of coal gasification considered in the HyPr-RING process.30 The following are assumed:30

1. Fixed carbon converted to char and volatile matter (VM) in the form of carbon, configuring the coal.
2. Char gasification with steam produces H₂ with k₂ (s⁻¹).
3. Tar and hydrocarbon gases (CₙHₙ), such as CH₄, C₂H₄, and C₂H₆, are produced in pyrolysis of VM in the form of carbon with kinetic constants k₃ and k₁ (s⁻¹), respectively.
4. Steam gasification and pyrolysis of tar produce H₂ and CₙHₙ with k₄ and k₅ (s⁻¹), respectively.
5. The product gas does not contain CO and CO₂ according to eqs 2 and 4.

The change in the logarithmic calculated line and observed plots of residual carbon in the gasification residue with relation to reaction time for Adaro coal char gasification with subcritical steam in the presence of CaO and a hydrogen separation membrane at 650 °C and 1.9–2.4 MPa are shown in Figure 8.

![Figure 8](image)

**Figure 8.** Changes in logarithmic calculated line and observed plots of residual carbon in the gasification residue with relation to reaction time for Adaro coal char gasification with subcritical steam in the presence of CaO and hydrogen separation membrane at 650 °C and 1.9–2.4 MPa.

In this case, by subtracting the rate of carbon conversion to gas from 100%, the observed plots of the residual carbon in the figure were evaluated. Material and heat transfer, as well as kinetics, generally control reactions.42 However, in the report, the kinetics of these step reactions are assumed to be of pseudo-first-order reaction with the components of VM and char in coal char and according to eqs 7–14,30 given that the mixing mole ratios of CaO/coal char and H₂O/coal char for Adaro coal char gasification with subcritical steam and CaO were 1.43 and 5.0 mol/molcarbon, respectively, which were in excess of the stoichiometric amounts.

\[ r_{\text{Char}} = -k_{2}C_{\text{Char}} \] (7)
show the values for activation energy (E) and k1 to k5 for each kinetic constant, computed from the plots for each kinetic constant at 1.9–2.4 MPa for subcritical steam gasification of Adaro coal char with/without CaO and/or a hydrogen separation membrane.

In Tables 1–3, a higher reaction temperature resulted in an increase of the values of k1–k5 for Adaro coal char gasification using subcritical steam with/without CaO and/or a hydrogen separation membrane.

The k1 values in Table 3 were less than 1.3–1.9 times those in Table 2, whereas the k3, k4, and k5 values in Table 3 were more than 0.5–3.0, 0.7–1.8, and 1.2–1.5 times those in Table 1, respectively. This suggests that CO2 sorption promotes pyrolysis of VM to tar and steam gasification of char and tar to hydrogen due to the catalytic effects of CaO,3,7 thereby inhibiting pyrolysis of VM to hydrocarbon gases at higher reaction temperatures.

In addition, the k1 values in Table 3 were less than 2.5–2.7 times those in Table 2, whereas the k3, k4, and k5 values in Table 3 were more than 0.5–1.5, 0.9–4.0, and 2.0–3.2 times those in Table 2, respectively. This suggests that hydrogen separation also promotes pyrolysis of VM to tar and steam gasification of char and tar to hydrogen, thereby inhibiting pyrolysis of VM to hydrocarbon gases at higher reaction temperatures.

Thus, CO2 sorption mainly promotes hydrogen production because of tar from VM with the catalytic effects of CaO, whereas hydrogen separation mainly promotes hydrogen production from char.

Application of the Results. As previously mentioned, the total H2 production amounts for subcritical steam gasification without and with CaO in the absence of the hydrogen separation membrane were 71 and 120 mL, respectively, whereas those without and with the hydrogen separation membrane in the presence of CaO were 120 and 760 mL, respectively. Thus, the effect of hydrogen separation with CaO on hydrogen production is higher than that of CO2 sorption without the hydrogen separation membrane. There has been no report focusing on the hydrogen production with both hydrogen separation and CO2 sorption under the HyPr-RING conditions in the previous studies.1–30 Therefore, the present work is useful for the efficiency of the HyPr-RING process.

### CONCLUSIONS

Adaro coal char gasification using subcritical steam was carried out with/without CaO as a CO2 sorbent and/or Pd-23% Ag as a hydrogen separation membrane in a batch/semibatch autoclave reactor to investigate the kinetics in terms of the effect of hydrogen separation at 590–650 °C and 1.9–2.4 MPa.
to investigate the application of the HyPr-RING method. The main conclusions are as follows

1. CO₂ sorption by CaO affects the production rate of H₂ but scarcely affected the carbon conversion to gas.
2. Hydrogen separation promotes the hydrogen production in spite of the absence of CO₂ sorption.
3. The effect of hydrogen separation on hydrogen yield and carbon conversion is higher than that of CO₂ sorption.
4. A higher gasification temperature increases hydrogen yield and carbon conversion.
5. Using a first-order reaction form in parallel, the gasification reaction mechanism is explained for the components of VM and char in coal char.
6. A higher reaction temperature results in an increase of the values of any kinetic constant for subcritical steam gasification of Adaro coal char with/without CaO and/or a hydrogen separation membrane.
7. CO₂ sorption promotes hydrogen production via tar from volatiles with the catalytic effects of CaO, whereas hydrogen separation promotes hydrogen production from char.

Table 2. Values of E at 1.9–2.4 MPa and k₁ to k₅ for 590–650 °C for Adaro Coal Char Gasification Using Subcritical Steam with CaO and No Hydrogen Separation Membrane.

|   | 590 °C × 10⁻³ [s⁻¹] | 620 °C × 10⁻³ [s⁻¹] | 650 °C × 10⁻³ [s⁻¹] | E [kJ/mol] |
|---|---------------------|---------------------|---------------------|------------|
| k₁ | 0.50                | 0.70                | 1.0                 | 76.5       |
| k₂ | 0.14                | 0.20                | 0.30                | 84.0       |
| k₃ | 0.20                | 0.60                | 0.80                | 154.0      |
| k₄ | 1.5                 | 1.9                 | 2.5                 | 56.3       |
| k₅ | 0.50                | 1.0                 | 2.0                 | 153.0      |
| k₁ + k₃ | 0.70 | 1.3 | 1.8 |
| k₄ + k₅ | 2.0 | 2.9 | 4.5 |

Table 3. Values of E at 1.9–2.4 MPa and k₁ to k₅ for 590–650 °C for Adaro Coal Char Gasification Using Subcritical Steam with CaO and Hydrogen Separation Membrane.

|   | 590 °C × 10⁻³ [s⁻¹] | 620 °C × 10⁻³ [s⁻¹] | 650 °C × 10⁻³ [s⁻¹] | E [kJ/mol] |
|---|---------------------|---------------------|---------------------|------------|
| k₁ | 0.20                | 0.27                | 0.38                | 70.8       |
| k₂ | 0.13                | 0.52                | 1.2                 | 245.9      |
| k₃ | 0.10                | 0.45                | 1.2                 | 274.8      |
| k₄ | 3.0                 | 5.0                 | 8.0                 | 108.3      |
| k₅ | 0.30                | 0.45                | 0.60                | 76.6       |
| k₁ + k₃ | 0.30 | 0.72 | 1.6 |
| k₄ + k₅ | 3.3 | 5.5 | 8.6 |

Table 4. Ultimate and Proximate Analyses of Adaro Raw Coal and Adaro Coal Char.

| coal sample       | ultimate analysis [wt %, dry ash-free basis] | proximate analysis [wt %, accepted basis] |
|-------------------|---------------------------------------------|-------------------------------------------|
|                   | C   | H   | N   | O (difference) | VM | fixed carbon | ash | moisture |
| Adaro raw coal    | 73.2 | 5.3 | 1.0 | 20.5 | 39.7 | 40.6 | 0.9 | 18.8     |
| Adaro coal char   | 85.2 | 3.5 | 1.2 | 10.1 | 17.5 | 78.2 | 1.7 | 2.6      |

Experimental Apparatus. A laboratory-scale batch autoclave reactor was used to investigate the subcritical steam gasification of Adaro coal char with/without CaO in the absence of a hydrogen separation membrane. Figure 10 shows the schematic diagram of the batch autoclave reactor, made of SUS-316 (stainless steel) and used in the present study. The reactor had a height of 10.6 cm, an outer diameter of 10.1 cm, and a volume of 110 cm³. It was externally heated to a given temperature using an electric furnace.

Figure 10. Schematic diagram of the laboratory-scale batch autoclave reactor used in the present study.
A laboratory-scale semibatch autoclave reactor was used to investigate the subcritical steam gasification of Adaro coal char with/without CaO in the presence of a hydrogen separation membrane. Figure 11 shows a schematic diagram of the semibatch autoclave reactor, made of SUS-316 (stainless steel) and used in the present study. The reactor had a volume of 110 cm³, a height of 10.6 cm, and an outer diameter of 10.1 cm. A Pd-23% Ag metallic membrane, which was 50 mm long with an outer diameter of 9.52 mm, inner diameter of 9.02 mm, and surface area of 14.9 cm², was used as a hydrogen separation membrane in the reactor (Takanaka Kikinzoku Kogyo, K.K., Japan). The reactor was externally heated to a given temperature using an electric furnace.

Experimental Procedure. The batch or semibatch autoclave reactor was loaded with a mixture of 0.307 g of Adaro coal char and 1.8 mL of distilled water, with or without 1.60 g of CaO prior to being sealed, at room temperature using an electric furnace.

For subcritical steam gasification without the hydrogen separation membrane, the batch reactor was heated to 590–650 degrees centigrade within 35 min, and then held at this temperature for each desired reaction time of 0.5–16.7 h for a reactor pressure of 1.9–2.4 MPa. After the desired reaction time, the reactor was cooled to room temperature using an electric fan to quench the reaction. The gaseous products were discharged from the reactor into a gas bag using a valve. Using a commercially available GC-TCD (Shimadzu GC-2014; using MS-SA and PPQ columns with the carrier gas of argon), the concentrations of hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, and ethane were analyzed. The total amount of the produced gas was estimated from the inner reactor volume, pressure, and temperature.

For subcritical steam gasification with the hydrogen separation membrane, the semibatch reactor was heated to 590–650 degrees centigrade within 35 min and then held in this temperature range with the reactor pressure set at 1.9–2.4 MPa. Immediately after heating, 500 mL/min of N₂ gas was introduced to the inside of the separation membrane as a sweep gas. The gas flow rate and H₂ concentration in the gas through the membrane were analyzed every 10 min using a wet gas meter (Shinagawa W-NK-0.5A) and the gas chromatogram, respectively. When H₂ was no longer detected in the gas, the reactor was cooled to room temperature using an electric fan to quench the reaction. The gaseous products were discharged from the reactor into a gas bag using a valve, followed by analysis using the gas chromatograph. The amount of produced gas that remained in the reactor after cooling was estimated from the inner reactor volume, pressure, and temperature.

Notes

The authors declare no competing financial interest.

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