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Short communication

Effect of carbon dioxide absorbent on initial hydrogen production from epoxy resin under high-temperature and -pressure steam conditions

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Abstract

Steam gasification employing a CO_2 absorbent was investigated using epoxy resin under high-temperature and -pressure conditions: 873 through 973 K, and 1 through 10 MPa. A newly designed drop tube reactor was introduced in order to achieve a rapid increase in sample temperature to simulate the initial stage of continuous reaction. Hydrogen generation was accelerated effectively with an addition of calcium hydroxide as a carbon dioxide absorbent, with efficiency of calcium utilization becoming higher under the higher pressure condition. Methane generation at the initial reaction step was suppressed by the addition of calcium to the drop tube reactor, while much methane was obtained in an autoclave-type reactor whose rate of temperature increase was small.

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1. Introduction

Hydrogen is a prospective primary energy resource for distributed energy systems. Taking account of the efficiency of current hydrogen production technology, more appropriate hydrogen producing methods should be developed for sustainable growth. Recently, a new hydrogen production process has been developed to produce more hydrogen from organic materials using carbon dioxide absorption under super-/sub-critical water conditions [1,2] and it has been named HyPr-RING.

In our previous studies, we used mainly a batch-type reactor, and obtained a mixture of high purity hydrogen and methane, 80% H_2 and 20% CH_4, respectively, from fossil fuel [1–3]. Carbon dioxide and carbon monoxide were trace products. Also, S and Cl compounds were not detected as they were lower than the detection limit of the gas chromatograph. However, these results were not concerned with the initial stage reaction mechanism because of the slow temperature increase and insufficient gas–solid contact. In this study, the initial stage reaction was investigated under a rapid temperature increase and sufficient gas–solid contact conditions.

1.1. HyPr-RING process

The guiding principle of the HyPr-RING process promotes water gasification, Eq. (1), and the water–gas shift reaction, Eq. (2), in a single reactor by combining the CO_2 absorbing process, Eq. (3).

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g), \quad \Delta H^{\circ}_{298} = 132\,\mathrm{KJ/mol} \tag{1}$$

$$CO(s) + H_2O(g) \rightarrow CO_2(g) + H_2(g), \quad \Delta H^{\circ}_{298} = -41.5\,\mathrm{KJ/mol} \tag{2}$$

$$CO_2(g) + CaO(s) \rightarrow CaCO_3(s), \quad \Delta H^{\circ}_{298} = -178\,\mathrm{KJ/mol} \tag{3}$$

With the coexistence of reaction (3), chemical equilibrium of reaction (2) should be shifted to the product side, and H_2 yield should be increased. Also, reaction (3) is exothermic and acts as a heat source of reaction (1) that is a strong endothermic reaction. A general expression for this new

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reaction system is given as

$$\mathrm{C(s)+2H_2O(g) + CaO(s) \rightarrow CaCO_3(s) + 2H_2(g)}, \quad \Delta H^{\circ}_{298} = -178\,\mathrm{KJ/mol} \qquad (4)$$

This total reaction is exothermic and proceeds spontaneously in the range of 873 through 973 K and higher pressure. The HyPr-RING process can be applied to not only coal but also other organic materials such as biomass and organic waste materials. Tar will be generated from such organic materials, which should be concerned for efficiency of gasification. In the present study, epoxy resin was investigated as typical source of tar using the newly designed reactor that realizes rapid temperature increase condition.

2. Experimental

A drop tube reactor (DTR) was used to rapidly increase the sample temperature, which made it possible to analyze the initial stage reaction. The outline of the apparatus is shown in Fig. 1. The DTR consisted of three zones: the sample holding zone, the reaction zone, and the quench zone. An electrical furnace was used to maintain the reaction zone temperature, and the interior pressure of the DTR was controlled by means of a backpressure regulator. The sample material used in the present study was epoxy resin (poly(bisphenol A-co-epichlorohydrin), average molecular weight; ca. 40,000, average particle diameter; ca. 3 mm, Aldrich) as a representative of the tar. Epoxy resin and $Ca(OH)_2$ (average particle diameter = 0.005 mm; Wako pure chemical) were set in a sample cage made of wire-mesh (SUS304). The sample cage was introduced to the reaction zone by opening the lower valve of the sample holding zone after reaching the desired temperature and pressure. In this work, the feed rate of water was fixed at 1.1 g/min. The typical reaction temperature and pressures were $T = 973$ K and $P = 1$, 5 and 10 MPa. The heating period of the epoxy resin was estimated as approximately 30 s through 60 s under the present condition, which was a relatively small value in comparison with reaction time. The typical weight of the epoxy resin was 250 mg. The molar ratio of calcium-to-carbon, Ca/C, was 0 and 0.5 through 0.6. The gases produced through the backpressure regulator were collected through the gas–liquid separator into the sampling bag in order to measure the gas production rate. During the reaction operation, the produced gases were collected by a

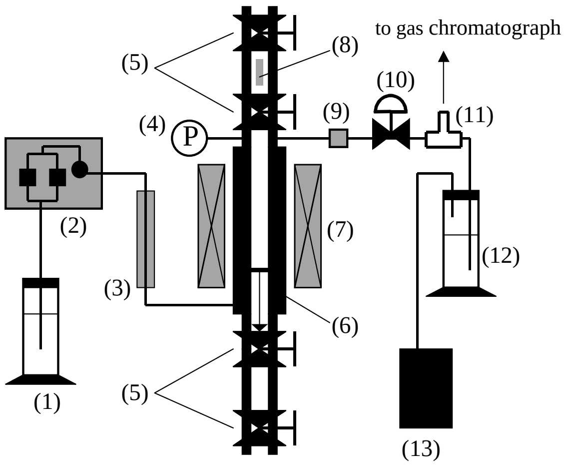

Fig. 1. Experimental apparatus: (1) water feed tank, (2) liquid feed pump, (3) pre-heater, (4) pressure gauge, (5)stop valve for sample insertion, (6) semi-batch reactor, (7) electrical furnace, (8) sample cell, (9) filter, (10) backpressure regulator, (11) gas-sampling port, (12) gas–liquid separator, (13) volume measurement device for generated gases.

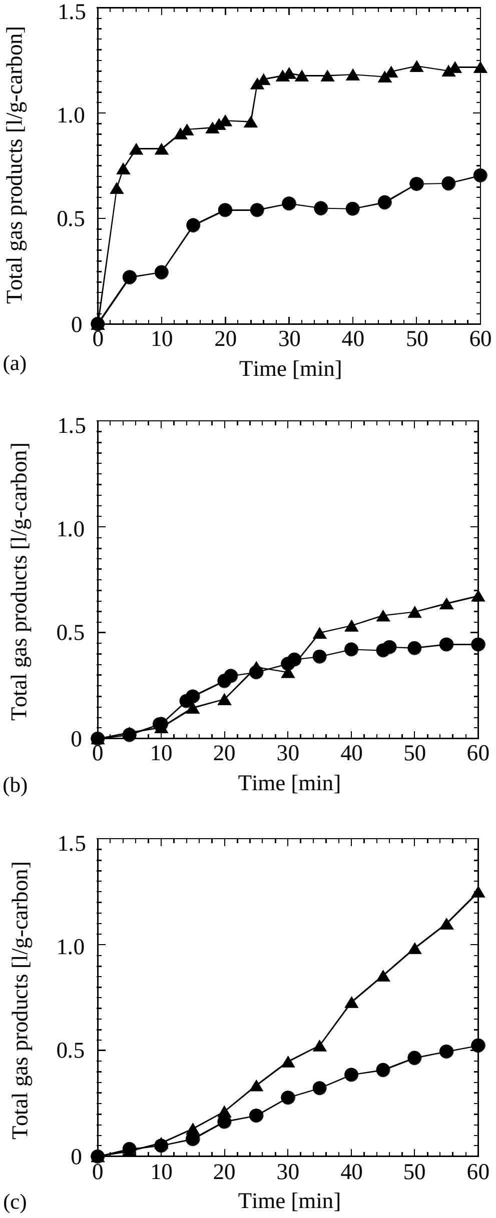

Fig. 2. Time dependence of total gas product. Temperature: 973 K. (a) Total pressure 1 MPa: (●) Ca/C = 0, (▲) Ca/C = 0.5. (b) Total pressure 5 MPa: (●) Ca/C = 0, (▲) Ca/C = 0.5. (c) Total pressure 10 MPa: (●) Ca/C = 0, (▲) Ca/C = 0.6. The gas compositions in the figure are water-free products.

sampling syringe every 5–10 min, and then analyzed by a gas chromatograph equipped with a thermal conductivity detector in order to obtain the time-series data. After the desired time had passed, 1 h for the present work, the upper valve of the quench zone was opened to withdraw the remaining solid sample and liquid. The total amount of carbon in the gas, liquid, and solid phases was analyzed in order to obtain a carbon balance. The amount of carbon in the liquid effluent and that remaining in the reactor vessel were analyzed by total carbon measurement (Shimadzu TOC-5000A). Hydrochloric acid solution was added to the remaining solid sample to release carbon dioxide and to measure that which had been absorbed. In some runs, batch tests were also performed in an autoclave-type reactor for comparison with the DTR.

3. Results and discussions

In the HyPr-RING process, hydrogen was observed as a main gas-product, and methane, carbon monoxide, and carbon dioxide were observed as by-products. Trace amounts of ethane and ethylene were also detected, and their molar fractions in the total gas-product were smaller than 1%, respectively.

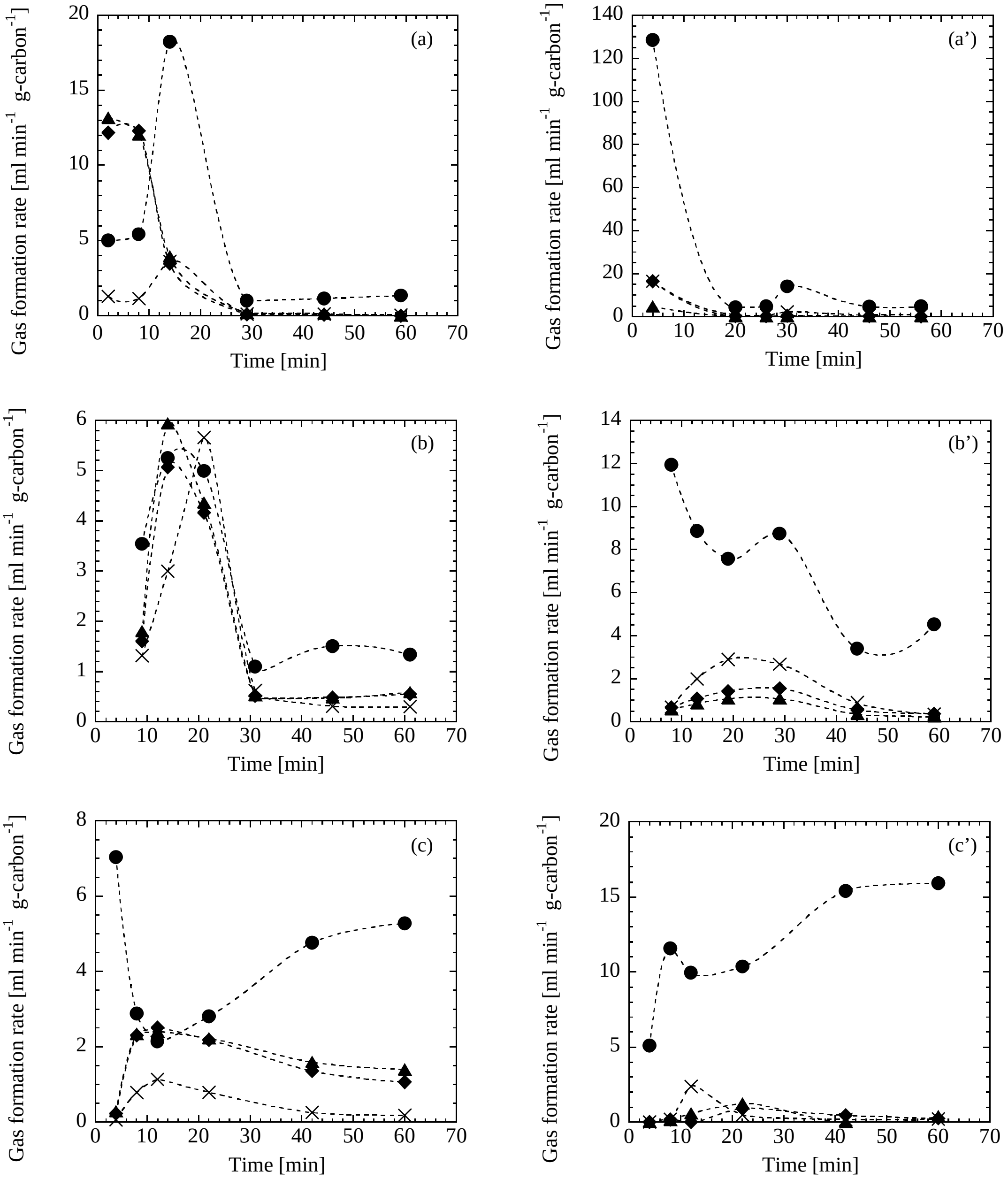

Fig. 3. Gas production rates vs. reaction time. Temperature: 973 K. (●) H_2, (▲) CO, (×) CO_2, (◆) CH_4. (a) Total pressure 1 MPa, Ca/C = 0; (a′) total pressure 1 MPa, Ca/C = 0.5; (b) total pressure 5 MPa, Ca/C = 0; (b′) total pressure 5 MPa, Ca/C = 0.5; (c) total pressure 10 MPa, Ca/C = 0; (c′) total pressure 10 MPa, Ca/C = 0.6. The gas compositions in the figure are water-free products.

Fig. 2 shows the cumulative volume of the produced gas with a series of total pressures of 1, 5, and 10 MPa. Under any pressure conditions, it is observed that gas production rates increase when calcium hydroxide is supplied into the system. In the cases of 5 and 10 MPa, the time delays of the gas productions are observed at the initial step. This may be caused by the systematical or capacitance delay of the reactor, because longer residence time is required at higher pressures under the constant steam feed rate condition. Hydrogen was generated continuously for over 1 h, and gas production rates were observed at periodic intervals for 1 h.

Fig. 3 shows the influence of the operating pressure on the gas production rate of hydrogen, carbon monoxide, carbon dioxide, and methane. Fig. 3(a)–(c) shows the results for $Ca/C = 0$, and Fig. 3(a′)–(c′) shows the results for $Ca/C =$ 0.5, 0.5, and 0.6, respectively. Though the experimental data are scattered, a significant increase of the hydrogen production is observed by the calcium hydrate addition. Especially for the 10 MPa, almost pure hydrogen was produced at the initial stage, which suggests that methane generated through a thermal decomposition reaction possibly decreases by adding the calcium hydroxide at the initial stage of the higher-pressure reaction. Changes in the gas production rates are almost similar among the carbon monoxide, carbon dioxide, and methane in each pressure condition. The yield of the carbonous gas-products against the total carbon amount decreases from 13% at 1 MPa to 5% at 10 MPa, while the yield of $CaCO_3$ increases from 17% at 1 MPa to 52% at 10 MPa. Thus, this also further demonstrates that the reaction (4) proceeds efficiently under the high-pressure steam condition.

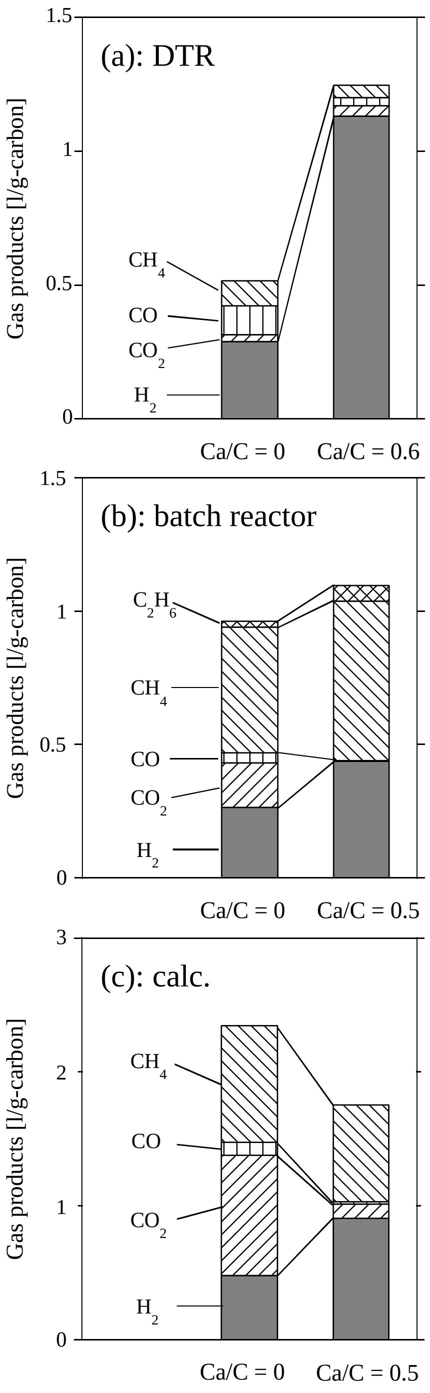

Fig. 4. Gas compositions in DTR and batch reactor. (a) Gas products in DTR; reaction temperature: 973 K, total pressure: 10 MPa, reaction time: 1 h. (b) Gas products in batch reactor; reaction temperature: 923 K, total pressure: 10 MPa ($S/C \approx 2$), reaction time: 1 h. (c) Equilibrium calculation at 923 K and total pressure 10 MPa. The gas compositions in the figure are water-free products.

In order to clarify the characteristics of the DTR results, the total amount of gas productions for a reaction time of 1 h in the DTR was compared with that in the batch reactor. Fig. 4 shows the gas compositions in the DTR and the batch reactor, and also shows those calculated by the equilibrium using HSC Chemistry ver. 4.1. Typical DTR result at 973 K with total pressure 10 MPa shows that hydrogen production significantly increases with the addition of calcium, and carbonous gases such as methane, carbon monoxide, and carbon dioxide decrease when calcium is added (Fig. 4a). Especially, remarkable decreases of methane and carbon monoxide are observed when calcium is added, and this tendency is also observed at 873 K under a total pressure of 10 MPa. Additionally, those decreases of methane and carbon monoxide are observed under total pressures of 1 and 5 MPa at 973 K. The same reaction was investigated in the batch reactor at 923 K under a total pressure 10 MPa (Fig. 4b). The result shows a tendency opposite that of DTR; the amounts of methane and ethane productions rather increase with the addition of calcium, although those of carbon dioxide and carbon monoxide decrease with calcium addition. The equilibrium calculations at 923 K show the results of calcium addition with the decrease of methane, carbon dioxide, and carbon monoxide while the hydrogen purity increases (Fig. 4c), which supports the DTR results. Therefore, it is considered that reaction (4) does not progress efficiently in the batch reactor. We also conducted a thermal decomposition of epoxy resin without the addition of calcium in an atmospheric N_2 flow condition at 973 K. This result showed that approximately the same amounts of hydrogen and methane were generated at the initial reaction period (i.e. during the first several minutes). Thus, in the batch reactor, most methane is generated at the initial reaction stage by thermal decomposition, and the produced methane stays in the reactor during the reaction period by the ineffective gas–solid contact. In contrast, as stated above, a larger amount of hydrogen is generated in the DTR than in the batch reactor. Effective hydrogen generation is observed through the reaction (4) in the DTR with the addition of calcium. This may be caused by the relatively high value of the ratio of steam-to-carbon, S/C, due to the water flow-condition, and by more efficient contact between the gas and the solid in the DTR than in the batch reactor. Additionally, we can point out that the addition of calcium suppresses methane generation at the initial reaction stage in the DTR, which probably occurs through thermal decomposition. This is first found using the newly designed DTR described here. This demonstrates the effectiveness of the HyPr-RING process for producing highly purified hydrogen.

4. Conclusion

Based on the data obtained by a newly designed drop tube-type reactor, the initial reaction for hydrogen production from epoxy resin under rapid temperature increase and high-pressure steam conditions has been discussed in regard to the effect of calcium addition. Effect of calcium addition on the hydrogen production rate is reconfirmed; namely, the hydrogen production rate is increased by the addition of calcium because the generated carbon dioxide is absorbed by calcium additives, leading to an enhancement of hydrogen production. The efficiency of calcium used as a CO_2 absorbent is higher under the higher pressure condition. It is found that calcium addition suppresses methane generation at the initial reaction stage, in particular, under high-pressure condition.

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