

Gasification of bamboo carbon with molten alkali carbonates

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Abstract—Solid carbon can be used as a fuel in the direct carbon fuel cell (DCFC). The chemical oxidation of carbon with alkali carbonates was investigated in this work. Decreasing the weight ratio of carbon to carbonate from 5 g : 5 g to 5 g : 20 g had an insignificant effect on the amount and concentration of gases. However, changing the amounts from 5 g : 5 g to 20 g : 20 g tripled the total amount of gases produced with similar gas compositions. The gas compositions ranged from 62.2-67.5 mol% CO, 13.9-14.7 mol% H₂, and 5.7-16.8 mol% CO₂ at 800 °C. Thus CO was the dominant gas species in the conditions. With increasing temperature, CO generation was activated, especially over 700 °C. The carbonate species did not affect carbon oxidation. Steam was supplied to the carbon and carbonate mixture at a fixed flow rate of N₂ or air. H₂ was the highest composition at both cases.

Key words: Gasification, Bamboo Carbon, Molten Carbonates, Nitrogen, Steam

INTRODUCTION

Recently, solid carbon has been used as a fuel for the direct carbon fuel cell (DCFC). In general, most fuel cells use hydrogen, as it is the most reactive gas, and thus a hydrogen-supplying unit is required for the fuel cell. However, the complexity of hydrogen units negatively affects the economics of fuel cells and their applications. Carbon, however, is a solid phase that has much higher energy density than gas fuel, and it can be obtained from all organic materials. Thus the source of carbon is in principle inexhaustible.

The DCFC was developed based on the molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and molten hydroxide technology [1,2]. Unlike hydroxide technology, DCFC with MCFC and SOFC technologies employs molten alkali carbonates as the catalyst for the solid carbon [3,4]. In previous studies, the alkali carbonates were reported to enhance the rate of carbon oxidation [5] and DCFC performance [3].

Nagase et al. [6] reported that different oxidation mechanisms act in the combination of carbon with Li₂CO₃ and Na₂CO₃. Carbon with Li₂CO₃ is oxidized by the following intermolecular redox reaction:



On the other hand, they suggested that carbon with Na₂CO₃ oxidizes to CO through a disproportionation reaction of the gas phase metal and metal peroxide path, with a comparable rate to the reverse Boudouard reaction (Eq. (2)).



They also reported that the rate of conversion of C to CO with Na₂CO₃ is about 23 times faster than that with Li₂CO₃.

In general, the characteristics of alkali carbonates of Li₂CO₃, Na₂CO₃, and K₂CO₃ are determined by the alkali metal ions. Li₂CO₃,

with the smallest Li ion, has the highest ionic conductivity among such ions, while the large ionic size of K allows high gas solubility [7]. Subsequently, the eutectic of Li₂CO₃-Na₂CO₃ (Li-Na) showed higher ionic conductivity than Li₂CO₃-K₂CO₃ (Li-K) whereas the Li-K carbonates showed greater gas solubility than Li-Na melt [7].

The alkali carbonates also catalyze carbon steam reforming (csr) (Eq. (3)) [5].



Carbon steam reforming changes carbon to H₂ and CO. Thus csr is a way of using carbon to supply H₂ and CO as fuel for the MCFC and SOFC.

In this work, activated carbon made from bamboo was oxidized with Li-K, Li-Na, and Li-Na-K eutectic carbonates under N₂ and H₂O environments. The resulting gas compositions were analyzed via gas chromatography. The concentrations and amounts of gases produced revealed the chemical oxidation behavior of the carbon.

EXPERIMENTAL SECTION

The carbon made from bamboo was a commercially available activated carbon supplied by Shinkwang Chemicals (Korea). Its average particle size was about 0.5 mm, and it was used as received. Carbonates of the following compositions were employed: 62 mol% Li₂CO₃+38 mol% K₂CO₃ (Li-K), 53 mol% Li₂CO₃+47 mol% Na₂CO₃ (Li-Na), 43.5 mol% Li₂CO₃+31.5 mol% Na₂CO₃+25 mol% K₂CO₃ (Li-Na-K). The carbon and carbonate mixtures were kept at 200 °C under vacuum prior to use. The mixed ratios of carbon and Li-Na carbonates were 5 g : 5 g, 5 g : 20 g, and 20 g : 20 g.

The carbon and carbonate mixture was held in an alumina crucible that was placed in a metal cylinder-type container with a volume of 1.25 L (Fig. 1), ca. 10 cm inner diameter and ca. 30 cm in length. The metal container was gas sealed and settled in a circular electric heater. The temperature of the metal container was controlled in the range 650-800 °C, and was measured with a K-type

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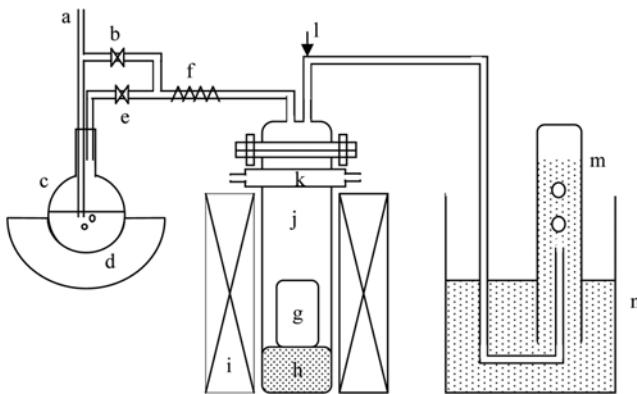


Fig. 1. Experimental apparatus for carbon gasification.

a. N ₂ or air inlet port	h. Thermal insulator
b. N ₂ or air direct inlet valve	i. Electric heater
c. Glass flask	j. Metal container
d. Electric heater	k. Water jacket
e. Steam inlet port	l. Gas sampling port
f. Line heater	m. Mass cylinder
g. Carbon- and carbonate-containing crucible	n. Water bath

thermocouple. The amount of evolved gas was measured by using the water substitution method; thus, cumulative gas amounts were obtained. The evolved gas was sampled by a gas syringe (250 μ L) at the gas outlet of the container and its composition was measured by gas chromatography (GC, HP model 5890II). The column material of the GC was Porapak Q and the detector was TCD. The metal container was initially filled with N₂ gas.

The carbon oxidation behavior was also measured by thermogravimetric analysis (TGA, Mettler Toledo 851). The temperature was increased by 20 $^{\circ}$ C min⁻¹ under N₂ purge conditions.

For carbon steam reforming, several carbon-to-carbonate ratios were prepared: 20 g + 0 g, 20 g + 1 g, 20 g + 2 g, 20 g + 10 g, and 20 g + 20 g. The carbonate was 62 mol% Li₂CO₃+38 mol% K₂CO₃ eutectics. The carbon and carbonate mixtures were placed in an alumina crucible and 0.2 L min⁻¹ N₂ or air was purged through a water bubbler at 85 $^{\circ}$ C. Thus, about 0.3 L min⁻¹ of steam was supplied to the mixture. The temperature and gas sampling method were the same as in the experiment without H₂O.

RESULTS AND DISCUSSIONS

1. Gasification of Carbon with Carbonate under N₂ Condition

Fig. 2 shows compositions of the gases evolved by the 5 g carbon and 5 g Li-Na carbonate mixture with increasing temperature. No gas generation was observed up to 300 $^{\circ}$ C. However, at 500 $^{\circ}$ C, CO₂, CO, and H₂ were produced. Among these gases CO₂ was dominant. Indeed, as carbonates melt at around 500 $^{\circ}$ C, carbon and carbonate may not have undergone any chemical reactions below 500 $^{\circ}$ C. Thus the CO₂ would be the result of the self-decomposition of carbonate (Eq. (4)) [8].



Another possibility is that carbon oxidation occurred via the functional oxygen species in the carbon [1]. Since carbon is a porous

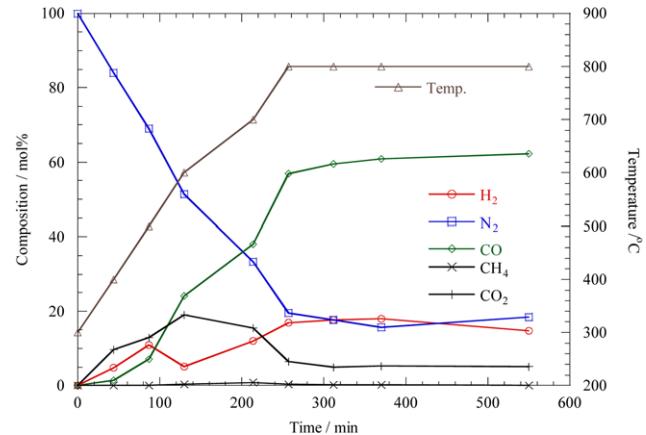


Fig. 2. Gas compositions with respect to temperature and time for the 5 g carbon and 5 g Li-Na carbonate mixture.

material, a significant amount of oxygen species would have been present in the carbon even though it was dried. In another experiment of this work, the CO₂ concentration only with 5 g carbon in the crucible at 500 $^{\circ}$ C was ca. 7 mol%. This indicates that some CO₂ was produced from the oxygen species on the carbon. The latter possibility is more acceptable because carbonate exists in a solid state below 500 $^{\circ}$ C and its decomposition is less plausible.

About 10 mol% of H₂ was observed, as shown in Fig. 2. This gas might have been discharged out of the carbon that was initially included during carbonization. Another possibility is that it was produced via the water-gas-shift reaction (Eq. (5)).



However, the carbon was dried and the cell was purged by N₂ gas. Thus the remaining H₂O would have been too small to generate such a high H₂ concentration.

A very small amount of CH₄ evolved from the carbon. In the experiment using carbon only, CH₄ was observed as the temperature increased, although only at a low concentration. Thus, it is plausible that CH₄, which initially existed in the carbon, was derived from the carbon.

Above 600 $^{\circ}$ C, CO generation became dominant. At such temperatures, the carbonate melts and the chemical reaction between the carbon and carbonate shown in Eq. (1) may take place. On the other hand, the reverse Boudouard reaction (Eq. (2)) is also activated at such temperatures [6]. Contrasting behaviors were observed for CO and CO₂; the CO concentration increased, whereas the CO₂ concentration decreased with temperature. This indicates the following two possibilities. With reaction (1) CO generation leads to the accumulation of oxide in the carbonate melts, and is regenerated by CO₂ recombination, the reverse reaction of Eq. (4). Reportedly, CO₂ recombination is much faster than the reaction of Eq. (1) [6]. Thus, CO₂ is consumed by the reverse reaction of Eq. (4) and its concentration is reduced. Another possibility involves the consumption of CO₂ by the reverse Boudouard reaction of Eq. (2). The reaction (2) with alkali carbonates such as Na⁺ and K⁺ is much faster than the intermolecular redox reaction of Eq. (1) [6]. Thus, CO₂ is consumed, and the CO concentration increases correspondingly.

The generation of CO also reduced the N₂ concentration in the

metal container. However, at a fixed temperature of 800 °C, all gas concentrations showed constant values. This indicates that gas evolution is halted at this temperature, and it also implies that gas generation is strongly dependent on temperature. The gas concentrations at 800 °C were as follows: CO, 62.2 mol%; H₂, 14.7 mol%; and CO₂, 5.7 mol%. The theoretical equilibrium constant of the reverse Boudouard reaction is about 7.0 at this temperature. The measured equilibrium constant of the Boudouard reaction was 6.8, which is very close to the theoretical value. This behavior indicates that the Na₂CO₃ in the carbonates enhanced CO production and that the rate reached the thermodynamic value of the reverse Boudouard reaction. The results also indicate that carbon with carbonate spontaneously produces CO at the temperature of 800 °C.

Fig. 3 shows the amounts of gas accumulated with increasing temperature. This was measured by water substitution, and thus is a total amount. Although CO₂ has a degree of solubility in water, the volume decrease due to CO₂ dissolution was ignored. Up to 800 °C gas generation rose monotonically. As shown in Fig. 2, CO₂ and H₂ were the main components below 500 °C, but CO dominated over this temperature. At 800 °C no further gas generation was observed. Since CO₂ gas was not supplied to the reactor, the recombination of oxide ion (O²⁻) with CO₂, which is the reverse reaction of

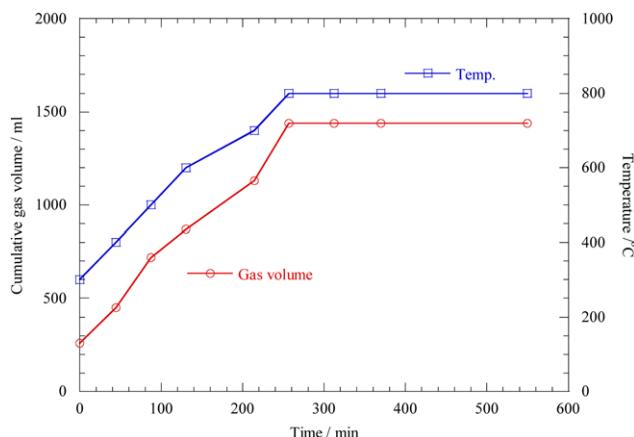


Fig. 3. Accumulated gas volume from the 5 g carbon and 5 g Li-Na carbonate mixture with increasing temperature.

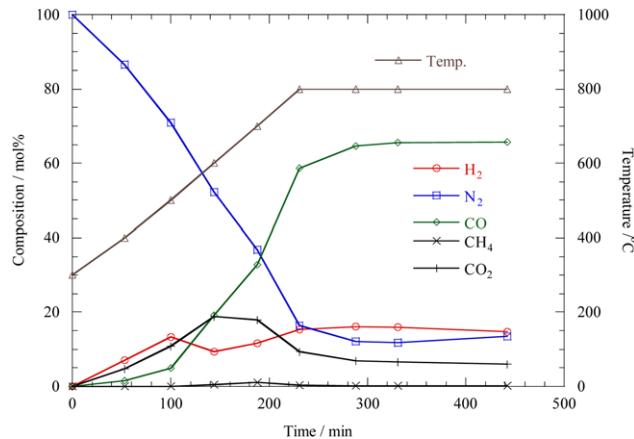


Fig. 4. Gas compositions with respect to temperature and time for 5 g carbon and 20 g Li-Na carbonate.

Eq. (4), and the reaction of Eq. (1) could not continue. Given the lack of CO₂, the reverse Boudouard reaction (Eq. (2)) was also unavailable. This behavior is in line with the results of a previous study that a helium gas environment did not allow continuous CO generation in the Li₂CO₃ and Na₂CO₃ conditions [6].

Fig. 4 shows the gas compositions obtained with 5 g carbon and 20 g Li-Na carbonate as temperature increased. The behaviors of composition were very similar to those in Fig. 2. Below 500 °C, CO₂ and H₂ were the main components, but CO became dominant over this temperature. At 800 °C, the compositions became constant, indicating that carbon oxidation could not continue. Although the amounts of carbonate were four times higher than those in Fig. 2, very similar behaviors of composition were observed. A previous study reported that the catalytic effect of alkali carbonate does not depend on the amount beyond a certain value [6]. The CO₂ compositions (in Fig. 2 and Fig. 4) at 500 °C were 12.9 and 10.8 mol%, respectively. Regardless of the difference in the amount of carbonate, similar CO₂ compositions were obtained. This indicates that CO₂ generation at this temperature is strongly dependent on the oxidation of carbon by the oxygen species inside the porous carbon rather than carbonate decomposition via Eq. (4). The gas compositions at 800 °C were CO, 65.7 mol%; H₂, 14.6 mol%; and CO₂, 6.0 mol%. The experimental equilibrium constant of Eq. (2) was 7.19, which is very close to the theoretical value of 7.0.

Fig. 5 shows the amount of gas accumulated with increasing temperature. This rose with temperature up to 800 °C. The total amount of gas at 800 °C was 1.63 L, which was close to 1.44 L of Fig. 3. Thus, gas generation does not depend on the amount of carbonate in this experimental range.

Fig. 6 shows the gas compositions produced by the 20 g carbon and 20 g Li-Na carbonate mixture as temperature increased. In particular, the CO₂ composition around 500 °C was 29 mol%, which was much higher than that at 5 g carbon, as shown in Figs. 2 and 4. Therefore, the CO₂ composition at 500 °C was strongly dependent on the amount of carbon. This strongly suggests that the carbon reacts with functional oxygen species in the carbon, resulting in CO₂ generation, although the carbon was stored in vacuum at 200 °C.

The CH₄ composition at 500 °C was 3.8 mol%, which is very

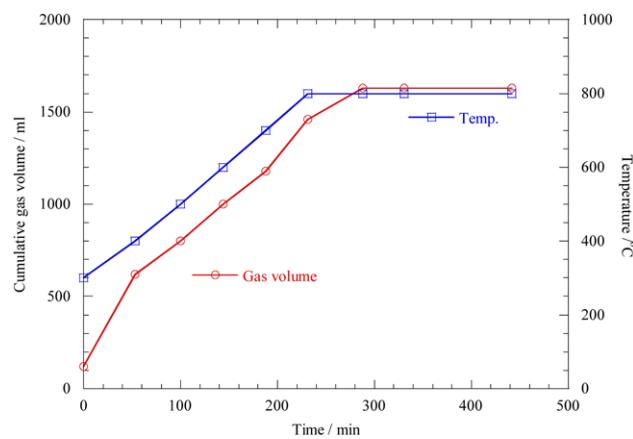


Fig. 5. Accumulated gas volume from the 5 g carbon and 20 g Li-Na carbonate mixture.

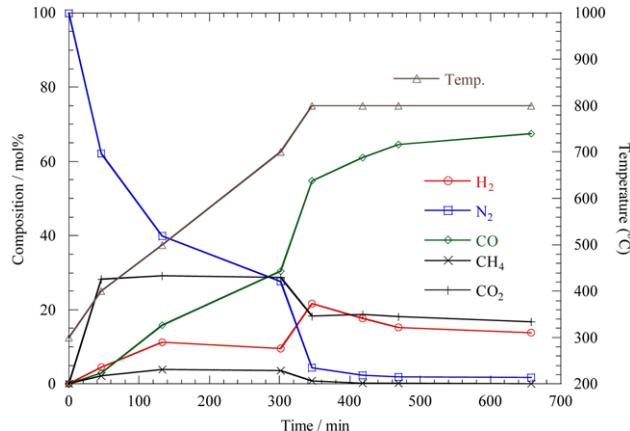


Fig. 6. Gas compositions with respect to temperature and time for 20 g carbon and 20 g Li-Na carbonate.

high compared with the value of zero in Figs. 2 and 4. The high CH_4 composition is due to the increasing amount of carbon. One possibility for the CH_4 generation is the chemical reaction of carbon with hydrogen (Eq. (6)):



The equilibrium constant of Eq. (6) was about 2.2 at 500 °C, so CH_4 formation is theoretically possible in such conditions. However, if the reaction (6) is active at 500 °C, CH_4 should be generated in the 5 g carbon conditions because solid carbon has one of activity. The zero composition of CH_4 in Figs. 2 and 4 indicates that reaction (6) may not be active in this condition. Another possible reason is the escape of CH_4 from the carbon. The CH_4 was initially stored in the carbon during carbonization. The ratio of CH_4 to carbon supports this hypothesis.

With increasing temperature CO increased and CO_2 decreased. Combinations of reaction (1) and (4) may be responsible for this behavior. The gas concentrations at 800 °C were CO, 67.5 mol%; H_2 , 13.9 mol%; and CO_2 , 16.8 mol%. It should be noted that the CO_2 composition was about triple those in Figs. 2 and 4. Although the reason for this is not yet clear, a relatively large amount of CO_2

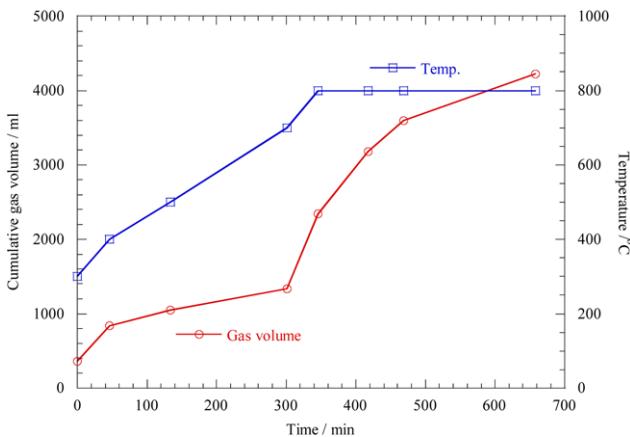


Fig. 7. Accumulated gas volume from the 20 g carbon and 20 g Li-Na carbonate mixture.

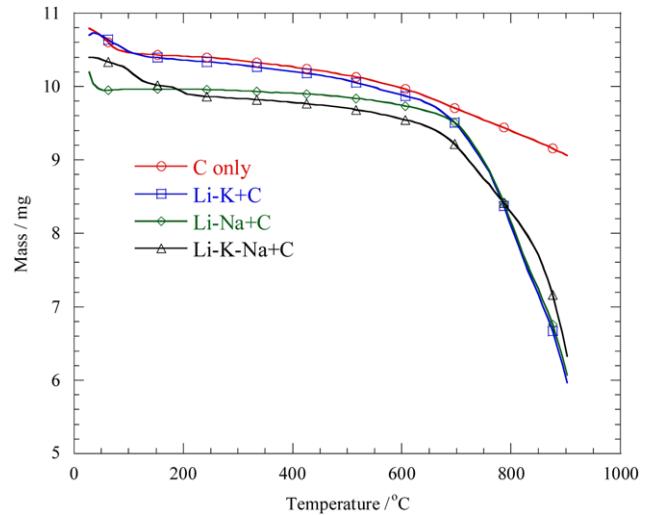


Fig. 8. TGA results of carbon and various carbon-carbonate mixtures under an N_2 environment.

is produced at higher carbon loading during CO generation.

Fig. 7 shows the gas produced by the 20 g carbon and 20 g carbonate mixtures. Over 700 °C steep increases in the amounts of gas were observed, mostly due to CO generation, as shown in Fig. 6. CO generation thus has a positive relation with carbon amount over the temperature.

Fig. 8 shows the TGA results of the carbon and carbon-carbonate mixtures under an N_2 environment. Three carbon and carbonate mixtures, C : Li-K=1 : 1 mass ratio, C : Li-Na=1 : 1 mass ratio, and C : Li-Na-K=1 : 1 mass ratio, were employed. The carbon/carbonate mixtures showed a steep decrease in mass over 700 °C, whereas carbon did not show any major decrease. This indicates that carbon is hardly oxidized over 700 °C but that carbon with carbonate is significantly oxidized over this temperature regardless of composition. All mixtures commenced carbon oxidation at around 700 °C and the slopes of mass decrease were very similar. Indeed, the melting point of Li-Na-K carbonate is ca. 100 °C lower than that of Li-K and Li-Na carbonates. Thus different mass decrease behavior could

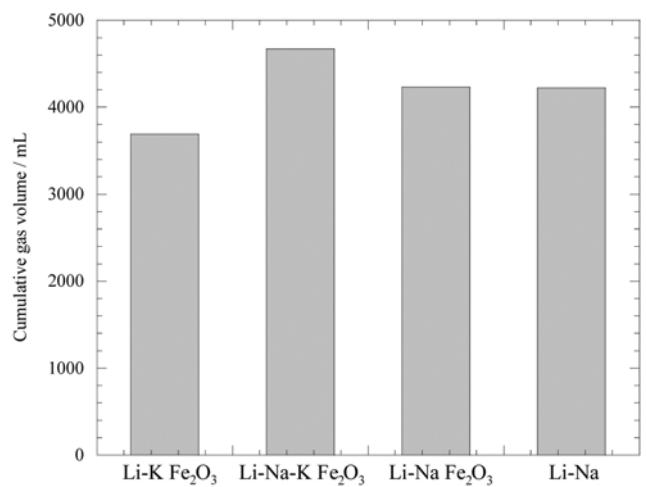


Fig. 9. Cumulative gas volume with 4 g of Fe_2O_3 in 20 g carbon and 20 g of various carbonates at 800 °C.

be expected. However, the similar slopes indicate that the carbon oxidation behavior is very similar among the carbonates. The TGA and gas concentration analysis gave consistent results regarding the carbon oxidation temperature of 700 °C.

Wu et al. reported that iron oxide behaved as a catalyst for carbon oxidation [9]. In the current study, 4 g of Fe_2O_3 was added to 20 g of carbon and 20 g of carbonate mixture. Three carbonate compositions were employed. Fig. 9 shows the total accumulated gas amounts up to 800 °C with respect to composition. About 65% of the total gas was composed of CO according to Fig. 6. Thus the amount of gas is a measure of the catalytic effect of Fe_2O_3 . As shown in this figure, the gas amounts produced by the carbonate species were within the ranges of error regardless of Fe_2O_3 addition, which indicates that Fe_2O_3 does not have a catalytic effect on carbon oxidation in the carbon/carbonate mixtures. Table 1 summarizes gas compositions from Fe_2O_3 added carbon and carbonate mixtures. The Li-Na-K carbonate shows rather higher CO composition compared with others, but insignificant differences in the gas generation behaviors are admitted among the carbonate compositions.

2. Gasification of Carbon with Steam

According to the reaction of Eq. (3) carbon can be reformed to H_2 and CO by steam. Fig. 10 shows the compositions of the gases produced from the carbon and steam with various amounts of carbonate at 800 °C. A fixed amount of N_2 (0.2 L min^{-1}) was supplied through an 85 °C water bubbler, so the gas flow contained 0.3 L

min^{-1} H_2O . The amounts of carbonate added to 20 g of carbon were 0, 1, 2, 10, and 20 g, respectively. Since N_2 is inert in these conditions, the gas evolution rate could be calculated from the composition ratio between N_2 and other gases. When CO and H_2 are produced by the reaction of Eq. (3), the gases generate CO_2 by the water-gas-shift reaction of Eq. (5). At 0 g of carbonate, CO_2 is the dominant species among H_2 , CO_2 , CO, and CH_4 . However, when the carbonates are added, H_2 is the dominant species and CO also rises. Above 2 g of carbonate, the H_2 composition reaches to a certain value and composition of other gases also converges. Thus about 10 wt% of carbonate to carbon has a sufficient catalytic effect on carbon steam reforming. The results indicate that carbonate addition increases the H_2 and CO production rate and that carbon steam reforming produces H_2 and CO species.

Fig. 11 shows the effect of temperature on carbon steam reforming with 20 g Li-K carbonate, 20 g carbon, and 0.2 L min^{-1} N_2 through an 85 °C water bubbler. At 650 °C CO generation is very low as is that of H_2 . With increasing temperature, H_2 and CO increase noticeably.

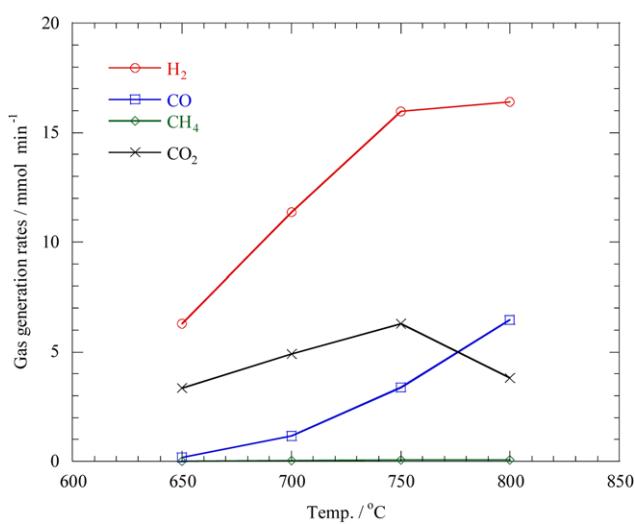


Fig. 11. Gas generation rates at various temperatures with 0.2 L min^{-1} N_2 through 85 °C water into 20 g Li-K carbonate and 20 g carbon.

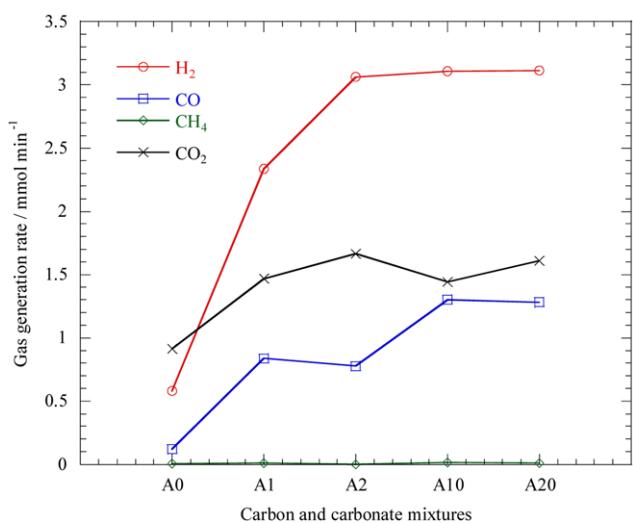


Fig. 10. Gas generation rates with 0.2 L min^{-1} N_2 through 85 °C water into various amounts of Li-K carbonate and 20 g of carbon mixtures at 800 °C. A0, 0 g of carbonate; A1, 1 g; A2, 2 g; A10, 10 g; A20, 20 g.

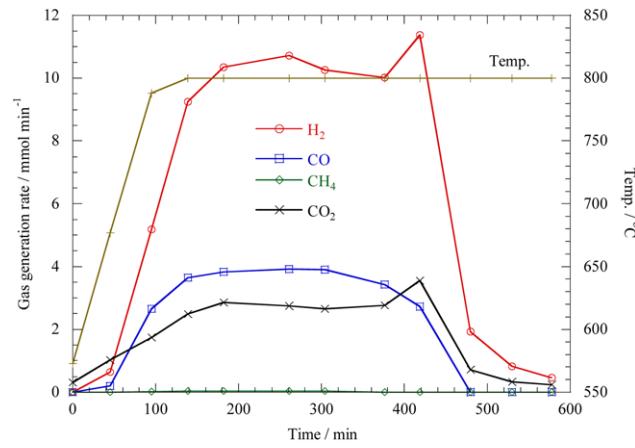


Fig. 12. Gas generation rates up to 800 °C with 0.2 L min^{-1} N_2 through 85 °C water into 20 g carbon and 20 g Li-K carbonate.

ably, while CO_2 is reduced at 800 °C. The equilibrium constant of the water-gas-shift reaction (Eq. (5)) decreases as temperature rises. Reduction of the constant may explain the decrease in CO_2 generation at 800 °C. Consequently, H_2 and CO generation increases with temperature and is a strong function of temperature.

Fig. 12 shows the gas generation rates with respect to time for 20 g Li-K, 20 g C, and 0.2 L min⁻¹ N_2 through an 85 °C water bubbler up to 800 °C. At about 100 min gas generation reaches a steady state. H_2 is the most generated species, and slightly more CO is generated than CO_2 . This is in line with the results shown in Fig. 11. Gas generation continues for about 10 hours. After the experiment, no carbon was observed in the alumina crucible and only white carbonates remained, indicating that the solid carbon was totally oxidized to a gaseous product.

The above results demonstrate that N_2 is an appropriate steam carrier in carbon steam reforming. The possibility of the substitution of N_2 with air was also investigated. Fig. 13 shows the gas compo-

sitions with 0.2 L min⁻¹ air through 85 °C water for the 20 g C and 20 g Li-K carbonate at various temperatures. Air contains about 80% N_2 , and thus other gas flow rates could be measured. At lower temperatures CO_2 is the dominant species because H_2 and CO production is relatively small and they are oxidized to H_2O and CO_2 by the oxygen in air. However, H_2 and CO generation greatly increases above 700 °C. At such temperatures, carbon steam reforming must be highly activated. On the other hand, the CO_2 flow rate is relatively invariant. This indicates that CO_2 generation is determined by the amount of O_2 in the air.

Fig. 14 shows the gas generation rates with 0.2 L min⁻¹ air through an 85 °C water bubbler for the 20 g C and 20 g Li-K carbonate up to 800 °C. Unlike in N_2 flow, the CO_2 generation rate is higher than that of CO . On the other hand, H_2 shows the highest rate of generation, indicating that air as a steam carrier produces H_2 as the dominant species, and that the gas species have relatively constant values. After gas generation ceased, only white carbonates were observed in the crucible. The carbon fuel was totally oxidized.

CONCLUSIONS

Carbon oxidation with alkali carbonates was investigated by analyzing compositions and measuring total gas evolution. The carbon-to-carbonate ratio, temperature, carbonate compositions, catalyst effect, and steam addition were considered. The investigation led to the following conclusions:

1. Carbon is oxidized to CO in the presence of carbonate according to the following reactions:
$$\text{C} + \text{CO}_3^{2-} \rightarrow 2\text{CO} + \text{O}^{2-}$$

$$\text{O}^{2-} + \text{CO}_2 \rightarrow \text{CO}_3^{2-}$$
2. CO generation is strongly dependent on the amount of carbon rather than carbonate.
3. CO generation is activated over 700 °C.
4. Carbon oxidation behavior is barely influenced by the carbonate species.
5. Fe_2O_3 as a catalyst had a negligible catalytic effect on carbon oxidation.
6. The supply of steam to a high temperature carbon and carbonate mixture resulted in H_2 and CO generation, referred to as carbon steam reforming.
7. Alkali carbonate catalyzed carbon steam reforming.
8. Carbon steam reforming was successfully carried out with N_2 and air as the steam carrier.

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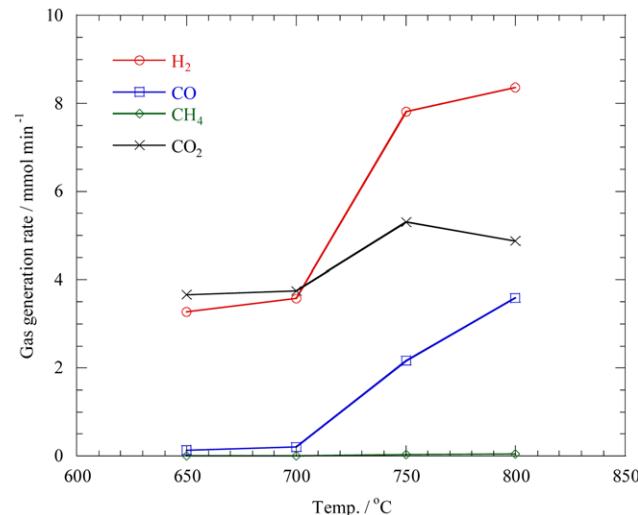


Fig. 13. Gas generation rates at various temperatures with 0.2 L min⁻¹ air through 85 °C water into 20 g Li-K carbonate and 20 g carbon.

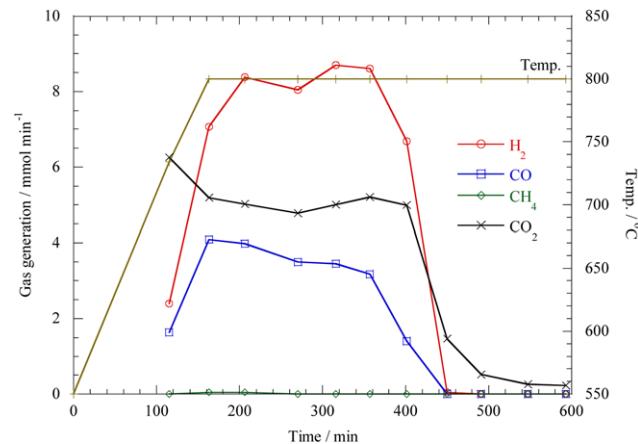


Fig. 14. Gas generation rates up to 800 °C with 0.2 L min⁻¹ air through 85 °C water into 20 g carbon and 20 g Li-K carbonate.

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