

# INFLUENCE OF THE MIXED MOLTEN CARBONATE COMPOSITION FOR HYDROGEN FORMATION BY STEAM GASIFICATION OF WASTE MATERIALS

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**Abstract:** Hydrogen is important as an energy source of a fuel cell and an energy storage medium. The hydrogen production process by using the steam reforming of naphtha or the partial oxidation of heavy hydrocarbon resources has already put in practical use. However, these processes are not suitable for hydrogen formation from waste materials, and development of small and high efficient new technology is expected.

The steam gasification of carbon residue was promoted in the presence of carbonates. Particularly, rate of the gasification was accelerated significantly by using mixed carbonates. The activation energy of the reaction with carbonates was smaller than that observed without carbonates. The effects of the mixed carbonates were caused not only by increasing of physical-contact-efficiency due to fluidization of molten salt, but also by increasing catalytic activity of the carbonates.

## 1. Introduction

A lot of useful resources, for instance gold, palladium, copper, and some rare metals, are used in electric devices. It is very important to recover these metals from the end-of-life electric devices, and to secure indispensable strategy materials to electronic industry. However, only a few electric devices such as mobile phones containing many noble metals, or some household appliances on which recovery duty is imposed by law have been disposed, because recovery metals from the end-of-life devices require high cost. The demand of rare metals is increasing rapidly, and we are anxious about future short supply of them. The end-of-life electric devices contain a lot of rare-metals. However, we cannot recover them by the conventional copper smelter. Moreover, plastics recovered from the end-of-life electric devices cannot be used as a feedstock or a fuel, because they are contaminated by toxic halogen compounds or heavy metals.

Our research group is developing the new technology to recover useful resources from the end-of-life electric devices efficiently by steam gasification. In our process, neither of manual recovery of the circuit-boards nor pulverizing of the boards is necessary, because all plastics parts are gasified by steam at the presence of molten carbonate. Toxic halogenated compounds hardly remain in gaseous or solid products, because bromine or chlorine is recovered as safe and stable inorganic salt. All plastic parts used in the electric devices, for instance circuit-board, insulation materials, case, can be converted into hydrogen and carbon dioxide mainly. We can use the gas products as energy for operating this process, and convert the surplus gaseous products into electricity by using a gas engine or a fuel cell.

In this work, I introduced influences of molten carbonate composition on steam gasification of activated carbon used as a model compound of organic solid waste.

## 2. Experiment

In the most of our experiments, activated carbon (ALDRICH, 20-40 mesh) was used. The activated carbon (0.4 g) and mixed carbonates (8.0 g) were charged in a reactor (30 cm<sup>3</sup>). Outline of our semi-batch reactor was shown in Fig.1 Detail of the apparatus was described in our previous paper [1].

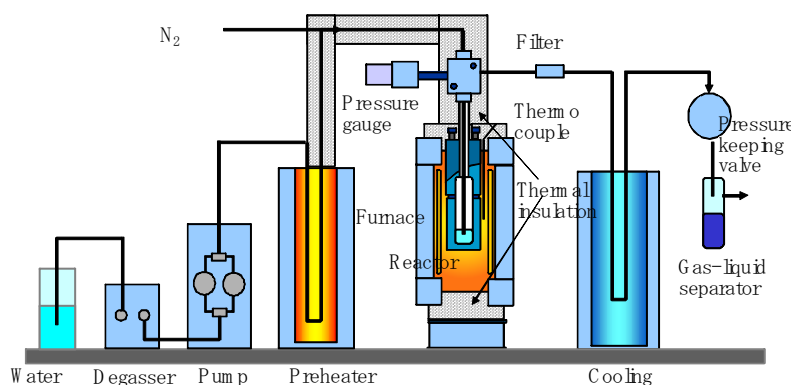


Fig.1 Outline of apparatus

Ultra pure water (0.2~1.3 g/min) and nitrogen gas (200~300 cm<sup>3</sup>/min) were introduced into the reactor through a preheater. Most of the experiments were carried out at 700 °C under 0.1 ~ 3.0 MPa. Each melting point of three carbonates (sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>)) is more than 700 °C. However, the melting points of the carbonate decrease easily by mixing other carbonates as shown in Fig. 2 [2]. The partial steam pressure was controlled by changing the flow ratio of water and nitrogen gas. Gaseous product was sampled for every constant period and analysed by a rapid analysis gas chromatograph (GL Science Micro GC-CP4900). Because

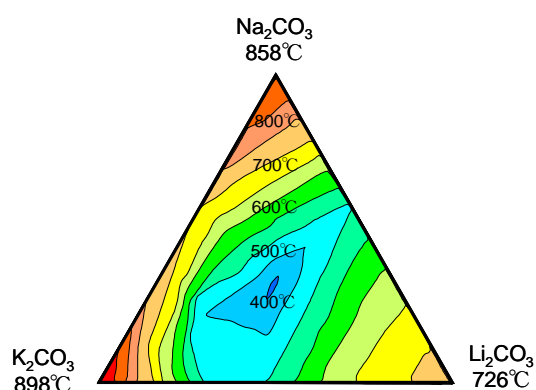


Fig. 2 Melting point of mixed carbonates

steam gasification was assumed to be pseudo first order reaction, gasification rate ( $k$ , 1/min) was derived from conversion ( $X_t$ ) and reaction time ( $t$ ) by using equation (1).

$$kt = \ln(1 - X_t) \quad (1)$$

### 3. Results and discussion

Hydrogen and carbon dioxide were produced mainly under our experimental condition. Carbon monoxide and methane were detected as trace products. Production rate of hydrogen and carbon dioxide derived from steam gasification of the activated carbon at the presence of various carbonate at 700 °C under 0.1 MPa are shown in Fig. 3. Slight formation of

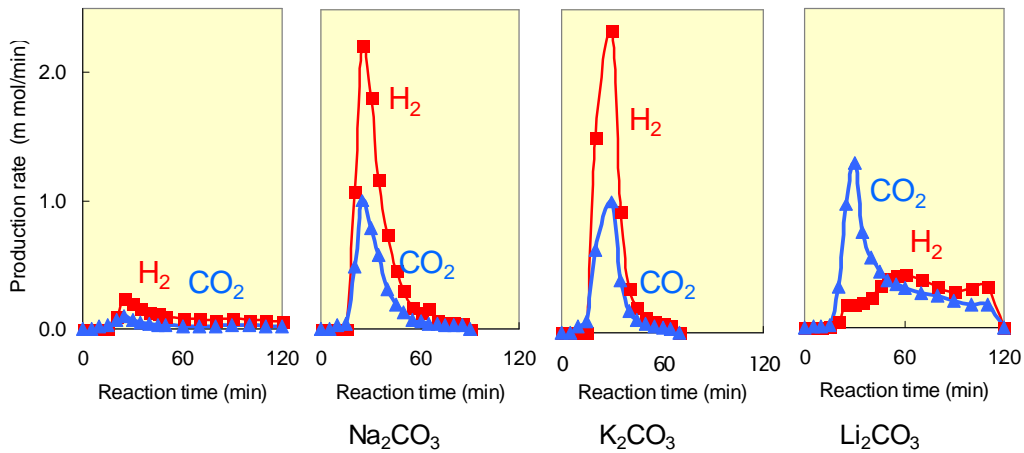


Fig. 3 Effects of carbonate for steam gasification of activated carbon at 700 °C.

hydrogen or methane was observed without carbonates. On the other hand, production rates of hydrogen and carbon dioxide increased significantly at the presence of sodium carbonate or potassium carbonate. The experimental results show that these carbonates have catalytic effect for the steam gasification. Amount of hydrogen formed in this steam gasification was almost twice amount of carbon dioxide. From the production ratio of hydrogen and carbon dioxide, chemical reaction formula of the steam gasification is summarized to (1). At the presence of lithium carbonate, carbon dioxide was observed dominantly in early stages of the gasification. Hydrogen increased gradually with reaction time and exceeded the amount of carbon dioxide in 50 minute of reaction. Thermodynamic equilibrium calculation indicated that approximately 10% of lithium carbonate decomposes to lithium hydroxide at 700 °C in excessive steam. We estimated that the carbon dioxide observed in early stages of the reaction was derived from lithium carbonate.



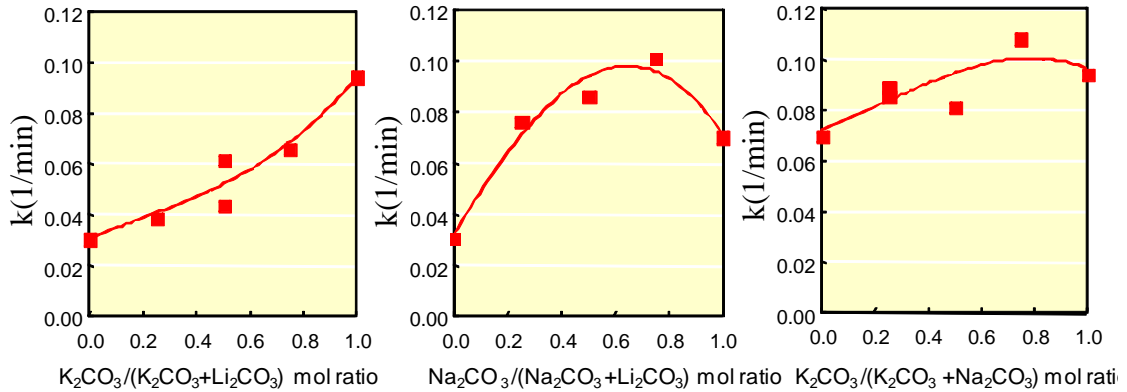


Fig.4 Effects of carbonate compositions for gasification rate. (700 °C, 0.1 MPa)

The rates of gasification observed at 700 °C under 0.1 MPa (partial steam pressure 0.09 MPa) in the presence of various carbonate mixture were shown in Fig.4. In the presence of lithium carbonate alone, the gasification rate was only 0.31/min. However, the gasification rate increased in proportion to the concentration of the potassium in the carbonate mixture, and it was 0.94 1/min at the presence of potassium carbonate alone. On the steam gasification in the mixture of carbonates, sodium carbonate and lithium carbonate or sodium carbonate and potassium carbonate, the maximum gasification rate was observed at 75% of sodium carbonate in the carbonate mixtures.

Effect of partial steam pressure in the gasification carried out under 8.0MPa was shown in Fig.5. The gasification rate increased in proportion to the partial steam pressure at the presence of three-carbonate-mixture ( $K_2CO_3/Na_2CO_3/Li_2CO_3=2/4/4$  mol ratio). On the other hand, effect of total pressure in the gasification was shown in Fig.6. The gasification was carried at a constant flow ratio of nitrogen and steam under various total pressures. Rate of the gasification increased with the total pressure gradually. However, the rate closed to a constant value at higher pressure than 0.4 MPa.

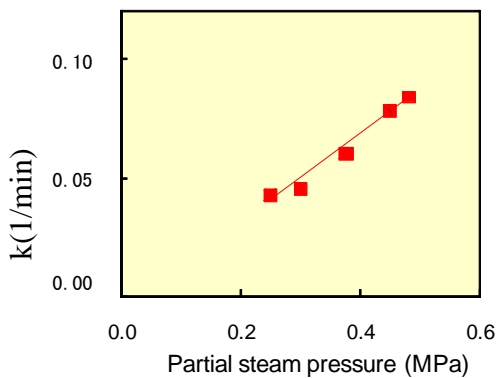


Fig.5 Effects of partial steam pressure for gasification rate (700 °C,  $P_{total}$ : 0.8 MPa)

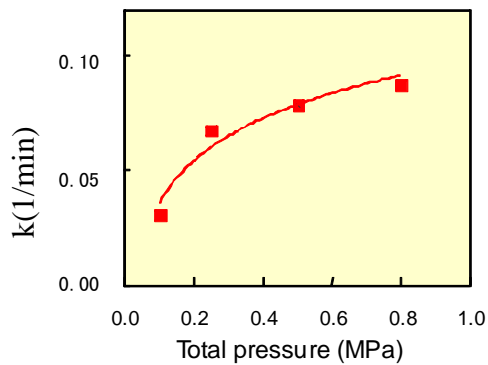


Fig.6 Effects of total pressure for gasification rate (700 °C,  $P_{steam}/P_{total}$ : 0.9)

### 4. Conclusions

Activated carbon was converted into hydrogen and carbon dioxide almost completely by steam gasification at the presence of mixed carbonate at 700 °C under 0.1-0.8 MPa. At the presence of carbonate, the gasification of the activated carbon was accelerated significantly. The gasification rate increased with partial steam pressure and total pressure, respectively. These experimental results suggest that, we can convert various plastics used in electric devices into hydrogen and carbon dioxide even under atmospheric pressure by choosing proper mixed carbonate.

### References

- [1] T. Kamo, K. Takaoka, J. Otomo, H. Takahashi, *Fuel*, **2006**, 85, 1052-1059.
- [2] J. R. Selman, H. C. Maru, *Advanced in Molten Salt Chemistry*, **1981**, 202.