Effective and selective hydrogen formation from biomass through hydrothermal reaction

Yasuyuki Ishida, Koichi Hata, Koji Tanifuji, Tatsuya Hasegawa and Kuniyuki Kitagawa*
EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan

The effects of various additives, such as an inorganic alkali and metal catalyst, on the hydrothermal process were examined to recover hydrogen from biomass with high efficiency and selectivity at relatively low temperatures around 400°C. At first, a cellulose sample as a model biomass was subjected to the hydrothermal process at 400°C under 25 MPa in the presence of an alkali, sodium carbonate (Na$_2$CO$_3$) and nickel catalyst (Ni/SiO$_2$). The combination of these two additives, Na$_2$CO$_3$ and the Ni catalyst, led not only to highly efficient formation of hydrogen but also to effective dissolution of CO$_2$ into a liquid layer. Similarly, the hydrothermal reaction of real biomass, such as wasted wood, sludges and food waste, in the presence of both the two additives resulted in highly effective and selective formation of hydrogen gas even at relatively low temperatures around 400°C.

I. Introduction

In recent years, a hydrothermal process, a reaction using super- or sub critical water as a medium, has been used for gasification of biomass. This process can be applied to gasification even for biomass with high moisture content without drying them. In addition, the fuels such as hydrogen and methane can be obtained in a form of compressed gas by means of the hydrothermal process with much higher reaction rate than that for the conventional fermentation technique. Therefore, this process has now attracted a great deal of attention as a powerful method to gasify various biomasses with a high efficiency.

So far, many researchers have reported the formation of various fuels including methane and hydrogen from biomass model compounds and real biomass through the hydrothermal process. For example, Lin et al reported that selective hydrogen formation was achieved by the hydrothermal reaction of various organic wastes, such as wood, salad oil, plastics and sewage sludge, at relatively higher temperatures around 700 °C. Furthermore, Elliot and Minowa et al applied the hydrothermal process to gasification of biomass at relatively lower temperatures from 350 - 400 °C. Particularly, Minowa et al revealed that cellulose was able to be gasified with a high efficiency in the presence of a reduced nickel catalyst or alkali. However, there has been no report focusing on a highly selective and effective formation of hydrogen at relatively low temperatures around 400°C, which can be obtained readily as the industrial wasted heat.

In this work, the hydrothermal process was applied to the gasification of cellulose and various real biomasses focusing on not only effective but also selective hydrogen formation at lower temperatures. At first, the effects of various additives, such as an inorganic alkali and metal catalyst, on the hydrothermal process were examined in detail in order to form hydrogen from cellulose with high efficiency and selectivity at relatively low temperatures around 400°C. Then the hydrothermal process under thus optimized conditions was used for the gasification of various real biomasses such as wasted wood, sewage sludge and food waste.

II. Experimental

Materials; A microcrystalline cellulose (Wako) was used as a model sample of biomass. As real biomass samples, wasted wood (supplied by Fuluhashi corp.), sewage sludge and food waste (supplied by INAX corp.) were also subjected to the hydrothermal process. Here, pulp components separated from soybean milk in the production of tofu were used as the food waste sample. These biomass samples were ground into fine powders by a freezer mill prior to the final reaction.

* Professor, EcoTopia Science Institute, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan, Kuni@esi.nagoya-u.ac.jp, AIAA Member Grade for First author.
According to the previous reports by Minowa et al.\textsuperscript{5-9}, sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}; Waco) and nickel compound (Ni/SiO\textsubscript{2}; 10-50 wt\% Ni) were used as an alkali and metal catalyst, respectively. The nickel catalyst was prepared by impregnating NiNO\textsubscript{3}·6H\textsubscript{2}O (Kishida Chemicals) onto SiO\textsubscript{2} supports followed by calcining at 450 °C for 4 hrs in air. This catalyst was reduced with H\textsubscript{2}/N\textsubscript{2} at 400 °C for 5 hrs before the usage.

Hydrothermal process: The hydrothermal reaction was performed in a stainless steel reactor (10 ml). About 0.1 g of a cellulose or real biomass sample was added into the reactor with 3 ml of water and additives such as Na\textsubscript{2}CO\textsubscript{3} or nickel catalyst. After the remaining air was purged by the flow of N\textsubscript{2} stream, the reactor was introduced into the hydrothermal furnace (Akico). The furnace temperature was programmed up to 400°C, and then maintained at the final temperature for 30 min. The pressure was kept at about 26MPa throughout the reaction. After cooling down to a room temperature, the evolved gases were sampled by a micro syringe through a gas sampler, and then subjected to a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

### III. Results and Discussion

A. Hydrothermal reaction of cellulose sample

At first, a cellulose sample as a model biomass was subjected to the hydrothermal process at 400°C under 26 MPa in the presence of an alkali, Na\textsubscript{2}CO\textsubscript{3}. Figure 1 shows the relationships between the molar yields of H\textsubscript{2}, CH\textsubscript{4}, CO and CO\textsubscript{2} formed during the hydrothermal reaction and the amount of Na\textsubscript{2}CO\textsubscript{3} added into the reactor. Here other gas species, such as C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}, were not shown since these amounts were too small enough to ignore their contribution. As shown in this figure, the addition of Na\textsubscript{2}CO\textsubscript{3} increased the amount of the hydrogen gas generated during the hydrothermal process from the cellulose sample. This increase in the hydrogen formation can be explained by considering the promoted hydrolysis of glycoside bonds present in the cellulose backbones shown in Scheme 1. As shown in this

![Scheme 1. Possible degradation mechanism of cellulose in the presence of alkali.](image-url)
scheme, hydrolysis of the glycoside bonds might be brought about not only by water but also by a hydroxide ion, which in turn resulted in the promoted hydrogen formation.

Furthermore, it should be noted that the formation of CO$_2$ in a gas layer was significantly suppressed by the addition of more than 200 wt% of Na$_2$CO$_3$ presumably due to the dissolution of CO$_2$ into an alkaline liquid layer. This observation indicates that the addition of alkali has a strong effect on the selective generation of hydrogen gas in a gas layer.

Next, the effects of the nickel catalyst (Ni/SiO$_2$) on the hydrothermal process of the cellulose sample at 400°C were also evaluated. By adding the catalyst into the reaction system, the amount of hydrogen became much larger (the molar yield of the hydrogen gas reached at about 1.2 mmol) than that obtained in the presence of Na$_2$CO$_3$. This increment is presumably due to the promoted water-gas shift reaction (CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$) as was reported earlier $^8,^9$. In the case of the nickel catalyst, however, other gas species such as CO$_2$ and methane were still formed to some extent, which led to a poor selectivity for the hydrogen formation.

Then the combination of the two kinds of additives, Na$_2$CO$_3$ and the nickel catalyst, was used for the hydrothermal process of the cellulose sample. Figure 2 shows the amounts of each gas species formed when both the two additives were added into the reactor, together with the data obtained without addition of any catalyst and in the presence of Na$_2$CO$_3$ or Ni/SiO$_2$ alone. Here the amounts of the catalyst and alkali reagent were experimentally optimized to yield the highest molar yield of the hydrogen gas. As shown in this figure, the addition of both the additives resulted in highly efficient and selective formation of the hydrogen gas. The hydrogen conversion rate was reached at about 90% due to the promoted gasification under the presence of the both additives. Furthermore, CO$_2$ was also effectively trapped into a liquid layer without releasing to a gas layer by the addition of the alkali reagent.

**B. Hydrothermal reaction of real biomass**

Finally, the real biomass samples, such as wasted wood, sledge and food waste, were subjected to the hydrothermal reaction in the presence of both the two additives at 400°C. As an example, the amounts of each gas species obtained from the wasted wood sample in the presence of both the two additives were shown in Figure 3. Similarly to the case of the cellulose sample, the hydrothermal process resulted in highly effective and selective formation of hydrogen although higher amount of Ni catalyst was required to promote the H$_2$ formation due to the deactivation of the catalyst caused by the degradation products from lignin$^{10,11}$. In a similar manner, the same process of the sledge and food waste samples generated the hydrogen gas with high efficiency and selectivity at relatively low temperatures around 400°C.
IV. Conclusion

By using a cellulose sample as a model biomass, the effects of the kind and amount of additional reagents on the hydrothermal gasification were evaluated in detail to form hydrogen gas formation at 400°C. As a result, the addition of the optimum amount of Na₂CO₃ led to the selective hydrogen formation by dissolving CO₂ gas into a liquid layer. On the other hand, it was revealed that the addition of the nickel catalyst significantly increased the yield of hydrogen gas during the hydrothermal reaction although the other gas species were also co-generated to some extent. As was expected from these observations, the use of these two additives resulted in the effective formation of hydrogen gas with enough selectivity. Furthermore, the combination of these two additives also promoted the formation of hydrogen even for the real biomass samples, such as wasted wood, sledges and food waste.

References