Study on Selective Hydrogen Generation from Real Biomass through Hydrothermal Process at Relatively Low Temperatures

Kuniyuki Kitagawa1,*, Koichi Hata2, Noriaki Sugimoto2, Yuta Shimizu2, Yasuyuki Ishida1 and Tatsuya Hasegawa1

1 EcoTopia Science Institute, Nagoya University, Nagoya, Japan
2 Graduate School of Engineering, Nagoya University, Nagoya, Japan

Abstract: The effect of additives, such as an inorganic alkali and a nickel catalyst, on the hydrothermal process was examined to generate hydrogen from biomass with high selectivity at relatively low temperatures around 400°C. At first, a cellulose sample as model biomass was subjected to the hydrothermal process at 400°C under 26 MPa in the presence of an alkali (Na2CO3) and a nickel catalyst (Ni/SiO2). The combination of these two additives led not only to highly efficient generation of hydrogen but also to effective dissolution of CO2 into an alkaline liquid layer. Similarly, the hydrothermal process of actual biomass samples, such as wasted wood, organic fertilizer and food waste, in the presence of both the two additives resulted in highly selective production of hydrogen even at 400°C. Moreover, isotope labeling followed by cryogenic gas chromatography (cryo-GC) was applied to the determination of hydrogen formed during hydrothermal reaction of biomass with differentiating two possible sources of hydrogen, namely biomass and water. As a result, it was revealed that the main source of hydrogen was not biomass itself but water utilized as a reaction medium under the gasification conditions used in this work.

Keywords: Hydrothermal Process, Biomass, Hydrogen, Isotope Labeling, Cryogenic GC

1. INTRODUCTION

In the fields of energy science, it has been an important issue to develop a highly effective process to generate hydrogen that can be used for clean power production including hydrogen-based fuel cells. Biomass is now attracting a great deal of attention as a source of hydrogen. Among various conversion methods, a hydrothermal gasification, using super- or subcritical water as a reaction medium, has become a promising technique to produce hydrogen from actual biomass with high efficiency. This process can be applied to the conversion of biomass samples with high moisture content without drying them. Furthermore, hydrogen can be obtained in a form of compressed gas with much higher reaction rate than those in the conventional fermentation processes.

There have been many reports on gasification and/or hydrogen generation from biomass through hydrothermal process. For example, Lin et al reported that hydrogen was produced effectively through the hydrothermal reaction of various organic wastes including wood, salad oil, plastics and sewage sludge [1,2]. They also enabled the selective hydrogen generation without emitting CO2 into a gas layer by adding CaO into a reactor as a CO2 absorbent. However, this process required significantly high temperatures over 650°C to convert biomass into hydrogen quantitatively. Other researchers have also attempted to generate hydrogen from model and actual biomass by hydrothermal process at relatively lower temperatures. Among them, Minowa et al revealed that cellulose was able to be gasified at low temperatures around 400°C [3-8], which could be obtained as the industrial wasted heat. Moreover, they investigated the effects of various additives such as a reduced nickel catalyst and inorganic alkalis on hydrothermal degradation of a cellulose sample in detail. So far, however, there has been no report to focus on a process to concurrently meet the following three conditions; (1) effective and (2) selective hydrogen generation at (3) relatively low temperatures around 400°C.

In this work, the effect of additives such as different contents of an inorganic alkali (Na2CO3) and Ni catalyst on a hydrothermal process was examined in detail in order to generate hydrogen from cellulose, used as a model biomass sample, with high selectivity at 400°C. Then the hydrothermal process under thus optimized conditions was applied to hydrogen generation from actual biomass samples such as wasted wood, organic fertilizer and food waste. Furthermore, isotope labeling followed by cryogenic gas chromatography (cryo-GC) was also applied to the analysis of hydrogen formed during hydrothermal process of biomass to determine H2 with differentiating its two possible sources, biomass itself and water.

2. METHODOLOGY

2.1 Materials

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

According to the previous reports by Minowa et al [3-8], sodium carbonate (Na2CO3; Waco) and nickel compound (Ni/SiO2; 10-50 wt% Ni) were used as an alkali and metal catalyst, respectively. The nickel catalyst was prepared by impregnating Ni(NO3)2·6H2O (Kishida Chemicals) onto SiO2 supports followed by calcining at 450°C for 4 hrs in air. This catalyst was reduced with H2/N2 at 400°C for 5 hrs before the usage.

2.2 Hydrothermal process

The hydrothermal reaction was performed in a stainless steel reactor (10 ml). About 0.1 g of a cellulose or actual biomass sample was added into the reactor with 3 ml of water and additives such as Na2CO3 or nickel catalyst. In the case of isotope labeling, deuterium oxide (99%std) purchased from Aldrich was added as a reaction medium instead of H2O. After the remaining air was purged by the flow of N2 stream, the reactor was introduced into the hydrothermal furnace (Akico). The furnace temperature was

* Corresponding author: kuni@esi.nagoya-u.ac.jp
programmed up to 400°C, and then maintained at the temperature for 30 min. The pressure was kept at about 26 MPa throughout the reaction. After cooling down to a room temperature, the evolved gas products 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).

2.3 Cryogenic GC measurements of gas products

According to the previous reports [9,10], cryo-GC system equipped with a thermal conductively detector (TCD) was applied to the analysis of hydrogen isotopes. In order to resolve hydrogen isotopes, a separation column packed with an alumina (coated with 19 wt% of MnCl2) was maintained at -196°C by immersing it into liquid N2. As a carrier gas, neon was selected in order to prevent its condensation at such a low temperature.

3. RESULTS AND DISCUSSION

3.1 Selective hydrogen formation from biomass through hydrothermal process

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, Na2CO3. Fig. 1 shows the relationships between the amount of Na2CO3 added into the reactor and the molar yields of H2, CH4, CO and CO2 formed during the hydrothermal reaction. Here other gas species, such as C2H4 and C2H6, were not shown since these amounts were too small enough to ignore their contribution. As shown in this figure, the addition of Na2CO3 increased the amount of hydrogen generated during the hydrothermal process from the cellulose sample. This increase in the hydrogen formation can be explained by the promoted hydrolysis of glycoside bonds in the cellulose backbones. Furthermore, it should be noted that the emission of CO2 into a gas layer was significantly suppressed by the addition of more than 200 wt% of Na2CO3 possibly due to the dissolution of CO2 into an alkaline liquid layer. This observation indicates that the addition of alkali is effective to the selective generation of hydrogen in a gas layer.

Next, the effects of the nickel catalyst (Ni/SiO2) on 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 hydrogen was about 1.2 mmol) than that obtained in the presence of Na2CO3. This increment is presumably due to the promoted water-gas shift reaction (CO + H2O → CO2 + H2) as was reported earlier [11]. In the case of the nickel catalyst, however, other gas species such as CO2 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, Na2CO3 and the nickel catalyst, was tested for the hydrothermal process of the cellulose sample. Fig. 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 Na2CO3 or Ni/SiO2 alone. Here the amounts of the catalyst and alkali reagent were experimentally optimized to yield the highest molar yield of hydrogen. As shown in this figure, the addition of both the additives resulted not only in highly efficient formation of hydrogen but also effective dissolution of CO2 into a liquid layer. Here, the hydrogen conversion rate was estimated as about 90%.

Finally, the real biomass samples, such as wasted wood, organic fertilizer 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 product obtained from the wasted wood sample in the presence of both the two additives were shown in Fig. 3. Similarly to the case of the cellulose sample, the hydrothermal process resulted in highly effective and selective formation of hydrogen. In a similar manner, the same process of the organic fertilizer and food waste samples generated the hydrogen with high efficiency and selectivity at relatively low temperatures around 400°C.
3.2 Determination of hydrogen by isotope labeling followed by cryo-GC

The gas products, formed from the hydrothermal process using D2O as a reaction medium, were analyzed by cryo-GC to obtain information on the sources of hydrogen. Fig. 4 shows typical chromatograms of (a) a standard hydrogen mixture consisting of H2, HD and D2, and (b) gas products obtained from hydrothermal reaction of the wasted wood sample in the presence of D2O. On the chromatogram of the standard sample (a), the peaks of each isotope were clearly observed as well-resolved ones. Furthermore, the good reproducibility of their peak intensities (R.S.D. < 1%) suggests that the composition of hydrogen isotopes can be determined precisely by means of this GC system. Next, in the chromatogram of the gas product from the wasted wood sample (b), the peaks of D2 and HD, which were presumed to be formed from D2O, were clearly observed while that of H2 was almost missing.

Table 1 summarizes the relative yields of hydrogen isotopes for the cellulose and wasted wood samples, determined from the peak intensities observed on the chromatograms. As shown in this table, the hydrogen isotopes were mainly consisting of D2, derived from D2O used as a reaction medium, for both the samples. This result suggests that the main source of hydrogen in the gas products is not biomass itself but water under the gasification conditions used in this work. Here, D2 was thought to be formed though the water-gas shift reaction, which had been reported to be the main route of hydrogen generation in the supercritical gasification of wood biomass [11].

\[ \text{CO} + \text{D}_2\text{O} \rightarrow \text{CO}_2 + \text{D} \]  

Table 1 Relative molar yields of hydrogen isotopes formed from hydrothermal reaction of biomass.

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<th>Relative molar yieldsa (mol%)</th>
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<tbody>
<tr>
<td></td>
<td>H2</td>
</tr>
<tr>
<td>cellulose</td>
<td>2.4</td>
</tr>
<tr>
<td>wasted wood</td>
<td>0.7</td>
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a determined from the peak intensities corrected by sensitiveness to TCD.
4. CONCLUSION

The effects of the additives such as Na₂CO₃ and Ni catalyst on the hydrothermal gasification of the model cellulose sample were tested in detail to achieve selective hydrogen generation at the relatively low temperature of 400°C. As a result, the addition of the optimum amount of Na₂CO₃ led to the selective hydrogen formation by dissolving CO₂ into the liquid layer. On the other hand, the use of the nickel catalyst significantly increased the yield of hydrogen during the hydrothermal process although the other gas species were also co-generated to some extent. Then, the concurrent use of these two additives resulted in the selective generation of hydrogen at low temperatures around 400°C even for the actual biomass samples.

Furthermore, isotope labeling followed by cryogenic GC was successfully applied to the determination of hydrogen generated during the hydrothermal reaction of biomass. By using this technique, it was shown that hydrogen was mainly derived from water as a reaction medium under the hydrothermal conditions used in this work.

5. REFERENCES