

Hydrogen Generation from Various Biomass Using Hydrothermal Gasification

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1. Introduction

In the fields of energy science, development of a highly effective process to generate hydrogen that can be used for clean power production, including hydrogen-based fuel cells has been an important issue. Biomass is now attracting a great deal of attention as a source of hydrogen. Among various conversion methods, a hydrothermal gasification, using super- or sub-critical water as a reaction medium, has become a promising technique to produce hydrogen from actual biomass with high efficiency. This process can be applied for 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 can be gasified at low temperatures around 400°C [3-6]. Moreover, they investigated the effect 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 temperature process of 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. Thus cellulose was used as a model biomass sample with demonstrated high selectivity at 400°C. The hydrothermal process under the optimized conditions was applied for hydrogen generation from real biomass samples such as wood waste, organic fertilizer and food waste.

2. Key Features

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 relationship between the amount of Na₂CO₃ added into the reactor and the molar yields of H₂, CH₄, CO and CO₂ formed during the hydrothermal reaction. As shown in this figure, the addition of Na₂CO₃ increased the amount of hydrogen generated during the hydrothermal process from the cellulose sample owing to promoted hydrolysis of glycoside bonds present in the cellulose backbones. Furthermore, it should be noted that the formation of CO₂ in a gas layer was significantly suppressed by the addition of more than 200 wt% of Na₂CO₃ presumably due to the dissolution of CO₂ into an alkaline liquid layer.

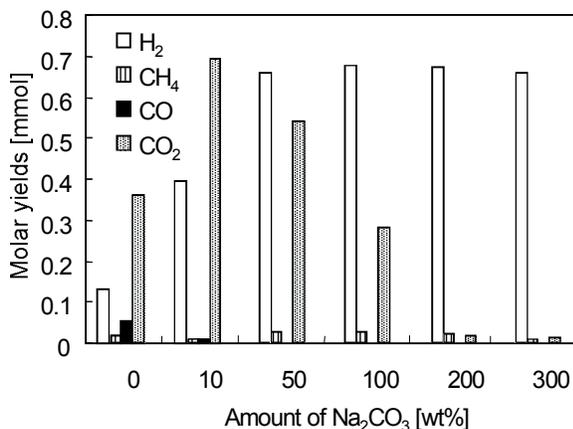


Fig. 1. Relationship between amount of Na₂CO₃ and molar yields of gas products from cellulose.

Next, the effect of the Ni catalyst (Ni/SiO₂) on the hydrothermal process at 400°C was also evaluated using the cellulose sample. By adding the catalyst into the reaction system, the amount of hydrogen became much larger (ca. 1 mmol of H₂ from 0.6 mmol of a glucose unit in the cellulose sample) than that obtained by using Na₂CO₃ although other gases, such as, CO₂ and methane were still formed to some extent.

Then the combination of the two kinds of additives, Na₂CO₃ and the Ni catalyst, was tested for the hydrothermal process of the cellulose sample. Fig. 2 shows the amount of each gas species formed when both the two additives were added into the reactor. Here the molar yields of evolved gasses obtained in the presence of Na₂CO₃ or Ni/SiO₂ alone are also presented. As was expected from these results, the addition of both the additives led not only to highly efficient formation of hydrogen (hydrogen conversion rate ≈ 90%) but also to effective dissolution of CO₂ into a liquid layer.

Finally, the actual 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. Similar to the case of the cellulose sample, the hydrothermal process resulted in highly effective and selective formation of hydrogen from such wastes.

3. Conclusions

The hydrothermal reaction in the presence of an alkali and Ni catalyst was significantly effective for the selective hydrogen formation from a model (cellulose) biomass sample. The formed CO₂ gas was almost quantitatively removed from the gas layer through the dissolution into an alkaline liquid layer. Furthermore, the combination of these two additives also promoted the formation of hydrogen even for the actual biomass samples, such as wood wast, organic fertilizer and food waste.

4. References and Bibliography

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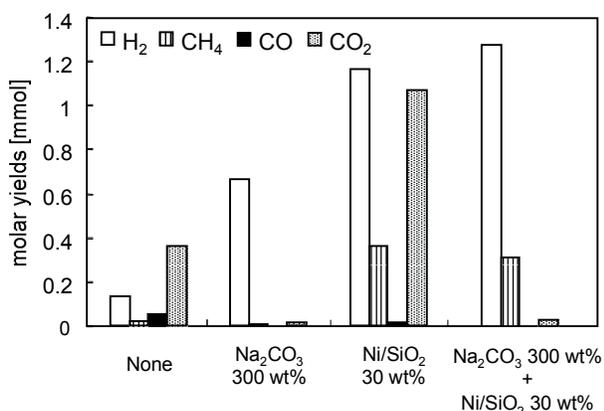


Fig. 2. Effect of addition of Na₂CO₃ and Ni/SiO₂ on the amount of gas products from cellulose.