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Conversion of rice straw into valuable products by hydrothermal treatment and steam gasification

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ABSTRACT

In order to obtain valuable products such as monosaccharides and hydrogen from rice straw (RS), the two-stage processing, hydrothermal treatment in the first stage and steam gasification in the second stage, was carried out. In the hydrothermal treatment, influence of hydrothermal treatment conditions and pretreatments to the raw RS sample on the product distribution was examined. Maximum yield of monosaccharides from the raw RS sample was 1.1 wt.% (C basis), which was obtained by the hydrothermal treatment at 220 °C for 5 min. A water treatment of raw RS sample was carried out before hydrothermal treatment to increase the yield of monosaccharides, so that 9.4 wt.% (C basis) of formic acid was extracted. Furthermore, in the subsequent hydrothermal treatment, the yield of monosaccharides increased up to approximately 4.5 wt.% (C basis). Simultaneously, 7.9 wt.% (C basis) of acids and furfural and 45.1 wt.% (C basis) of other water-soluble products were also formed. In the second stage, conversion of hydrothermal-treated rice straw residue (HT-RSR) into hydrogen was performed by steam gasification using fixed-bed reactor and influence of nickel catalyst was examined. Hydrogen from HT-RSR sample without catalyst was produced above 800 °C, while hydrogen from the 7.5 wt.% nickel-loaded sample was evolved at lower temperature (500 °C). The peak top temperature of the hydrogen evolution was shifted from 850 °C for the 1.5 wt.% nickel-loaded sample to 750 °C for the 7.5 wt.% nickel-loaded sample. Total amount of hydrogen evolved from the samples loaded with nickel more than 2 wt.% was 50–60 mmol/g-RSR and about three times larger than that from HT-RSR sample without catalyst. In addition, e.g. for the 2.3 wt.% nickel-loaded sample, the CO, CO_2, and other gaseous products were also evolved and their yields were 9.4, 21.1, and 3.1 wt.% (C basis), respectively.

1. Introduction

Biomass has lately attracted considerable attention as future resources of energy and chemical materials for the solution of the global warming issue, because the biomass is a carbon neutral. Rice straw, which is a kind of the lignocellulosic biomass, is produced by about nine million tons a year in Japan, but most of them are not effectively used. The rice straw is mainly composed of three constituents (hemicellulose, cellulose, and lignin), the reactivity of which is quite different. Therefore, the development of an effective conversion process for each component is considered to be necessary. In this study, we tried to convert the rice straw into valuable products by two-stage processing: the first stage is the production of monosaccharides (glucose and xylose) as a raw material of bioethanol, and the second stage is the production of hydrogen from the residue after hydrothermal treatment. In order to obtain the saccharides from the holocellulose (hemicellulose and cellulose) present in the lignocellulosic biomass, the following three methods have been researched: acid hydrolysis [1–3], the enzymatic saccharification [4–6], and hydrothermal treatment [7–9]. The acidic hydrolysation has some problems such as the waste water treatment, the corrosion of reactor and so on. The enzymatic saccharification is not turned to practical use because it takes a long time for conversion and the enzyme is high in price. On the other hand, the hydrothermal treatment is very rapid process and the dry process is unnecessary in the case of biomass having high moisture content. In this study, in the batch method using simple equipment (autoclave) we examined the influence of the hydrothermal conditions such as reaction temperature and time without any acidic catalysts and enzymes on the yields of monosaccharides. In addition, we investigated the influence of pretreatments such as grinding and water washing of rice straw in order to increase the yield of monosaccharides. It is expected that the grinding treatment lowers the crystallinity of cellulose and the water washing at room temperature reduces the influences of the water-soluble components on the product distribution. In the hydrothermal treatment, however, not all rice straw can be converted into the water-soluble organic compounds including monosaccharides. In other words, a large amount of the carbonaceous

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residue remains even if the rice straw is treated under a severe condition. The production of hydrogen by the steam gasification is thought to be the most expectable conversion process. In the steam gasification of coal, the transition metals such as iron and nickel are well-known to be effective [10,11]. In this study, the effect of the impregnated nickel catalyst on the amount of hydrogen evolved from the hydrothermal-treated residue during steam gasification was also investigated.

2. Experimental

2.1. Sample

Rice straw (RS) from Akita, Japan was ground below 250 μm and dried at 110 °C for 1 h. The elemental analysis of RS is shown in Table 1. The ash content was calculated from the residual amount when 1 g of the RS sample was calcined at 815 °C for 1 h in the air. The lignin was obtained as follows: 1 g of the RS sample was stirred in 15 mL of sulfuric acid (72%), the suspension was settled at 20 °C for 4 h, the distilled water was added to the suspension, and this mixture was refluxed for 4 h. The lignin content was calculated from the amount of this sulfuric acid-insoluble component. The holocellulose component was obtained by treating 1.5 g of the RS sample with the mixture of sodium chlorite and glacial acetic acid. The cellulose content was calculated from the residual amount after the holocellulose component was treated with 17.5% NaOH solution. The hemicellulose content was evaluated by subtracting the cellulose content from the holocellulose content. The chemical composition of RS is also shown in Table 1.

2.2. Pretreatments to rice straw sample

The grinding treatment and water washing were carried out as pretreatments in this study. The grinding was performed by using vibrational mill equipment under the conditions of a frequency of 1000 p.c.m., a swing length of 8.5 mm, and a milling time between 30 and 240 min. The average diameters of the RS samples were measured by a wet-type laser diffraction analyzer (Nikkiso Microtrac HRA X-100). The crystallinity of cellulose was determined by the following Segal method from the X-ray diffraction patterns (Rigaku RAD-C) [12]:

$$X_{CR} = (I_{CR} - I_{AM})/I_{CR} \times 100$$

where x_{CR} is the crystallinity of cellulose (%), I_{AM} the intensity at $2\theta = 18°$, I_{CR} the intensity at $2\theta = 22.8°$. As for the water treatment, 10 g of the RS sample was immersed in 400 mL of the distilled water and the suspension was stirred at room temperature for 4 h. Then, the solid was separated from the suspension by filtering, and dried at 110 °C.

Table 1
Elemental analysis and chemical composition of raw rice straw.

	RS	HT-RSR
Elemental analysis (wt.%, dry basis)		
C	41.7	36.2
H	5.8	4.9
N	0.7	2.8
O (diff)	41.6	43.0
Chemical composition (wt.%, dry basis)		
Hemicellulose	32.0	24.2
Cellulose	29.9	49.8
Lignin	18.8	11.4
Ash	10.2	13.1

2.3. Hydrothermal treatment

Two kinds of reactors with different capacity were used for the hydrothermal treatment of the samples. In a large-scale autoclave (TOYO KOATSU), 10 g of sample and 90 mL of distilled water were put into a reactor. After the gas in the reactor was purged by nitrogen gas, it was pressurized up to 3 MPa. The reactor was heated to the desired temperature (60–220 °C) at the heating rate of about 1 °C/min and cooled to room temperature. The products were filtered and the liquid components were analyzed by the liquid chromatograph. In a small-scale autoclave (Fig. 1), 0.3 g of sample and 3 mL of distilled water were inserted into a reactor (9 mL of inner volume) made of stainless steel. After the gas in the reactor was purged by nitrogen gas, it was pressurized up to 3 MPa. The reactor was heated up to 220 °C at the heating rate of about 100 °C/min and kept at the temperature for the desired time (0–20 min). Then, the reactor was cooled rapidly to room temperature, the products were filtered and the liquid components were analyzed by the liquid chromatograph.

2.4. Steam gasification

Nickel nitrate was impregnated to the hydrothermal-treated rice straw residue (HT-RSR). The nickel-impregnated samples were dried at 110 °C for 1 h, and then preserved in desiccator. As the result of TG measurement (Bruker AXS TG-DTA2000SA), the moisture contents in the nickel-impregnated samples were 5–7 wt.%. The nickel loadings were determined to be 1.5–7.5 wt.% from the results of ultimate analysis and the ash content. A quartz boat

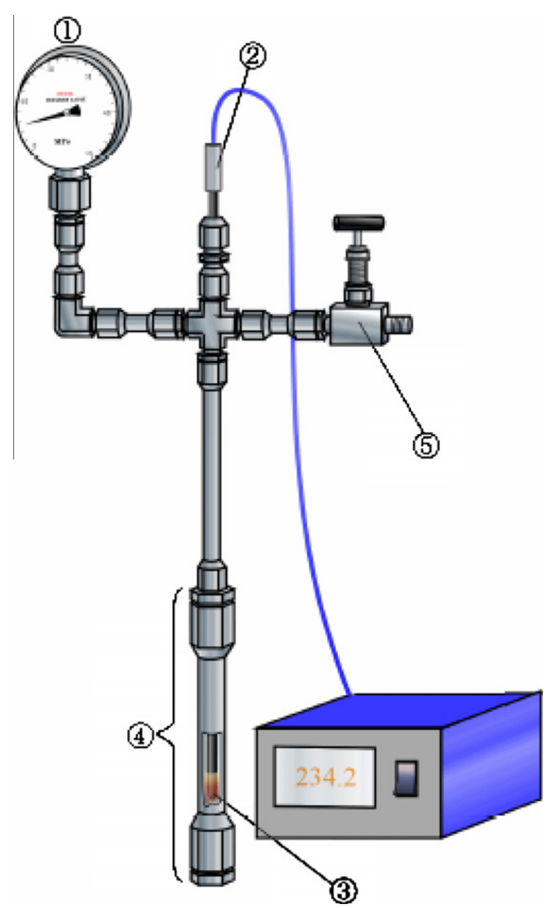

Fig. 1. Schematic illustration of the small-scale autoclave. 1. Pressure gauge. 2. Thermocouple. 3. Sample. 4. Reactor (SUS316). 5. Valve.