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Direct Saccharification of Rice Straw Using a Solid Acid Catalyst

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A direct saccharification process via hydrolysis of rice straw using a solid acid catalyst was developed and its feasibility was investigated. The effects of various reaction parameters and reuse of the catalyst on yields of monosaccharide and organic acid in saccharification of rice straw were evaluated. Saccharification was carried out using an 80 cm³ stainless autoclave. The main monosaccharides produced were xylose and glucose; and the main organic acids were acetic acid, formic acid and levulinic acid. The yields of monosaccharide and organic acid increased with increasing reaction temperature from 110 to 150 °C. The yields of organic acids increased with increasing reaction time from 1 to 6 h, while the yields of monosaccharides initially increased then decreased. It was observed that the particle size of rice straw and solid content of rice straw to water also affected saccharification. The maximum yield of monosaccharides was 148.7 g-sugar / kg-rice straw, obtained at 150 °C for 3 h with the 10 % solid content of rice straw to water. Based on composition analysis of rice straw before and after saccharification, it was found that most of the monosaccharide came from the decomposition of hemicelluloses.

Key Words

Saccharification, Rice straw, Solid acid catalyst

1. Introduction

Fossil fuels play an important role in modern society, but they are a limited resource and their reserves are diminishing. At the same time, with their use, significant emissions of the greenhouse gas CO₂ contribute to global warming problem. Therefore, it is becoming urgent that alternative energy sources to fossil fuel are developed. Utilization of biomass, especially inedible lignocellulosic biomass, is highly desirable for the sustainable development of human society. Lignocellulosic biomass is a renewable and carbon neutral resource¹⁾ and many technologies for its utilization have been developed, with the production of bio-ethanol offering good prospects for the future²⁾.

Extensive research has been carried out on conversion of lignocellulosic biomass to bio-ethanol³⁾, which includes two steps: saccharification of the biomass to monosaccharides and fermentation of monosaccharides to bio-ethanol. Because the first step is the most difficult and costly, an economic saccharification technology will play a key role in the bio-ethanol production process⁴⁾. Several hydrolysis technologies, including the use of inorganic ac-

ids, enzymes and high temperature compressed water have been widely studied, with each having its advantages and disadvantages. Dilute-acid hydrolysis is a rapid process, but the resistant equipments is necessary, selectivity is poor, overpass decomposition occurs easily, and waste liquid is produced in this process⁵⁾⁶⁾. Enzymatic hydrolysis uses mild reaction condition and has high selectivity, but long reaction times and pretreatment are necessary. In addition, enzymes are costly⁷⁾. Thus, it is necessary to develop an efficient and economic process for saccharification of lignocellulosic biomass.

Currently, research into lignocellulosic biomass hydrolysis using solid acid catalysts attracted significant attention because solid acid catalysts offer the advantages of recovery, low or even no corrosion, and mild reaction conditions. Patents describing methods for lignocellulosic biomass saccharification and liquefaction have been developed by our group⁸⁾⁹⁾. Various solid acid catalysts have also been investigated by other groups, including sulfonated carbon materials¹⁰⁾, ion-exchange resins¹¹⁾, heteropolyacids¹²⁾ and layered transition-metal oxide¹³⁾. However, most previous research used α -cellulose as a substrate. It is well known that lignocellulosic biomass includes α -cellulose, hemicelluloses, lignin, extractives and other components. Thus, it

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is not sufficient to use α -cellulose alone as a substrate for studies. Therefore, it is necessary to investigate the feasibility of using the solid acid catalysts for lignocellulosic biomass saccharification.

The feasibility of rice straw saccharification using a solid acid catalyst was investigated in the present study. The aim was to determine the effects of reaction temperature, reaction time, solid content of rice straw to water, particle size of rice straw and recycle of catalyst on the release of monosaccharides and organic acids, and to find the basic character of rice straw saccharification using a solid acid catalyst.

2. Experiments

2.1 Materials and catalyst

Rice straw was supplied by the Agricultural Faculty of the Tokyo University of Agriculture and Technology. The chemical composition of rice straw was analyzed following the procedure described in the NREL Chemical Analysis & Testing procedure¹⁴⁾ and is given in **Table 1**. Rice straw was washed thoroughly using tap water to remove surface dust and then dried to a constant weight at 105 °C, then chopped into small pieces of about 0.83-2.8 mm. Amberlyst 15Dry (Rohm and Hass Co., USA) catalyst was bought from Takacho Company, with properties as shown in **Table 2**. This catalyst is in spherical bead form and is a strong acid ion exchange resin, developed for heterogeneous acid catalysis of a wide variety of chemical reactions.

2.2 Saccharification

Saccharification of rice straw was carried out as follows. First, Amberlyst 15Dry catalyst, distilled water and rice straw were placed into a stainless autoclave of volume 80 cm³ and this then was placed into a shock-heated incubator (Isuzu, EPEC-75-Y). The reaction conditions for rice straw saccharification were: 1 g of Amberlyst 15Dry catalyst, a solid content of rice straw to water of 3.3-16.7 %, particle size of rice straw 0.83-2.8 mm, 30 g distilled water, a reaction time of 1-6 h, and a reaction temperature

of 110-150 °C.

After saccharification, the reacted mixture was separated into solid and liquid fractions using a 0.2 μ m membrane filter (Sartorius Stedim, 17761). The solid was dried at 105 °C in the oven until no further change in weight of the sample was observed. The liquefaction rate of rice straw was then calculated using equation (1).

2.3 Analysis method

The separated liquid sample was diluted and analyzed using high-performance liquid chromatography (HPLC) equipped with refractive index detectors (Tosoh, RI-8020). Monosaccharide was determined with a TSKgel Amide-80 column (Tosoh, K0131) at 50 °C using 10 mM KH₂PO₄ solution (Acetonitrile/distilled water = 3/1) as an eluent at a flow rate of 1.0 cm³/min. Organic acids were analyzed on a TSKgel Opak-A column (Tosoh, N0001) at 40 °C using an eluent of 75 mM sulfuric acid flowing at 0.7 cm³/min.

Standard samples were used to identify the saccharification products in the solution. The main products of rice straw saccharification are xylose, glucose, acetic acid, levulinic acid and formic acid. All values were calculated on the basis of dried rice straw without ash. All reported data are the average of two replications.

The definition of the liquefaction rate of rice straw, yield of monosaccharide and yield of organic acid are given by in equations (1), (2) and (3).

$$\text{Liquefaction Rate (\%)} = \frac{W_{RS}(\text{g}) - W_R(\text{g})}{W_{RS}(\text{g})} \times 100\% \quad (1)$$

$$\text{Monosaccharide yield (g/kg)} = \frac{W_M(\text{g})}{W_{RS}(\text{kg})} \quad (2)$$

Table 2 Properties of Amberlyst 15Dry catalyst

Item	Content
Physical form	opaque beads
Concentration of acid sites	≥ 4.7 eq/kg
Surface area	53 m ² /g
Average pore diameter	300 Å
Total pore volume	0.40 cc/g

Table 1 Change in chemical composition of reacted rice straw

Content % (w/w)	Rice straw (unreacted)	Reacted rice straw (110 °C/3 h)	Reacted rice straw (135 °C/3 h)	Reacted rice straw (150 °C/3 h)
Hemicellulose	18.5	11.4	5.8	0.0
Cellulose	34.9	33.8	30.2	28.6
Acid insoluble lignin	14.4	14.0	13.9	13.1
Acid soluble lignin	1.6	0.6	0.4	0.1
Ash	19.4	13.2	12.8	12.6
Extractives	3.4	2.5	2.1	1.9

All data in Table 1 were calculated on the basis of 1 g rice straw.

$$\text{Organic Acid Yield (g/kg)} = \frac{W_{\text{OA}} (\text{g})}{W_{\text{RS}} (\text{kg})} \quad (3)$$

Where W_{RS} is the weight of the rice straw sample without ash, W_{R} is the weight of reacted rice straw residue without ash, W_{M} is the weight of monosaccharide (xylose, glucose), and W_{OA} is the weight of organic acid (acetic acid, levulinic acid, formic acid).

3. Results and discussion

3.1 Saccharification of rice straw in the presence of solid catalyst

Saccharification of rice straw was first carried out in the presence of Amberlyst 15Dry catalyst and absence of Amberlyst 15Dry catalyst. The reaction conditions were: 1 g of catalyst, 30 g of distilled water, 3 g of rice straw (1.18 mm), at 110 °C for 3 h. A blank experiment was also carried out under the same reaction conditions without the catalyst. The results are given in Table 3. For saccharification in the absence of the catalyst, no glucose and little of organic acids or xylose were detected. In contrast, in the presence of the catalyst, the main products detected were xylose and glucose and a little of byproducts such as acetic acid, formic acid and levulinic acid etc. The results indicate that it is more feasible and efficient to carry out saccharification of rice straw in the presence of a solid catalyst.

3.2 Effect of reaction temperature on saccharification of rice straw

As discussed in the section 3.1, saccharification of rice straw using the solid acid catalyst is feasible. Thus, the effect of reaction temperature on saccharification of rice straw using the solid acid catalyst was investigated further in this section. The reaction conditions were: 1 g of catalyst, 30 g of distilled water, 3 g of rice straw (1.18 mm), at the temperature range from 110 to 150 °C for 3 h.

The effect of increase in reaction temperature is shown in Fig. 1.

In fact, as shown in Table 1, the cellulose content (34.9 %) is higher than that of hemicellulose (18.5 %), hence it is possible that little of the cellulose decomposed at the reaction temperature range and xylose and glucose mostly

came from hemicellulose decomposition. To confirm this, both the untreated and reacted rice straw was also analyzed by the procedure described in the NREL Chemical Analysis & Testing procedure¹⁴⁾. As shown in Table 1, the hemicellulose content in rice straw after reaction decreased from 18.5 to 0 % at 150 °C for 3 h, whereas the cellulose content changed only from 34.9 to 28.6 %. This means that the monosaccharide mainly originated from hemicelluloses conversion.

Fig. 1 Liquefaction rate of rice straw and yield of monosaccharide (a), yield of organic acid (b) in saccharification of rice straw at different reaction temperatures

Fig. 2 Hydrolysis mechanism of rice straw using solid acid catalyst

Table 3 A comparison between solid-acid catalyzed hydrolysis (a) and auto-catalyzed hydrolysis (b)

Content	Liquefaction Rate (%)	Yield of xylose (g/kg)	Yield of glucose (g/kg)	Yield of acetic acid (g/kg)	Yield of formic acid (g/kg)	Yield of levulinic acid (g/kg)
a	26.3	40.9	25.8	17.5	1.6	2.8
b	14.1	6.0	0.0	8.2	0.5	0.8

a-in the presence of catalyst, b-absence of catalyst

Based on the results mentioned above, hydrolysis mechanism of rice straw using solid acid catalyst in the present work was shown in Fig. 2. As shown in Fig. 2, in Stage I, part of hemicellulose and cellulose were converted into oligosaccharide and a small amount of monosaccharide via hydrothermal hydrolysis and/or catalytic hydrolysis. In Stage II, oligosaccharide produced and dissolved in water was hydrolyzed and further mainly converted into monosaccharide. In Stage III, part of monosaccharide would be converted into byproducts such as furfural, 5-HMF, levulinic acid and formic acid because of overreaction. At the same time, acetyl group in hemicellulose may be hydrolyzed into acetic acid in Stage I. Acetic acid and solid catalyst could perform a catalytic hydrolysis of part of hemicelluloses, but the hydrothermal hydrolysis performed the main role in Stage I. The stirring style, particle size of rice straw and solid content of rice straw to water etc. played a minor role due to mass transfer between rice straw, water and catalyst. In addition, it is considered that catalytic hydrolysis by solid acid catalyst performed the main role in Stages II and III.

3.3 Effect of reaction time on saccharification of rice straw

It was found that most of the hemicellulose was removed with increasing temperature from 110 to 150 °C. However, there seemed to be no apparent effect on cellulose in rice straw. Therefore, the effect of reaction time was investigated in this section. The reaction conditions were: 1 g of catalyst, 30 g of distilled water, 3 g of rice straw (1.18 mm), at 150 °C for 1-6 h.

The effect of increase in reaction time is shown in Fig. 3.

It was reported that under mild reaction conditions for a short reaction time, hemicellulose was almost completely converted to xylose, glucose, arabinose and other monosaccharide. At the same time, acetyl groups decomposed to acetic acid¹⁵⁾. However, it seemed the rate of xylose formation was higher than that of acetic acid, thus yields of xylose and acetic acid both increased over the range of reaction time of 1-3 h. When the reaction time exceeded 3 h, it is possible that the structure of rice straw became loose with the hemicelluloses decomposition and a slight decrease in the content of lignin in rice straw (Seen in Table 1). This would aid the conversion of cellulose into glucose, the product glucose would then decompose into levulinic acid and formic acid. In addition, as shown in Fig. 2, with the increase in reaction time, overreaction happened in Stage III because of catalytic hydrolysis. Thus, monosaccharide was converted into organic acids and other byproducts. Therefore, yields of xylose and glucose decreased; and yields of levulinic acid and formic acid increased. Overall, the maxi-

Fig. 3 Liquefaction rate of rice straw and yield of monosaccharide (a), yield of organic acid (b) in rice straw saccharification for different reaction times

imum relative monosaccharide yield was obtained at 150 °C for 3 h.

3.4 Effect of solid content of rice straw to water on saccharification of rice straw

It is shown above that saccharification of rice straw using a solid acid catalyst is effective. Next, we investigated the effects of solid content of rice straw. In this section, the reaction conditions were: 1 g of catalyst, 30 g of distilled water, solid content of rice straw (1.18 mm) to water of 3.3-16.7 % (w/w), at 150 °C for 3 h.

The effect of solid content of the rice straw is shown in Fig. 4.

According to the mechanism as shown in Fig. 2, the results shown in Fig. 4 are explained as follows. In this case, because the amount of catalyst in all reactions was constant, thus the conversion yield of rice straw decreased with the increase in the solid content of rice straw to water from 3.3 to 16.7 %. In fact, the liquefaction rate of rice straw decreased slightly in the whole range of solid content of rice straw to water, and the yields of all the products decreased in the range of solid content of rice straw to water from 10.0 to 16.7 %. However, the yields of glucose and the organic acids were low when the solid con-

Fig. 4 Liquefaction rate of rice straw and yield of monosaccharide (a), yield of organic acid (b) in rice straw saccharification with different solid content of rice straw to water

tent of rice straw to water was 3.3 %. It could be attributed to the overreaction taking place in Stage III as shown in Fig. 2, resulting in that the monosaccharide was converted into the byproducts such as furfural, 5-HMF, organic acids and some other unknown compounds which were not determined. Therefore, the yields of organic acids and glucose were low with a low solid content of rice straw to water of 3.3 %. In addition, xylose came from xylan conversion; and the content of xylan was higher than that of glucan in hemicellulose. In the present work, monosaccharide mainly came from hemicellulose decomposition. It was possible that the rate of xylose formation was faster than that of xylose degradation. Thus, the yield of xylose did not decrease. In all cases, currently, a 10 % (w/w) seemed to be a superior solid content of rice straw to water.

3.5 Effect of particle size of rice straw on saccharification of rice straw

In fact, the particle size of rice straw also plays an important role in the process of rice straw saccharification¹⁶⁾. The proper size is beneficial to the yield of monosaccharide. In this section, the reaction conditions were: 1 g catalyst, 30 g distilled water, 3 g rice straw with average par-

Fig. 5 Liquefaction rate of rice straw and yield of monosaccharide (a), yield of organic acid (b) in rice straw saccharification with different particle size of rice straw

ticle size of 0.83-2.8 mm, at 150 °C for 3 h.

The effect of particle size of the rice straw is shown in Fig. 5.

The surface area of rice straw decreased with the increase in the particle size of rice straw. Firstly, hydrothermal hydrolysis in Stage I as shown in Fig. 2 became weak due to the decrease in the surface area of rice straw. Thus, little of oligosaccharide was produced, resulting a decrease in monosaccharide via catalytic hydrolysis in Stage II as shown in Fig. 2 and a decrease in organic acids in Stage III. Therefore, the yields of monosaccharide and organic acids decreased. However, the yield of glucose was low in the case of the particle size of rice straw of 0.83 mm than that in the case of 1.18 mm. It was possible that the reaction rate of hydrothermal hydrolysis in Stage I and catalytic hydrolysis in Stages II and III was accelerated when the particle size of rice straw was 0.83 mm. Thus, overreaction happened and monosaccharide was converted to other unknown products and organic acids in Stage III as shown in Fig. 2. In this section, 1.18 mm seems to be the best particle size for saccharification of rice straw.

3.6 Reuse of the solid catalyst

As mentioned in the introduction, the solid acid cata-

lysts offer great advantages of recovery. In this section, the reuse of Amberlyst 15Dry catalyst was investigated. The reaction conditions were: 1 g of catalyst, 30 g of distilled water, 3 g of rice straw (1.18 mm), 150 °C for 3 h. A blank experiment was carried out under the same reaction conditions without catalyst.

As shown in Fig. 6 and Table 4, the catalyst was reused for four times, while the blank sample was used only as a reference and obtained from saccharification of rice straw without catalyst. With the reuse of the catalyst, the liquefaction rate and all the products from saccharification of rice straw appeared to decrease. However, the yield of xylose decreased faster from 74.9 to 9.0 g/kg than that of

glucose from 73.7 to 26.8 g/kg; and the yield of acetic acid decreased faster from 22.1 to 9.8 g/kg than those of levulinic acid from 13.1 to 3.7 g/kg and formic acid from 2.6 to 1.9 g/kg.

Amberlyst 15Dry catalyst is an ion change catalyst and clearly with the reuse, its acid sites decreased. Hence, the liquefaction rate of rice straw decreased. However, it was found that the yield of xylose decreased faster than that of glucose. As discussed above, the yield of xylose was always higher than that of glucose. It is possible that hemicellulose and cellulose have different accessibility to the different types of acid site. At the same time, the unknown products from saccharification of rice straw may adversely affect the active sites of the catalyst. In addition, the silica and lignin¹⁷⁾ in rice straw also negatively affected the activity of Amberlyst 15Dry catalyst. It is possible that with reuse of Amberlyst 15Dry catalyst, the unknown products, silica and lignin accumulated on the surface of the catalyst, as can be seen in Table 1, leading to catalyst poisoning and sudden loss of activity.

4. Conclusions

The effects of various reaction parameters and reuse of catalyst on yields of monosaccharide and organic acids in the saccharification of rice straw were investigated. The main monosaccharides produced were xylose and glucose, and the main organic acids were acetic acid, formic acid and levulinic acid. The yields of monosaccharide and organic acid increased with increasing reaction temperature from 110 to 150 °C. With increasing reaction time from 1 to 6 h, yields of organic acids increased, while yields of monosaccharide initially increased then decreased. It was observed that particle size of rice straw and solid content of rice straw to water also affected the saccharification of rice straw. The maximum yield of monosaccharide was 148.7 g-sugar/kg-rice straw, obtained at 150 °C for 3 h with a 10 % solid content of rice straw to water. Based on a composition analysis of rice straw before and after saccharification, it was found that most monosaccharide came from the decomposition of hemicelluloses in rice straw, and part of lignin and ash was removed in the present study. Activity of Amberlyst 15Dry catalyst decreased with its reuse.

Fig. 6 Yields of monosaccharide (a) and organic acid (b) in rice straw saccharification with reuse of Amberlyst 15Dry

Table 4 Reuse of solid catalyst

Run time	Liquefaction rate (%)	Yield of total organic acid (g/kg)
run 1	39.3	37.6
run 2	30.7	18.9
run 3	26.1	17.2
run 4	22.8	15.4
blank	21.3	20.7

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