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Research Paper

Effects of Reactive Condition and Mechanochemical Treatment on Xylose Production from Rice Husk by Dilute Acid Hydrolysis

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ABSTRACT

Rice husk is one of lignocellulosic biomass wastes. In this study, effects of hydrolysis condition with dilute acid and mechanochemical treatment on xylose production from rice husk were investigated. The xylan content in the rice husk used in this study was 11.3%, and assuming that this was completely hydrolyzed, 128 g of xylose can be obtained per kg of rice husks. When the hydrolysis of rice husk was conducted for 4 hours with the nitric acid (0.01-0.10 mol/L) at 70-100°C, the highest xylose yield (64.5%) could be obtained with 0.10 mol/L nitric acid at 100°C. By mechanochemical treatment in a planetary ball mill, microfibril structure of rice husk collapsed and became amorphous. The xylose yield reached 93.1%, when the mechanochemically treated rice husk was hydrolyzed with 0.10 mol/L nitric acid at 100°C for 4 hours.

HIGHLIGHTS

- Rice husk, one of the lignocellulosic biomass wastes, was subjected to mechanochemical treatment.
- When the treated rice husk was hydrolyzed with dilute nitric acid, the yield of xylose reached 93.1%.

Keywords: Biorefinery, Rice husk, Acid hydrolysis, Xylose, Pretreatment

Massive consumption of fossil resources is causing an increase in the concentration of carbon dioxide in the atmosphere. As a result, in recent years, abnormal weather events such as heat waves, torrential rains, and droughts have been occurring frequently in many parts of the world, and climate change such as global warming is progressing. Therefore, there is a strong need to develop biorefinery technology to convert raw materials for energy (e.g., electricity) and chemical products (e.g., fibers and plastics) from fossil resources to renewable biomass resources. The development of this technology is expected to make a significant contribution not only to solving climate change problems but also to the formation of a sustainable society.

Among bio-refinery technologies, bioethanol has been the subject of vigorous research for the past several decades since it was positioned as carbon neutral by the United Nations Framework Convention on Climate Change (Silalertruksa and Gheewala, 2011; Byun *et al.* 2022; Chang *et al.* 2010). In Brazil and the United States, bioethanol has already being produced on a large scale from sugarcane and corn. The increase in bioethanol production has led to an increase in the prices of various livestock products and grains. Therefore,

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there is an urgent need to develop the use of biomass resources that do not compete with food production. Currently, there is a strong need to develop a process to convert inedible biomass, lignocellulose, into a resource.

Global rice production was about 600 million tons in 2000 and increased to about 780 million tons in 2018. In Japan, although there is a declining trend in production, nearly 10 million tons are still produced annually in recent years. Rice husk is the outer hard protective covering which surrounds the paddy grain and accounts for 20% of its weight (Hongo *et al.* 2021). Therefore, about 2 million tons of rice husks are generated every year in Japan. Rice husks are effectively used as soil conditioner and barn bedding, but it is estimated that 20-30% of rice husks are disposed of without being effectively utilized.

The main components of lignocellulose are cellulose, hemicellulose, and lignin. Hemicellulose is a heteropolysaccharide and is composed primarily of xylan, a homopolymer of xylose (Saha, 2003). Since xylitol, a widely used non-cariogenic sweetener, is synthesized from xylose, active research is being conducted to produce xylose from lignocellulose-based biomass (Zhang *et al.* 2012; Morinelly *et al.* 2009; Rahman *et al.* 2007). Hemicellulose can be hydrolyzed with dilute acid solution and is generally studied by hydrothermal treatment methods at temperatures above 100°C. Hydrothermal treatment is a processing method under high-temperature and high-pressurer, which requires a pressure-resistant container and a lot of energy. Temiz and Akpinar reported that hydrothermal treatment of rice husks at 127°C produced xylose in 87.7% yield (Temiz and Akpinar, 2016).

Various pretreatment methods have been investigated for efficient enzymatic saccharification of lignocellulosic biomass (Sun *et al.* 2016; Elgharbawy *et al.* 2016; Gu *et al.* 2018; Zhang *et al.* 2021; Xu *et al.* 2019). However, very few pretreatment methods have been studied for acid hydrolysis. Mechanochemical treatment by ball milling, one of the pretreatment methods for biomass samples, is expected to advance acid hydrolysis reactions because it can alter the polymer structure at the molecular level (Wu *et al.* 2021). In this study, we investigated a method to produce xylose from rice husks using dilute acid at lower temperatures and in higher yields without pressurization. We also examined the effect of mechanochemical treatment on acid hydrolysis.

EXPERIMENTAL PROCEDURE

1. Material

Rice husk was obtained from a rice mill at Fukaya in Japan. It was washed thoroughly with distilled water to remove adhered soil and dust. It was dried at 70 °C overnight in a drying oven and pulverized by milling cutters.

2. Rice husk composition

The moisture and ash contents were determined by the dry weight method (110 °C) and direct ashing method (575 °C), respectively. The amount of cellulose, hemicellulose, and lignin in the rice husk was determined by the detergent method (Van Soest and Wine, 1968).

The polysaccharides in the rice husk were hydrolyzed according to Browning (Browning, 1967), and the xylose composition was determined. The rice husk (300 mg) was mixed with 72 % sulfuric acid (3 mL), and the mixture was held at 30 °C for 1 h with stirring. The concentration of acid in the mixture was adjusted to 40 % by adding distilled water, ant the mixture was hydrothermally treated at 120 °C for 1 h. The xylose in the aliquot of the hydrolysate was assayed by high performance liquid chromatography (HPLC) as described below.

3. Mechanochemical treatment

The rice husk was subjected to mechanochemical treatment using a planetary ball mill (Fritsch P7), a tungsten carbide container, and a tungsten carbide grinding medium. The rice husk (1.0 g) was placed in a ball milling container and subjected to mechanochemical treatment at a rotation speed of 500 rpm for 10 min. The treated rice husk was characterized by powder X-ray diffraction (XRD) measurements (Rigaku, RINT-Ultima III) and scanning electron microscopy (SEM, Hitachi, TM3000).

4. Dilute acid hydrolysis

1.0 g of rice husk sample was placed in a 500 mL nitrate solution (0.01, 0.05, 0.10 mol/L) and refluxed at 70 to 100 °C for 4 hours with stirring at 500 rpm. Sampling of the suspension during refluxing was conducted intermittently using a 0.2-μm nitrocellulose filter. The concentrations of xylose in the filtrates were determined using the HPLC as described below.

5. Analytical method

Ion exchange resin (Amberlite, Organo) was used to remove sulfate and nitrate ions contained in the hydrolysate samples. The xylose in the aliquot of the treated hydrolysate were assayed by with the Shimadzu HPLC system, using refractive index detector (RID-10A) and Shodex HPLC column SUGAR SP0810. Xylose was eluted from the column with the use of distilled water as the mobile phase at 80 °C, with a flow rate of 0.5 mL/min.

RESULTS AND DISCUSSION

The composition of rice husks is known to vary depending on several variables, including the rice variety, and the regional climate and geographical conditions experienced during the rice cultivation process. According to the previously reported papers, the contents of cellulose, hemicellulose and lignin contained in rice husks are 29-43%, 12-29% and 15-26%, respectively (Tabata *et al.* 2017; Ilhamy *et al.* 2020; Karim *et al.* 2012). In addition, the high ash content (15-20%) is a characteristic of rice husks. Table 1 shows the chemical composition of rice husk. Cellulose, hemicellulose, lignin, and ash were found to be 41.3%, 17.7%, 15.7%, and 19.1%, respectively, within the reported chemical composition distribution.

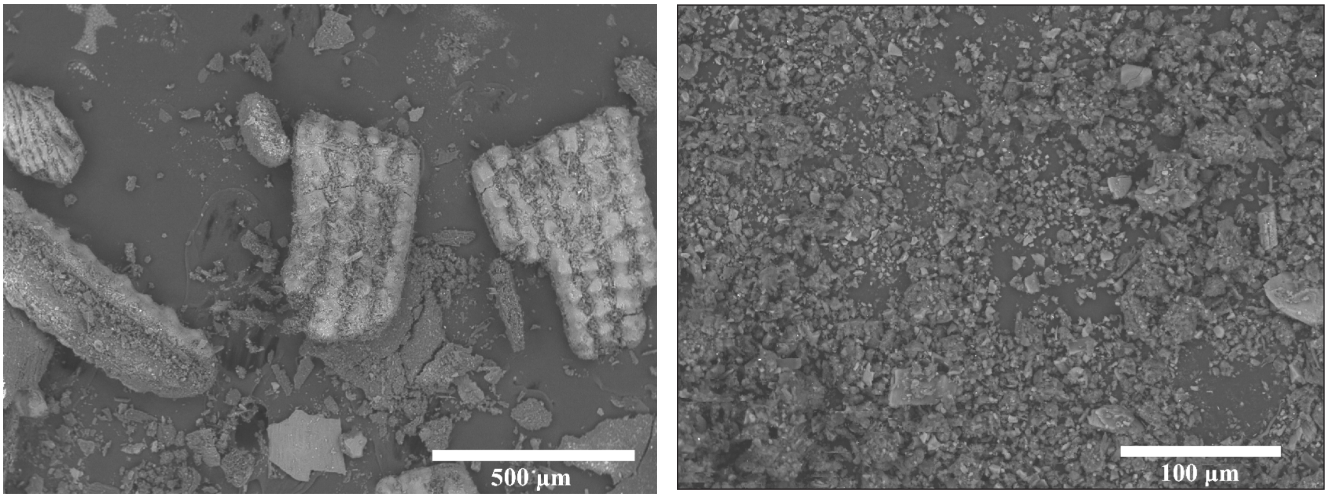
Table 1: Composition of the rice husk

Component	Content (%)
Cellulose	41.3
Hemicellulose	17.7
Lignin	15.7
Moisture	1.7
Ash	19.1
Others	4.5

The xylose yield determined by the Browning method was 128 g per kg of the rice husk. The molecular weights of xylose and anhydrous xylose units in xylan are 150.130 g/mol and 132.114 g/mol, respectively. From these values, the xylan content in the rice husk was estimated to be about 11.3%. Xylan was found to account for 63.8% of hemicellulose, since it was contained in hemicellulose (17.7%).

SEM images of the untreated and treated rice husk samples by the planetary ball mill are shown in Fig. 1. The particle size of untreated rice husks was less than 1 mm (Fig. 1a). On the other hand, the particle size of treated rice husks was found to be less than 40 μm (Fig. 1b). From this result, it was expected that the hemicellulose fiber could be shortened by the treatment with the planetary ball mill.

XRD patterns of the untreated and treated rice husk samples by the planetary ball mill are shown in Fig. 2. The XRD pattern of the untreated rice husk sample had broad diffraction peaks at around 2θ = 16°, 22°,



(a) (b)

Fig. 1: SEM images of the **(a)** untreated and **(b)** treated rice husk samples by the planetary ball mill

and 35°, corresponding to the 110 and 110, 200, and 004 reflections of cellulose I crystal, respectively (Sri Bala *et al.* 2016). This indicates that the rice husk sample before the mechanochemical treatment had a microfibril structure of cellulose. On the other hand, the XRD pattern of the treated rice husk sample did not show diffraction peaks attributed to cellulose I crystal, and a halo peak was observed around 2θ = 21°. This is due to amorphization, meaning that the microfibril structure of the cellulose in the rice husk had disrupted by the mechanochemical treatment. Cellulose and hemicellulose are the major components and are tightly connected and intertwined in cell walls of plants (Murashima *et al.* 2003). Therefore, the microfibril structure of the hemicellulose was considered to have disrupted by the mechanochemical treatment as well as cellulose.

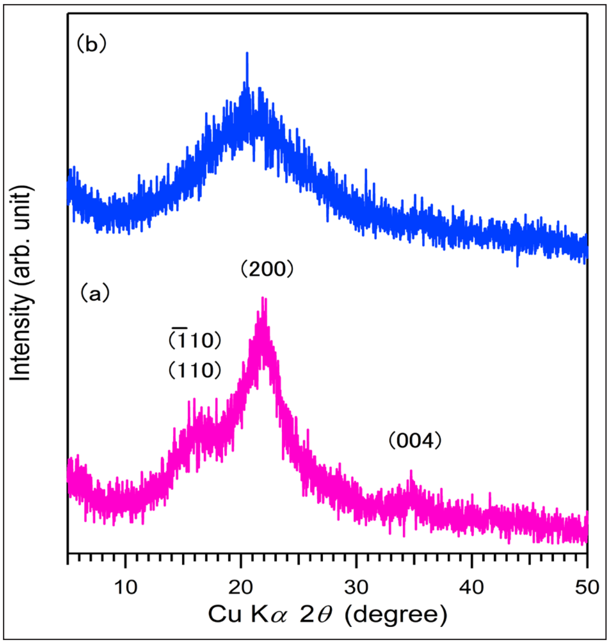


Fig. 2: XRD patterns of the **(a)** untreated and **(b)** treated rice husk samples by the planetary ball mill

Fig. 3 shows the time variation of xylose yield with varying nitric acid concentration (0.01-0.10 mol/L) at 90°C using untreated rice husk samples. At nitric acid concentrations of 0.01 mol/L and 0.05 mol/L, xylose production was observed, whereas the xylose yield did not increase significantly with time. The xylose yields after 4 hours were 6.2% and 6.9%, respectively. When the nitric acid concentration was increased to 0.10 mol/L, the xylose yield after 1 hour was 3.2 %. The xylose yield continued to increase with time, and the yield after 4 hours was 15.9%.

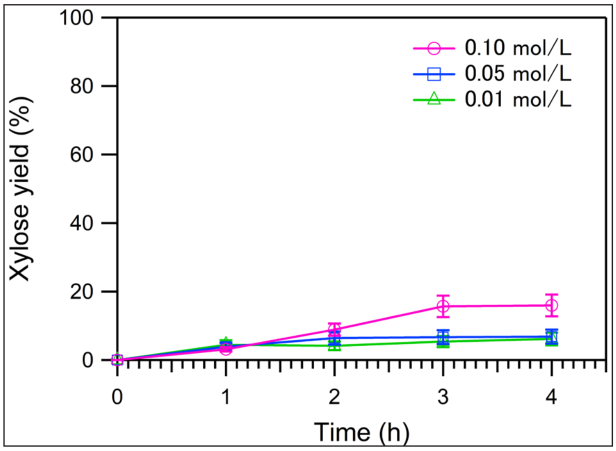


Fig. 3: Time variation of xylose yield with varying nitric acid concentration at 90°C using untreated rice husk samples

Next, the temperature dependence of xylose yield was examined. Fig. 4 shows the time variation of xylose yield when the reaction temperature was varied (70-100°C) at a nitric acid concentration of 0.10 mol/L using untreated rice husk samples. Xylose production was observed at 70°C and 80°C, however the yields after 4 hours were very low, 0.6% and 2.3%, respectively. On the other hand, when the reaction temperature was increased to 100°C, the xylose yield after 1 hour was 13.3%. The xylose yield increased with time, and the xylose yield after 4 hours was 64.5%. By increasing the reaction temperature from 90°C to 100°C, the xylose yield after 4 hours increased approximately 4-fold.

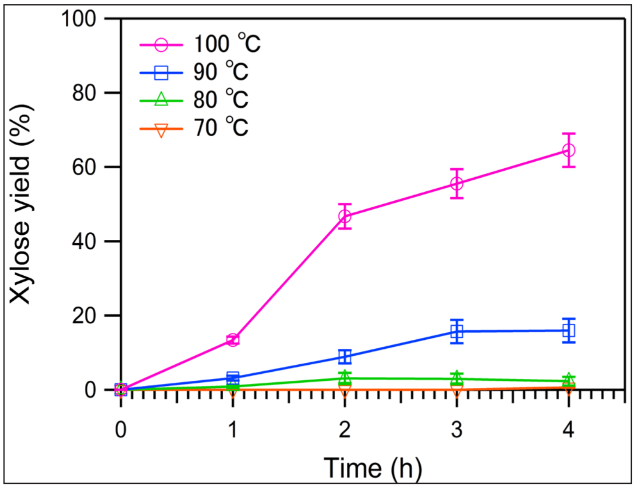


Fig. 4: Time variation of xylose yield when the reaction temperature was varied (70-100°C) at a nitric acid concentration of 0.10 mol/L using untreated rice husk samples

To further increase the xylose yield, the effect of mechanochemical treatment of rice husk samples with a planetary ball mill was investigated. Fig.

5 shows the time variation of xylose yield when the reaction temperature was varied (70-100°C) at a nitric acid concentration of 0.10 mol/L using treated rice husk samples. At a reaction temperature of 70°C, little xylose production was observed, whereas the xylose yield increased dramatically as the reaction temperature increased. At a reaction temperature of 100°C, the xylose yield reached 44.5% in 1 hour and continued to increase, reaching 93.1% in 4 hours.

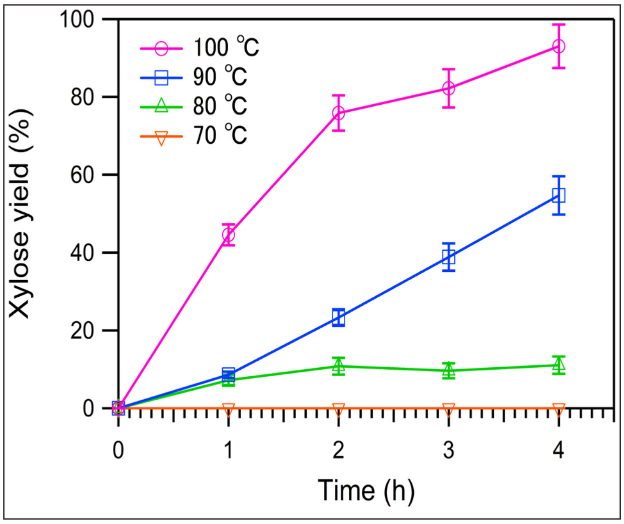


Fig. 5: Time variation of xylose yield when the reaction temperature was varied (70-100°C) at a nitric acid concentration of 0.10 mol/L using treated rice husk samples

Xylose production from lignocellulosic biomass by dilute acid has been often conducted by hydrothermal treatment. In a study of lignocellulosic biomass other than rice husk, Roberto *et al.* reported the production of xylose in 77% yield by hydrothermal treatment of rice straw at 121°C with sulfuric acid solution at 1% concentration (Roberto *et al.* 2003). Similarly, studies on the production of xylose from corn stover and cotton stalks by hydrothermal treatment with dilute sulfuric acid (120-140°C) have been reported (Fehér *et al.* 2017; Akpinar *et al.* 2011). Their yields were 81.9% and 47.88%, respectively. In this study, a xylose yield of 93.1% was achieved at a lower temperature (100°C) and without pressurization by mechanochemical treatment of rice husk samples in a planetary ball mill. This is due to the disruption of the microfibril structure of the rice husk and the cleavage of the xylan in the hemicellulose by the mechanochemical treatment, which effectively caused a hydrolysis reaction from the cleavage surface.

CONCLUSION

The rice husks used in this study contained 17.7% hemicellulose, of which about 63.8% was xylan. When all the xylan in the rice husks was hydrolyzed, 128 g of xylose was found to be produced per kg of rice husks. The production of xylose by acid hydrolysis could be confirmed even with a 0.01 mol/L nitrate aqueous solution, but a higher xylose yield could be obtained by increasing the nitrate concentration to 0.10 mol/L. Xylose yield was also greatly affected by the temperature. At a nitric acid concentration of 0.10 mol/L, almost no xylose was produced at 70°C, however at 100°C, xylose yield reached 64.5% after 4 hours. To obtain higher xylose yields, the rice husks were mechanochemically treated by the planetary ball mill. The mechanochemical treatment resulted in the miniaturization of the rice husk particles and the disruption of their microfibril structure. Xylose yield reached 93.1% when mechanochemically treated rice husks were hydrolyzed with 0.10 mol/L nitric acid at 100°C for 4 hours.

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