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Microwave-assisted Acid-catalyzed Hydrolysis of Hemicelluloses in Rice Husk into Xylose

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Abstract. The development of an environmentally benign process for the hydrolysis of hemicelluloses into xylose could be one of the key technologies for making full use of biomass in the future. This paper studies dilute acid hydrolysis of hemicelluloses in rice husk (RH) into xylose using microwave radiation. Fourier transform infrared-attenuated total reflection spectroscopy was employed to quantitatively analyze xylose. The influences of hydrolysis parameters such as temperature, time, acid concentration, and ratio of RH to sulfuric acid on the yield of xylose in acid hydrolysis of RH were also investigated. The optimum hydrolysis conditions of hemicelluloses in RH to xylose are as follows: 4 wt% of H_2SO_4 concentration, 150 °C hydrolysis temperature, 25 min reaction time, and 1:7 ratio of RH (g) to H_2SO_4 (mL). Under optimum hydrolysis conditions, a yield of 32.96% xylose is obtained.

1. Introduction

Rice husk (RH), which represents 20% of the dry weight of a rice harvest, is an agricultural byproduct abundant in all rice-producing countries [1]. However, most RH is not sufficiently utilized because of its poor protein content. In fact, RH arouses more environmental concern for its lack of usefulness. Therefore, research on how to utilize RH comprehensively is urgent [2].

RH is rich in hemicellulose $(C_5H_8O_4)m$ and cellulose $(C_6H_{10}O_5)n$, in which the content of hemicellulose is approximately 20 wt% and cellulose is 40 wt% [3]. Compared with cellulose, Hemicellulose is amorphous and relatively easy to hydrolyze into mono sugars [4-6]. hemicellulose in RH is made up of substituted arabinoxylan, which can be converted into xylose by diluted acid hydrolysis under certain conditions. Xylose products are widely used in the food and pharmaceutical industries for their low calorific value and acceptable organoleptic properties [2]. Cellulose, another main component of RH, is a valuable energy resource, and can be transformed into ethanol by hydrolysis and by fermentation [4, 7, 8].

Dilute acid hydrolysis of biomass has a long industrial history. It hydrolyzes hemicelluloses and cellulose in biomass into useful chemicals, such as pentose and hexose. Compared with cellulose hydrolysis, hemicellulsoe in biomass requires shorter time for complete hydrolysis because of its amorphous structure. Additionally, hemicelluloses could be further decomposed to other chemicals, such as HMF, before complete hydrolysis of cellulose. Therefore, the whole process of biomass hydrolysis consists of the steps in the hydrolysis of hemicellulose into xylose and the subsequent hydrolysis of cellulose into glucose, xylose, and other byproducts, such as HMF [9]. Today, hydrolysis with dilute acid is the primary pretreatment technology for altering or removing structural and compositional impediments to hydrolysis to improve the rate of enzyme hydrolysis and to increase yield of fermentable sugars from cellulose [8]. Most studies focus on dilute acid pretreatment of biomasses, such as bagasse [10], silvergrass [11], corn stover [12], rice straw [13], RH, and bean husk [9], to enhance the digestibility of cellulose in residual solids, which is able increase yield of fermentable sugars from cellulose. During pretreatment, addition of dilute acid removes hemicelluloses from biomass either in combination with the breakdown of cellulose to glucose or prior to acid hydrolysis of cellulose. However, little attention has been paid to dilute acid hydrolysis of hemicelluloses in RH into xylose. In addition, the past decades have witnessed the use of microwave irradiation to accelerate organic reactions, which has been attracting interest as a type of environmentally benign process. In particular, this technique has been successfully applied to promote dilute alkalis, dilute acids, and catalyzed hydrolysis of various materials [14, 15]. The utilization of emerging microwave-assisted chemistry techniques in conjunction with benign reaction media has dramatically reduced chemical waste and reaction time in several organic syntheses and chemical transformations [16]. Such technology is very effective in accelerating acid-catalyzed hydrolysis of RH because both thermal (rapid heat generation) and non-thermal effects (particle collision) are involved [17]. Therefore, in the present work, hemicelluloses in RH is hydrolyzed into xylose using acid with microwave assistance, and the influences of hydrolysis parameters such as temperature, time, acid concentration, and ratio of RH to sulfuric acid on the yield of xylose are studied.

2. Method

2.1Feedstock preparation and pretreatment

RH was obtained from China; its components are listed in **Table 1**. Analytically pure sulfuric acid was from Sigma. Prior to hydrolysis, RH was washed thoroughly with distilled water to remove adhering soil and dust, and then dried to a constant weight at 105 ºC. Hemicellulose is relatively easy to hydrolyze. Crushing RH may increase the chances of cellulose decomposition. As such, in this experiment, we hydrolyze RH directly without crushing.

Table 1. Composition of raw RH

Component	Composition (wt%)
Moisture	0.97%
Cellulose	42.49%
Hemicellulose	19.34%
Lignin	15.05%
Ash	15.49% (SiO_2 12.84%)
Benzene alcohol extract	6.66%

2.2Hydrolysis of RH under microwave irradiation

In our experiment, RH (0.5-3 g) and dilute sulfuric acid (1-5 wt%, 20 mL) were mixed and transferred to a Teflon reactor. Then, the reactor was sealed and placed in a 600 W microwave oven (MDS-6, Sineo Microwave Chemical Technology Co. Ltd.). Heating time should be considered and deducted from hydrolysis time. The following heating times were investigated under different acid hydrolysis temperatures: 2, 3, 4, 5, and 6 min under 100, 120, 140, 160, and 180 ºC, respectively. Heating time at different acid hydrolysis temperatures was deducted from hydrolysis time in the present experiment. After hydrolysis, the reaction mixture was cooled down in cold water and filtered. Because cellulose in RH is hard to hydrolyze in a short time and in a low acid concentration, we assume that sugar in the hydrolysis solution was xylose.

2.3FTIR-ATR analysis

Spectra for the filtrate solution were obtained using Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectrometer (Bruke Tensor 27) by averaging 16 scans at 2 cm^{-1} resolution. Because xylose reacts with NaOH to form double-bonded enol with identical stoichiometric characteristics, double-bonded C=C in the range of 1616.88–1501.75 cm^{-1} was selected for the analysis of enol (**Figure 1**). The quantity of xylose was calculated using the amount of enol produced. To depict the performance of hydrolysis reaction, the yield of xylose is defined as the percent of M_d/M_x, in which M_d represents the mass of xylose in hydrolyzate and M_x represents the mass of hemicellulose in RH.

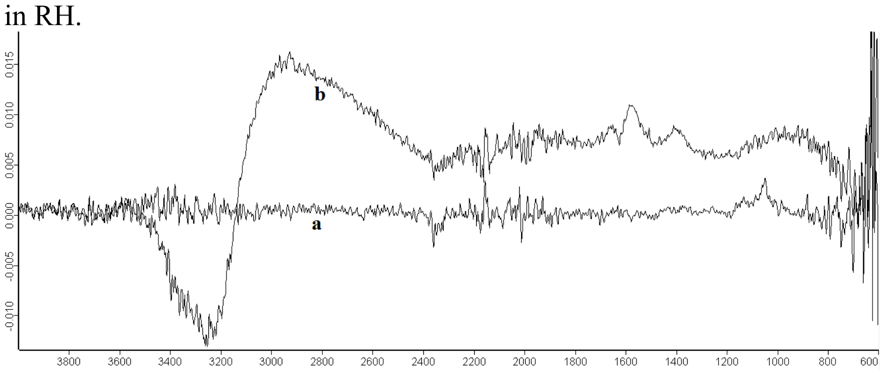

Fig. 1. IR of (a) xylose solution (5 g/L) and (b) xylose in NaON solution (1:1 v/v, 1 mol/L NaOH concentration, heating condition: 100 ºC, 20 min)

3. Results and discussion

Many factors influencing the hydrolysis degree of hemicellulose have been considered, such as acid concentration, hydrolysis temperature, and time. Therefore, the effects of these parameters on the hydrolysis of hemicellulose in RH are discussed first. Optimization is then conducted by orthogonal test.

3.1Hydrolysis temperature

Figure 2 shows the effect of temperature (100–180 ºC) on the yield of xylose under three factors (hydrolysis time, sulfuric acid concentration, and ratio of RH to sulfuric acid) fixed at 15 min, 1 wt% (20 mL), and 1:10, respectively. The yield of xylose increases with an increase in hydrolysis temperature, and reaches the maximum value (53.8%) at 180 ºC. This phenomenon may be attributed to the endothermic character of hemicellulose hydrolysis reaction. Therefore, higher hydrolysis rate with higher temperature. At high temperatures, cellulose hydrolyzes as well. However, the FTIR detector cannot distinguish between xylose and glucose; thus, the curve does not decrease rapidly. At hydrolysis temperature above 160 ºC, the residue turns black. This result indicates that RH has been carbonated. High temperatures convert xylose into other chemicals, such as HMF [9]. When the temperature is below 120 ºC, the yield of xylose is very low. Thus, hydrolysis temperature within the range of 130–150 ºC was selected for the next optimization.

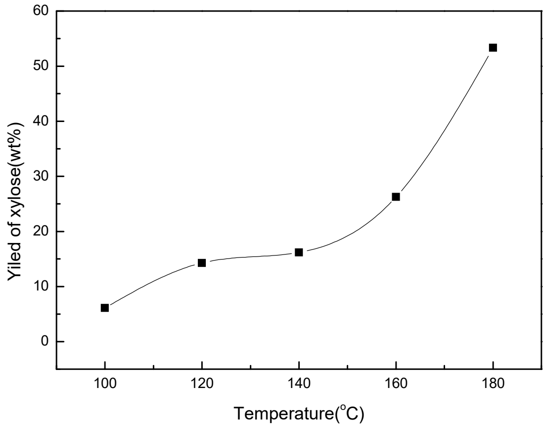

Fig. 2. Effect of temperature on the yield of xylose

3.2Acid concentration

The yield of xylose affected by different concentrations of sulfuric acid (1–5 wt%, 20 mL) is shown in **Figure 3**. With three factors (temperature, time, and ratio of RH to sulfuric acid) fixed at 120 ºC, 15 min, and 1:10, respectively, the yield of xylose increases as a function of sulfuric acid concentration, and reaches the maximum value (96.85%) at a sulfuric acid concentration of 4 wt%. Hemicelluloses cannot be hydrolyzed completely in low-concentration sulfuric acid; thus, the yield of xylose increases with an increase in sulfuric acid concentration. When sulfuric acid concentration reaches 4%, hemicellulose is hydrolyzed completely, and reaches maximum yield. When sulfuric acid concentration exceeds 4 wt%, xylose degrades rapidly, causing a decrease in xylose yield. Thus, sulfuric acid concentration within a range of 2–4 wt% was selected for the next optimum experiment.

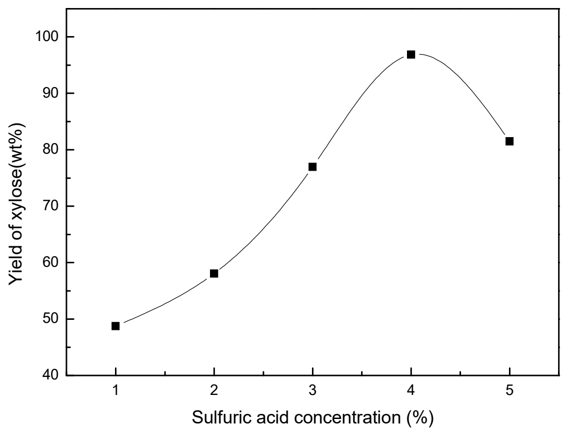

Fig. 3. Effect of sulfuric acid concentration on the yield of xylose

3.3 Hydrolysis time

The yield of xylose affected by different hydrolysis times (5-45 min) is shown in Figure 4. When three factors (temperature, sulfuric acid concentration, and ratio of RH to sulfuric acid) are fixed at 120 ºC, 1 wt% (20 mL), and 1:10, the yield of xylose increases with increase in hydrolysis time, and reaches the maximum value (19%) at hydrolysis time of 25 min. With prolonged time, the yield of xylose is reduced slightly because of xylose decomposition. With energy conservation considered, hydrolysis time within a range of 15–35 min was selected for the next optimum experiment.

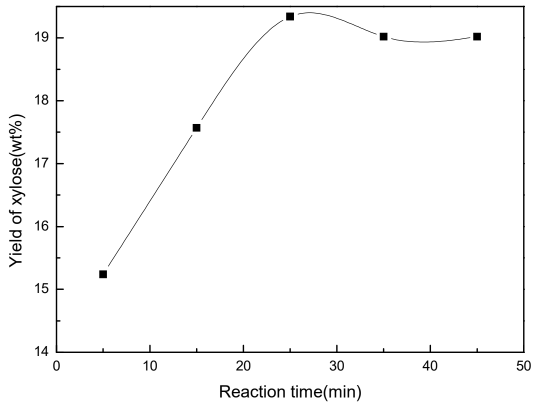

Fig. 4. Effect of reaction time on the yield of xylose

3.4Ratio of RH to sulfuric acid

Figure 5 presents the yield of xylose as a function of the ratio of RH to sulfuric acid (g/mL). When three factors (temperature, sulfuric acid concentration, and hydrolysis time) are fixed at 120 ºC, 1 wt% (20 mL), and 15 min, respectively, the yield of xylose increases to the maximum value (36%) at the point of 1:8. The yield then continually decreases with an increase in ratio with the mass of RH, with a range of 0.5–3 g. This phenomenon is explained by the catalysis of sulfuric acid in the reaction system. An appropriate amount of sulfuric acid favors hemicellulose degradation reaction; however, excessive sulfuric acid causes side reactions, such as xylose dehydration to HMF [9]. Thus, the optimum ratio within a range of 1:7–1:10 was selected.

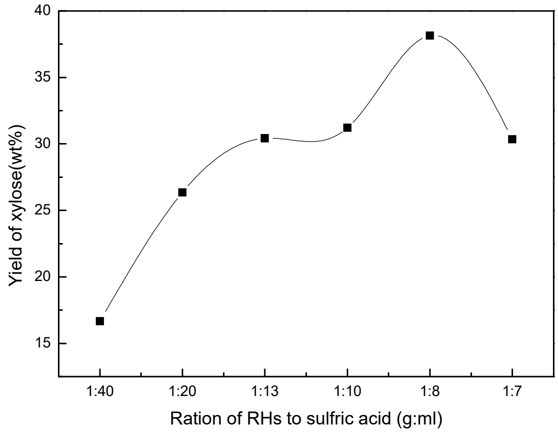

Fig. 5. Effect of ratio on the yield of xylose

3.5Orthogonal test design

The influences of temperature, time, acid concentration, and ratio of RH to sulfuric acid on the yield of xylose were investigated in previous experiments. The results could neither determine the best hydrolysis condition nor demonstrate which factor most influences the yield of xylose; therefore, an orthogonal test was used to address this problem [2, 18]. An orthogonal test is a scientific and systematic method in which a concise test set with fewer test cases is created. The investigated levels of each factor are selected based on experimental results. An orthogonal test with four factors and three levels was designed to screen hydrolysis conditions, including A (hydrolysis temperature), B (hydrolysis time), C (ratio of RH to acid), and D (sulfuric acid concentration), and is listed in **Table 2**. The parameters of an $L_9(3)^4$ orthogonal test are shown in **Table 2**. The total evaluation index was analyzed by statistical method. The final analysis results of the orthogonal test are presented in **Table 3**.

Table 2. Factors and levels for $L_9(3)^4$ orthogonal test

Variables	Levels		
	1	2	3
Hydrolysis temperature (°C)	130	140	150
Hydrolysis time (min)	15	25	35
Sulfuric acid concentration (%)	2	3	4
Ratio of RH to sulfuric acid (g:mL)	1:10	1:8	1:7

Table 3. Analysis of L_9 $(3)^4$ orthogonal test results

No.	(A) Temperature (°C)	(B) Time (min)	(C) Ratio (g/mL)	(D) Concentration (wt%)	Yield of xylose (%)
1	1	1	1	1	9.93
2	1	2	2	2	12.30
3	1	3	3	3	19.35
4	2	1	2	3	24.90
5	2	2	3	1	34.47
6	2	3	1	2	15.82
7	3	1	3	2	46.06
8	3	2	1	3	29.94
9	3	3	2	1	17.84
T1	41.58	80.89	55.69	62.24	
T2	75.19	76.71	55.04	74.18	
T3	93.84	53.01	99.88	74.19	
	A3	B2	C3	D3	

The maximum yield of xylose was obtained at hydrolysis temperature of 150 ºC, sulfuric acid concentration of 4 wt%, hydrolysis time of 25 min, and ratio of RH to sulfuric acid of 1:7. To save on cost of production and time for industrialization, the following should be the optimum technology: A3B2C3D3 (150 ºC, 4 wt%, 25 min, and 1:7). Through acid hydrolysis, hemicellulose in RH was utilized to produce xylose. Under optimum hydrolysis conditions (150 ºC, 25 min, 4 wt%, and 1:7), a yield of 32.96% was obtained.

4. Conclusions

Through acid hydrolysis, hemicelluloses in RH were utilized to produce xylose. Under optimum hydrolysis conditions (150 ºC, 25 min, 4 wt%, and 1:7), hydrolysis yield of xylose is 32.96%. This study is the first to focus on process optimization of microwave-assisted acid hydrolysis of hemicelluloses in RH into xylose. The results under optimized reaction conditions can provide guidance to operations such as reaction temperature and time for microwave-assisted processes. Moreover, as another primary component of RH, the hydrolysis of cellulose in RH for glucose production after hemicellulose hydrolysis is significant. A study on the hydrolysis of cellulose in RH by microwave assistance is currently being undertaken in our laboratory.

Acknowledgments

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