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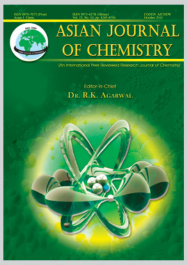

Preparation of Furfural Through the Hydrolysis of Rice Hull Using a Combined Biological and Chemical Approach

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Furfural was prepared through the combined hydrolysis of rice hull with cellulase and SO_4^{2-}-TiO_2 clay solid acid. An optimization analysis of the key factors was carried out with the methods of orthogonal experimentation and response surface analysis. The orthogonal experiment result of enzymolysis showed that the average pentose content was 17.54 g L^{-1} under the following conditions *i.e.*, granularity of raw materials, 120 grit; solid-to-liquid ratio, 1:13; zymohydrolysis temperature, 55 ºC; enzymolysis time, 8 h and amount of enzyme solution, 30 U g^{-1} dry rice hull powder. The response surface analysis of the preparation of furfural with solid acid showed that the yield of furfural was 70.87 % under a reaction temperature of 152 ºC, reaction time of 125 min and 6.1 % of solid acid. Compared with the technology that does not use cellulase hydrolysis, the yield of furfural was increased by 18.41 %.

Key Words: Furfural, Rice hull hydrolysis, Biological and chemical approach, Response surface analysis.

INTRODUCTION

The molecular structure of furfural consists of a furan ring, an aldehyde group, two double bonds and a cyclic ether link in the furan ring[1]. Thus, furfural can undergo hydrogenation, oxidation, chlorination, nitration, condensation and other reactions and it is widely used in food, medical treatments, chemicals and other fields. As crop waste, most rice hulls are disposed off by burning, which not only wastes many resources, but also pollutes the environment. There are abundant hemicelluloses in rice hull. It is hydrolyzed into pentose, which generates furfural through acid catalysis and dehydration[2].

At present, a strong acid is commonly used as a catalyst to prepare furfural, but there exists several problems with this method, such as low yield, long reaction time, too many byproducts and a lot of furfural residue that can not be used as fertilizer but as boiler fuel. Meanwhile, the liquid inorganic acid not only corrodes equipment, but is also challenging to separate from the products. Although acetic acid, modified sulfuric acid, acid salt, basic salt and metal oxides are also used as catalysts, they still negatively impact the environment[3]. In recent years, biodegradation and solid acid catalysis technology have developed rapidly in order to conform to the requirements of "green chemistry". Solid acid is a new type of reusable acid catalyst that is easily separated from liquid[4,5] and bio-enzymatic hydrolysis requires mild conditions, consumes little energy and causes no pollution[6]. Currently, there is still no report about the preparation of furfural through the chemical and biological hydrolysis of rice hull. In this study, furfural is prepared through the degradation of rice hull with the combined catalysis technology with cellulase and catalysts of SO_4^{2-}-TiO_2 clay solid acid. Such disadvantages as high cost, low yield and environmental pollution existing in the traditional preparation methods are thus improved.

EXPERIMENTAL

After air drying, rice hull, collected from villages of Hunan, P.R. China is crushed, screened and set aside; cellulase is obtained from Novozymes (Biotechnology Co. Ltd., China). The SO_4^{2-}-TiO_2 clay solid acid catalyst is prepared with the method described[7]. The main reagents are of analytical purity and the clay is an industrial product.

The test and inspection equipment include a UV-visible spectrophotometer (Waters Corp. America), a SHZ-82 digital water bath thermostatic oscillator (China), a stainless steel reaction kettle with the diameter of φ 80 mm and volume of 200 mL (China), 170 electronic balance (Sartorius, Germany), TDL-40B centrifuge (Anke, America).

Pretreatment of rice hull: Dried rice hull powder with granularity of 30, 60, 90, 120 and 150 grit were sieved. After that, the powder was soaked with diluted hydrochloric acid at a solid-to-liquid ratio of 1:10 and concentration of 5 % for 1 h and then it was filtered. After the residue was washed with water, it was dried at 80 ºC until constant moisture content was obtained and then was ready for use.

Enzymolysis of rice hull: A certain amount of enzyme solution was added to 5 g of pretreated rice hull powder and the solid-to-liquid ratio was adjusted with distilled water. The reaction was operated in the water bath oscillator at the set temperature for some time and then the reaction solution was centrifuged. The amount of pentose in the centrifugal liquid was determined.

Synthesis of furfural: The rice hull degraded by enzyme and its residue, as well as a certain amount of solid acid, were added to the magnetic stirred autoclave to undergo a heating reaction, during which various reaction factors were strictly controlled. At the end of the reaction, the autoclave was quickly placed in ice water to be cooled to room temperature and was detected after it was filtered. At the same time, comparative tests were carried out by directly hydrolyzing rice hull powder with solid acid.

Detection: Pentose in rice hull hydrolyzate was detected with the method using 3,5-dinitrosalicylic acid reagent. The concentration of furfural in the received liquid was determined with a UV-visible spectrophotometer and the mass and yield of the obtained furfural were calculated according eqns. 1 and 2, below.

The pentose in the reaction solution

= Quality of pentose in reaction solution/quality of reaction solution × 100 % (1)

Furfural yield = The actual quality of furfural in the reaction solution/the theory quality of rice hull × 100 % (2)

RESULTS AND DISCUSSION

Determination of the conditions of enzymatic degradation of rice hull: The single-factor experiment was conducted to study the effect of various factors-such as material granularity, solid-to-liquid ratio, hydrolysis temperature, enzyme dosage and hydrolysis time-on the content of pentose to determine the optimal conditions for enzymatic hydrolysis of rice hull.

Mechanical grinding can damage the binding layer of lignin, hemicellulose and cellulose; reduce the degree of crystallinity of the three and change their crystal structures partly, which can facilitate the rupture of glycosidic bond and the degradation of rice hull powder[8]. Meanwhile, smaller granularity increases the area of contact surface with the enzyme solution and accelerates the degradation.

A comparative test was carried out with pretreated rice hull powder with grits of 30, 60, 90, 120 and 150 under the same conditions and the results are shown in Table-1. The pentose contents with grits of 120 and 150 were similarly as high as 16.33 and 16.90 g L^{-1}, respectively. According to the experimental data and the cost of rice hull crushing, the granularity of rice hull was determined as 120 grit under the conditions of this experiment.

TABLE-1
EFFECTS OF REACTION CONDITIONS
ON THE CONTENT OF PENTOSE

Item	Reaction condition	Pentose content (g L^{-1})
Material granularity (grit)	30	9.86
	60	12.76
	90	14.92
	120	16.33
	150	16.90
Solid-to-liquid ratio	1: 19	8.87
	1:17	13.88
	1:15	16.22
	1:13	16.88
	1:11	17.33
Enzymolysis temperature (ºC)	45	10.62
	50	13.95
	55	17. 33
	60	16.02
	65	14.94
Enzymolysis time (h)	4	12.12
	6	15.02
	8	16.83
	10	15.05
	12	14.38
Enzyme dosage (U g^{-1})	20	6. 53
	25	9.92
	30	16.98
	35	17.19
	40	17.27

The solid-to-liquid ratio plays an important role in the reaction. The yield of pentose in the systems with different solid-to-liquid ratios-under the conditions of the reaction temperature of 55 ºC, the amount of enzyme solution of 30 U g^{-1} dry rice hull powder, enzymolysis time of 8 h and the granularity of rice hull powder of 120 grit-is shown in Table-1. The yield increased with the increase of solid-to-liquid ratio. The yield of pentose was the greatest with the solid-to-liquid ratio of 1:13; the yield increased as the solid-to-liquid ratio further increased, but with a slow growth rate. This would mean that the change of solid-to-liquid ratio is actually that of the concentration of enzyme in the system and when the solid-to-liquid ratio was high, the concentration of enzyme solution was also high; excess enzyme solution could not participate in the reaction, so the increase of pentose yield slowed down. The activity of the reaction system is related to enzymolysis temperature. The reaction was operated in the water bath thermostatic oscillator at different temperatures for 8 h with the solid-to-liquid ratio of 1:13, the amount of enzyme solution of 30 U g^{-1} dry hull powder and rice hull powder with the granularity of 120 grit. The result of this reaction is shown in Table-1. When the temperature was 45-55 ºC, the amount of pentose in the enzyme solution gradually increased with the increase in temperature and the yield reached 17.33 g L^{-1} at 55 ºC; when the temperature was higher than 55 ºC, the amount of pentose tended to decrease. This was because the increase in temperature induced the increase in activation energy of the reaction system and the reaction yield, but the enzyme was inactivated when the temperature was too high.

The content of pentose in the reaction system is related to enzymolysis time. Under the conditions of the reaction temperature of 55 ºC, the amount of enzyme solution of 30 U g^{-1} dry rice hull powder, the solid-to-liquid ratio of 1:13 and the granularity of 120 grit, the content of pentose in the reaction system with different enzymolysis times is shown in Table-1. The content of pentose gradually increased as the reaction time increased; however, when the reaction time exceeded 8 h, the yield of pentose was significantly reduced. This was because the amount of by-products in the reaction system was gradually increased as the enzymolysis time increased, which resulted in the decomposition of pentose and the increase of by-products.

The amount of enzyme solution is directly related to hydrolysis speed, the content of pentose, production cost and other problems. The pretreated rice hull powder with the granularity of 120 grit, the solid-to-liquid ratio of 1:13 and different amounts of enzyme solution reacted in the water bath thermostatic oscillator at 55 ºC for 8 h and the results of this experiment are shown in Table-1. When the amount of enzyme solution was less than 30 U g^{-1} dry rice hull powder, the amount of released pentose increased significantly. But when the amount of enzyme solution exceeded this value, the release of pentose increased slowly. This was because the increase in enzyme solution actually led to the increase of the contact area between the enzyme solution and the rice hull powder. When the contact area between the enzyme solution and the rice hull powder reached the peak value, the excess enzyme solution could not participate in the reaction, so the release of pentose increased slowly.

Under the above conditions, the optimal technology was obtained through the L_{16} (4^5) multi-factor orthogonal experiment: raw material granularity of 120 grit, the solid-to-liquid ratio of 1:13, hydrolysis temperature of 55 ºC, vibrating reaction time of 8 h and the amount of enzyme solution of 30 U g^{-1} dry rice hull powder. Three duplicate tests were carried out in these conditions and the average content of pentose was 17.69 g L^{-1}.

Optimization of the technological conditions of furfural synthesis: Furfural was synthesized with the hydrolysate and its residue, with solid acid as the catalyst. Based on the exploratory experiments, the response surface experiment combination of three factors and three levels in Table-2 were designed with three factors-hydrolysis temperature, hydrolysis time, the amount of solid acid-as independent variables.

TABLE-2
LEVEL AND CODE OF VARIABLES CHOSEN FOR RSM DESIGN

Name	Code	-1	0	1
		Level	Level	Level
Hydrolysis temp. (ºC)	X_1	140	150	170
Hydrolysis time (h)	X_2	90	120	150
Solid acid dosage (%)	X_3	3.0	5.0	7.0

Based on the requirement of the response surface experimental design, 17 experiments were carried out with 5 replicates of the center.

A regression analysis of the test data was conducted with the software of Design-Expert 7.1.3. The result of this analysis is shown in Table-3 and a quadratic regression eqn. 3 was obtained.

$$Y = 70.98 - 3.00X_1 + 2.57X_2 + 2.07X_3 - 12.63X_1^2 - 2.47X_2^2 - 3.67X_3^2 \quad (3)$$

Table-3 showed that X_1, X_3 and all three factors' quadratic terms had significant ($p < 0.05$) impacts on furfural yield. In addition, all quadratic terms were negative, indicating the existence of optimum condition. The quadratic terms coefficient of the quadratic regression equation was negative, suggesting the equation has the largest value.

In order to simplify the explanation regarding furfural yield and those predictors, the response surfaces 3D are used, as shown in Figs. 1-3.

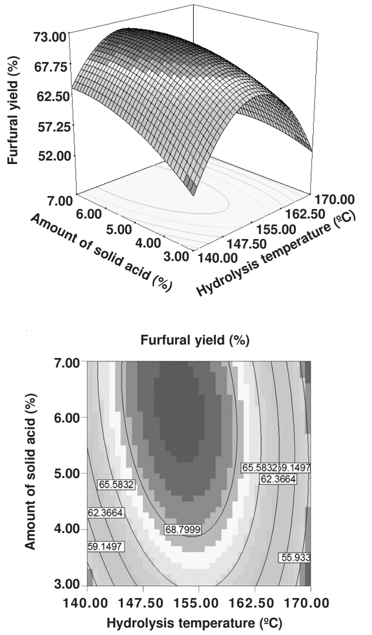

Fig. 1. Effects of solid acid amount and hydrolysis temperature on the furfural yield

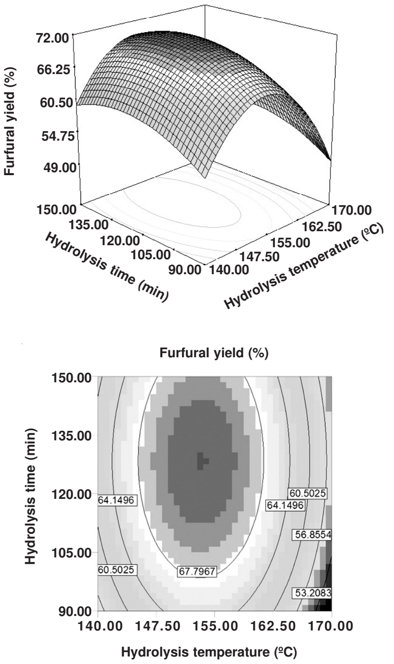

Fig. 2. Effects of solid hydrolysis time and temperature on the furfural yield

TABLE-3
ANALYSIS OF VARIANCE FOR REGRESSION MODEL

Source	Sum of squares	Mean squares	F value	*p*-Value	Significant
Model	993.27	110.36	24.23	0.0002	**
X_1	72.12	72.12	15.83	0.0053	**
X_2	52.69	52.69	11.56	0.0114	–
X_3	34.16	34.16	7.50	0.029	*
$X_1 X_2$	23.09	23.09	5.07	0.0591	–
$X_1 X_3$	9.025E-3	9.025E-3	1.981E-3	0.9657	–
$X_2 X_3$	11.76	11.76	2.58	0.1521	–
X_1^2	671.76	671.76	147.46	$<$0.0001	**
X_2^2	25.66	25.66	5.63	0.0494	*
X_3^2	56.82	56.82	12.47	0.0096	**
Residual	31.89	4.56	–	–	–
Lack of fit	8.63	2.88	0.49	0.7051	–
Pure error	23.26	5.81	–	–	–

R^2 = 0.9689, *Significant, **Very significant.

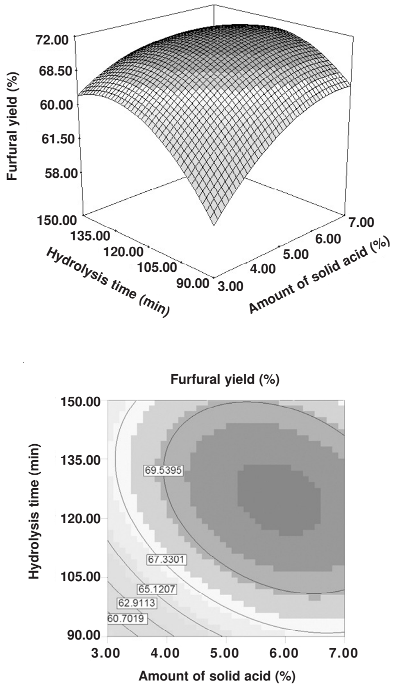

Fig. 3. Effects of hydrolysis time and amount of solid acid on the furfural yield

Fig. 1 is the response surface figure of the interaction between the amount of solid acid and hydrolysis temperature. According to Fig. 1, the yield of furfural increased with the increase of amount of solid acid because the increase of the H^+ concentration in the reaction system accelerated the reaction. Under the condition of a fixed amount of solid acid, the yield of furfural was first quickly increased with the increase of temperature and then decreased subsequently. This was because the activity of the reaction system was raised at increased temperatures, which facilitate the generation of furfural. However, at excessively high temperatures, furfural is further hydrolyzed into acetylpropionic acid and acetic acid[9]. Thus, the phenomenon that the yield of furfural decreased at high temperatures was observed. Under this experimental condition, the yield of furfural was maximized when the amount of solid acid was approximately 6 % and the temperature was about 155 ºC.

Fig. 2 is the response surface figure of the interaction between reaction time and reaction temperature. The figure demonstrates that the furfural yield gradually increased with the increase of reaction time and temperature. The yield reached its maximum value at about 150 ºC and 120 min and decreased sharply subsequently. This phenomenon can be explained as follows. Increases in reaction temperature and time can promote the progress of the dehydration reaction; as the reaction continues, the amount of by-products in the reaction system will gradually increase, thus inhibiting the reaction[10]. Then, with the increase in reaction temperature, the decomposition of furfural at high temperature increases. In conclusion, higher temperature and longer reaction time will decrease the yield of furfural.

Fig. 3 shows the influence of the interaction between reaction time and the amount of solid acid on the yield of furfural. With a fixed amount of solid acid, the yield of furfural increased sharply and then decreased slowly as the reaction time continued. During the fixed reaction time, the yield of furfural showed the same characteristics and even revealed a decreasing trend with the increase in solid acid amount. This is explained by the fact that the increase of the solid acid amount can increase the synthesis speed of furfural and excessively high concentrations of solid acid can accelerate the polymerization, condensation and resinification of pentose and furfural[11]; this affects the yield of furfural. Under the conditions of this experiment *i.e.*, the reaction time of 125 min and the solid acid amount of approximately 6.1 %-the yield of furfural might be maximized.

Optimization analysis of the parameters that influence the yield of furfural was conducted with multiple regression models. The obtained optimal technological conditions were as follows: reaction temperature of 152.43 ºC, reaction time of 124.54 min and 6.1 % amount of solid acid. Under the conditions above, the yield of furfural was 72.10 %. A verification test was conducted three times under the conditions of reaction temperature, 152 ºC; reaction time, 125 min and the amount of solid acid, 6.1 %. The mean value for the furfural yield of these three experimental results was 70.87 %, which was close to the predictive value and indicated that the established multiple regression model accurately predicts the test results. Under the same conditions, the yield of furfural using technology without enzymolysis was only 62.46 %, an apparently low value. Fig. 4 shows the contrast between the predictive value of the model and the true value; the R square is 0.9689. The data points were basically distributed in a straight line, which indicates that the established model displays excellent predictability.

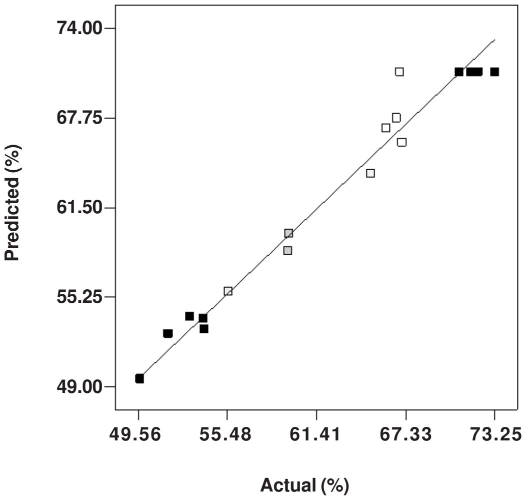

Fig. 4. Predicted *versus* actual models

Conclusion

When rice hull was hydrolyzed with cellulase, the average content of pentose was 17.69 g L^{-1} with raw material granularity of 120 grit, a solid-to-liquid ratio of 1:13, enzymolysis temperature of 55 ºC, shaking reaction time of 8 h and the amount of enzyme solutions of 30 U g^{-1} dried rice hull powder. The yield of furfural prepared through the hydrolysis of rice hull can be improved though enzymolysis.

The optimum technological conditions of the preparation of furfural by hydrolyzate and its residue with the catalyst of SO_4^{2-}-TiO_2 clay solid acid are as follows: reaction temperature, 152 ºC; reaction time, 125 min and 6.1 % amount of solid acid. Under such conditions, the yield of furfural is 70.87 %, which is 18.41 % more than that obtained under the same technological conditions without enzymolysis.

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