



Furfural production from rice husk using sulfuric acid and a solid acid catalyst through a two-stage process

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ABSTRACT

This study aimed to optimize the conditions for furfural production from rice husk via a two-stage process: acid hydrolysis followed by dehydration using an orthogonal test design and response surface methodology, respectively. Orthogonal test design was utilized in the hydrolysis step; optimum conditions were as follows: 2.5% sulfuric acid (mass fraction), 110 °C reaction temperature, sulfuric acid to rice husk (*L/S*) ratio of 8 (g/mL), and a reaction time of 3 h. According to the Box–Behnken design, the temperature, amount of catalyst, extractant volume, and reaction time were chosen as four important factors with three levels for the dehydration step. Conditions were further optimized by response surface analysis. The results showed that the optimal conditions were 177 °C, 120 mL extractant volume, 2.1 g of catalyst, and a reaction time of 4.8 h. Under the optimal conditions, the furfural yield reached 8.9%, which is consistent with the estimated value, 8.97%.

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1. Introduction

Biomass is one of the world's most important renewable energy sources. It has been reported that the sustainable production of 1.3 Pg of biomass per year can be achieved without significant changes in agricultural practices or food supplies.^{1–3} Since annually renewable biomass contains 75% carbohydrates, converting these carbohydrates into organic chemicals to ultimately replace those derived from petrochemical resources is a major challenge for green chemistry.⁴

Furfural is produced from the hemicellulosic fraction of biomass,⁵ and has been identified as one of the top 30 high-value, bio-based chemicals. Furfural is a versatile furan platform compound comprised of a heteroaromatic furan ring and an aldehyde functional group.⁶ Commercial furfural production is currently carried out by acid catalytic dehydration of pentosan-containing lignocellulosic materials in a batch or continuous reactor. Lignocellulose materials from agricultural waste that are rich in pentosans, such as rice husks, oat hulls, cottonseed hull bran, almond husks, and bagasse, have generally been preferred for the commercial production of furfural.^{7–13} Rice husk is a renewable, cheap, and widely available biomass. The majority of rice husk is burnt in China, resulting in severe environmental pollution. To enhance the value of rice husk and to decrease pollution, new indus-

trial uses of rice husk should be developed. As a major source of carbohydrates, including cellulose, hemicellulose and lignin, rice husk can be used directly for furfural production, thereby greatly reducing the production cost.

Furfural can be produced through a one- or two-stage process.^{14–16} In the one-stage process, pentosan is hydrolyzed to xylose and dehydrated to furfural within the same reactor. The disadvantage of this method is that it gives a low furfural yield (0.7–3.3%, mass fraction).¹⁴ In the two-stage process, hydrolysis and dehydration reactions occur in separate reactors. There are two advantages of the two-stage process: a higher furfural yield, and utilization of the solid residue for the production of cellulose, glucose, and ethanol via fermentation.¹⁵ Homogenous acids, such as sulfuric acid and phosphoric acid, are widely-used catalysts for the conversion of lignocellulosic materials to furfural.^{17,18} However, this results in several problems, including difficulties in acid recovery, complicated separation of products, and environmental pollution. Solid superacid is a type of acid with many advantages over a liquid acid. For example, a solid superacid is easy to separate from a reaction mixture and easy to regenerate and reuse. Due to these advantages, a number of studies have focused on the solid acid-catalyzed production of furfural from lignocelluloses.^{19,20} Due to the high pentosan content of rice husk and the employment of functionalized solid acid catalysts, this study aimed to optimize the conditions in both the hydrolysis and dehydration stages for the efficient production of furfural using SBA-15, a solid superacid with high catalytic activity, by an orthogonal test design and response surface methodology (RSM).

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2. Results and discussion

2.1. Optimization of the hydrolysis process by orthogonal test design

Independent variables with three variation levels are listed in Table 1: A (reaction temperature), B (sulfuric acid concentration), C (reaction time), and D (L/S ratio). In the present study, all selected factors were examined using an orthogonal $L_9(3)^4$ test design. The total evaluation index was analyzed by statistical methods.

Results of the orthogonal test are presented in Table 2. According to the *R* value, the factors affecting the hydrolysis rate are listed in decreasing order as follows: $C > B > A > D$. The maximum hydrolysis rate was obtained when the factors were A2B2C3D1 (110 °C, 2.5%, 4 h, and 1:8), respectively. According to the *R* value, hydrolysis time was the most important determinant of hydrolysis rate. To reduce production costs and avoid side reactions, the optimum parameters were: A2B2C2D1 (110 °C, 2.5%, 3 h, and 1:8). After confirmation, a yield of 97.89% was obtained.

2.2. Optimization of the dehydration process by RSM

The statistical treatment combinations of the test variables, along with the measured response values, are summarized in Table 3, and expressed as the yield of furfural corresponding to each combination. The application of RSM yielded the following regression equation, which indicated an empirical relationship between furfural yield and the test variable in coded units:

$$Y = 8.59 - 0.414167X_1 + 1.12833X_2 + 0.401667X_3 + 0.569167X_4 - 2.21208X_1^2 - 1.52333X_2^2 - 1.03833X_3^2 - 0.949583X_4^2 - 0.425X_1X_2 - 0.3775X_1X_3 - 0.32X_1X_4 - 0.985X_2X_3 + 0.21X_2X_4 + 0.3125X_3X_4, \quad (1)$$

where *Y* was the response, and X_1 , X_2 , X_3 , and X_4 were the coded values of temperature, solvent volume, catalyst amount, and reaction time, respectively. The coefficients above Eq. 1 were calculated using RSM, and their values are listed along with the parameter estimates in Table 4.

The significance of each coefficient was determined using Student's *t*-test and *P*-values. The *P*-values were used to determine the significance of each coefficient, which, in turn was necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of the *t*-value and the smaller the *P*-value, the more significant the corresponding coefficient was. From Table 4, it is evident that the first-order main effect of solvent volume (X_2) was highly significant, as indicated by its *P*-value. This suggested that the solvent volume was directly related to the production of furfural. The quadratic main effects of temperature, solvent volume, catalyst amount, and time were also significant, with *P*-values of 0.000, 0.000, 0.002, and 0.004, respectively.

The three-dimensional response surface plots represent the regression equation, which were drawn to illustrate the main and interactive effects of the independent variables on the dependent variable (Figs. 1–6). The maximum predicted values were

Table 1
Variables and levels used according to $L_9(3)$ 4 orthogonal experimental design

Variables	Symbol	Levels		
		1	2	3
Reaction temperature (°C)	A	100	110	120
Sulfuric acid concentration (% mass fraction)	B	2	2.5	3
Reaction time (h)	C	2	3	4
L/S ratio (mL/g)	D	8	10	12

Table 2
Experimental results of rice husk hydrolysis

Experiment	Coded level				The yield of xylose (%)
	A	B	C	D	
1	1	1	1	1	76.02
2	1	2	2	2	82.18
3	1	3	3	3	87.42
4	2	1	2	3	80.24
5	2	2	3	1	97.04
6	2	3	1	2	89.94
7	3	1	3	2	87.97
8	3	2	1	3	88.54
9	3	3	2	1	73.18
K1	81.873	81.410	84.833	82.080	
K2	89.073	89.253	78.533	86.697	
K3	83.230	83.513	90.810	85.400	
R	7.200	7.843	12.277	4.617	

Table 3
Result and design table of Box–Behnken

Trial	x_1	x_2	x_3	x_4	Yield (%)
1	A	B	C	D	The yield of furfural (%)
2	0	1	1	0	6.33
3	0	0	1	1	8.30
4	1	0	1	0	4.62
5	-1	1	0	0	6.27
6	0	0	0	0	8.65
7	0	-1	-1	0	3.72
8	1	0	0	1	4.86
9	0	-1	0	-1	4.18
10	1	1	0	0	5.65
11	-1	-1	0	0	3.64
12	-1	0	0	-1	5.32
13	0	0	-1	1	7.00
14	0	0	0	0	8.62
15	0	-1	0	1	4.41
16	-1	0	1	0	6.53
17	1	0	0	-1	4.40
18	0	-1	1	0	6.56
19	-1	0	0	1	7.06
20	1	0	-1	0	4.51
21	0	0	1	-1	6.01
22	1	-1	0	0	4.72
23	-1	0	-1	0	4.91
24	0	1	0	-1	7.01
25	0	0	0	0	8.50
26	0	1	0	1	8.08
27	0	0	-1	-1	5.96

Table 4
Significance of regression for furfural yield

Variables	Coefficient	Stand error	<i>T</i>	<i>P</i> value
Constant	8.59	0.3529	24.344	0.000
X1	-0.414167	0.1764	-2.348	0.037
X2	1.12833	0.1764	6.395	0.000
X3	0.401667	0.1764	2.277	0.042
X4	0.569167	0.1764	3.226	0.007
X1*X1	-2.21208	0.2646	-8.359	0.000
X2*X2	-1.52333	0.2646	-5.756	0.000
X3*X3	-1.03833	0.2646	-3.924	0.002
X4*X4	-0.949583	0.2646	-3.588	0.004
X1*X2	-0.425	0.3056	-1.391	0.190
X1*X3	-0.3775	0.3056	-1.235	0.240
X1*X4	-0.32	0.3056	-1.047	0.316
X2*X3	-0.985	0.3056	-3.223	0.007
X2*X4	0.21	0.3056	0.687	0.505
X3*X4	0.3125	0.3056	1.023	0.327

indicated by the surface confined in the smallest ellipse in the contour diagram. Elliptical contours were obtained when there was a perfect interaction between the independent variables.²¹ These

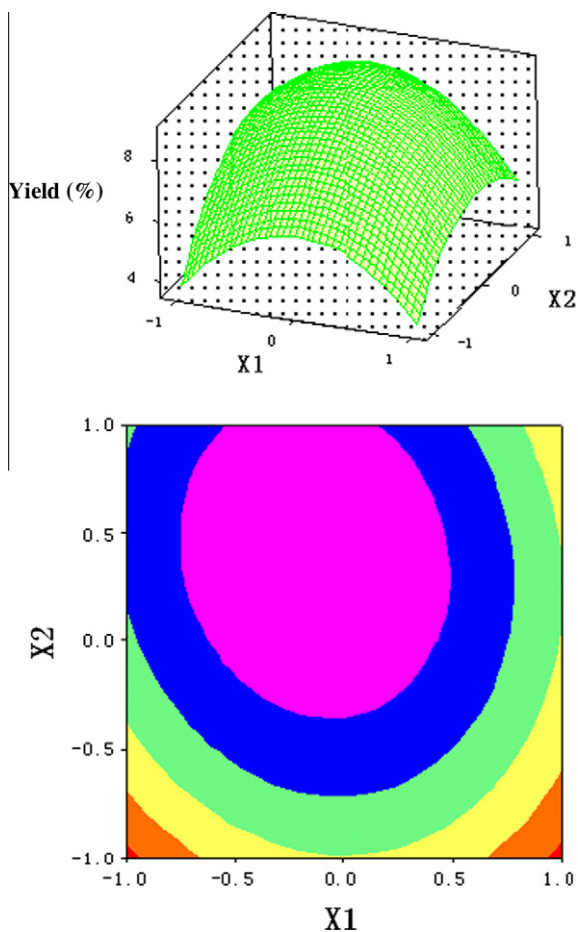


Figure 1. 3D graphic surface optimization of furfural yield versus temperature and amount of solvent.

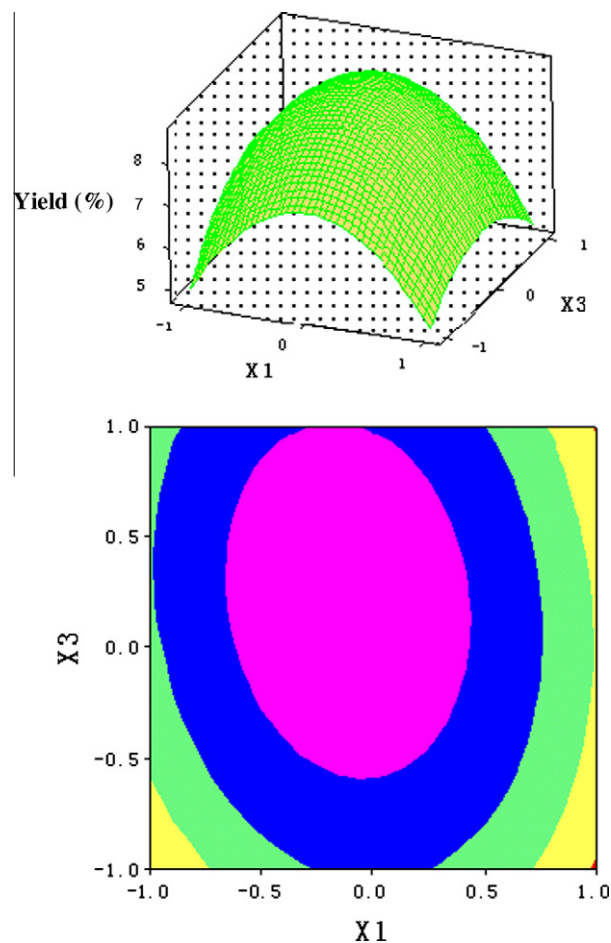


Figure 2. 3D graphic surface optimization of furfural yield versus temperature and amount of catalyst.

graphs were drawn by imposing two other variables at the zero levels.

There was a relative significant interaction between every two variables, and a maximum predicted yield, indicated by the surface confined in the smallest ellipse in the contour diagrams. The amount of solvent played an important role in the experiments, as was evident from its *P*-value. We observed a quadratic effect of solvent amount on the response (Figs. 1, 4, and 5), which suggested that an increased amount of solvent may not be able to boost the yield of furfural under the experimental conditions. As shown in Figures 1–3, the reaction temperature showed similar results to that of the solvent amount. At temperatures above 180 °C, the yield of furfural began to decrease. Although high temperatures could accelerate the rate of conversion of carbohydrates to furfural, unwanted side reactions may also build simultaneously. Theoretically, a higher amount of catalyst should obtain a higher yield of furfural. However, it was determined that the yield of furfural decreased after a certain ratio was reached due to this factor (Figs. 2, 4, and 6). Reaction time exhibited a relatively significant interaction with other variables. The temperature, solvent amount, and amount of catalyst significantly affected the time required for the overall reaction. As shown in Figures 3, 5, and 6, there was an optimal conversion process time. This suggests that if hydrolysis continued for too long, the yield would decrease again as the result of side reactions of furfural.

According to the Minitab software response optimizer analysis, the maximum estimate of *Y* was 8.97%. The values of the four main factors were: 177 °C reaction temperature, 120 mL extraction

dosage, 2.1 g of catalyst, and a 4.8 h reaction time. Based on the results from the verification experiment, an actual furfural yield of 8.9% was achieved. These data show that the predicted and actual values were similar, and so indicated that the experimental model has significance. Additional results regarding the yield of furfural from alternate substrates are shown in Table 5.

3. Conclusions

A two-stage process that consisted of hydrolysis followed by dehydration was used for the production of furfural. In the first step, the optimum conditions were 2.5% sulfuric acid and an *L/S* ratio of 8 mL/g for 3 h. The maximum yield of xylose was 97.89%. In the second step, we concluded that the effect of solvent amount was highly significant for furfural production. The quadratic main effects of temperature, reaction time, and catalyst amount were also significant. By employing the optimum experimental conditions, a furfural yield of 8.9% was achieved.

4. Experimental

4.1. Materials

Rice husk was obtained from Zhengzhou City (China), washed thoroughly with distilled water to remove adhering soil and dust, and dried at 105 °C for over 12 h and porphyzied to 60 mesh before use. The hemicellulose, cellulose, lignin, and 'other' contents

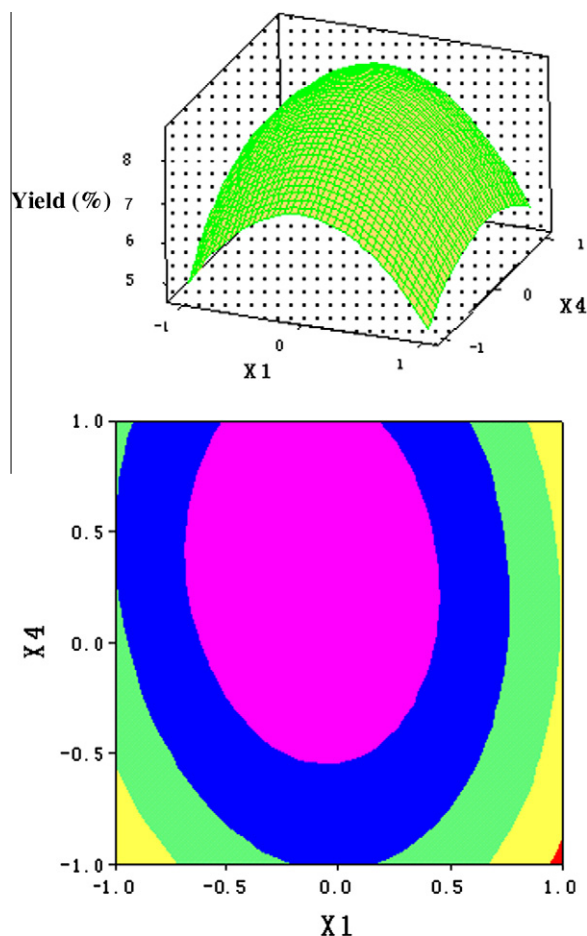


Figure 3. 3D graphic surface optimization of furfural yield versus temperature and reaction time.

(e.g., ash) of dry rice husk were 18.5%, 35.8%, 25.3%, and 20.4%, respectively.

4.2. Experimental process

4.2.1. Synthesis of functionalized solid acid catalyst SBA-15

The procedure for solid acid catalyst synthesis was as described previously.²² Mercaptopropyltrimethoxysilane (MPTMS; Sigma Aldrich) was added as the sulfonic group precursor. The molar composition of the mixture for 4 g of pluronic 123 (P123) was: 0.0328 tetraethoxysilane (TEOS), 0.0082 MPTMS, 0.0738 H₂O₂, 0.24 HCl, and 6.67 H₂O. The MPTMS/(TEOS + MPTMS) ratio was set to 0.2. The silica precursor was hydrolyzed at 40 °C for 20 h. These materials were prepared at an aging temperature of 100 °C for 24 h. After solvent extraction, the wet material was suspended in 1 M sulfuric acid for 2 h at room temperature. The solid product, SBA-SO₃H, was re-filtered, washed with ethanol, and dried.

4.2.2. Furfural production by a two-stage process

The scheme of the two furfural production reactions is shown in Figure 7. For acid hydrolysis, rice husk and dilute sulfuric acid were mixed into a 100 mL stainless steel autoclave with a Teflon inner lining. The autoclave was closed and placed into a pre-heated oven. The autoclave was kept in the oven for a given period of time to hydrolyze the xylan in the rice husk. After the reaction, the autoclave was removed and allowed to cool by natural convection. The solid rice husk residue and liquid were then filtered. For dehydration, the collected filtrate (50 mL) and functionalized solid acid

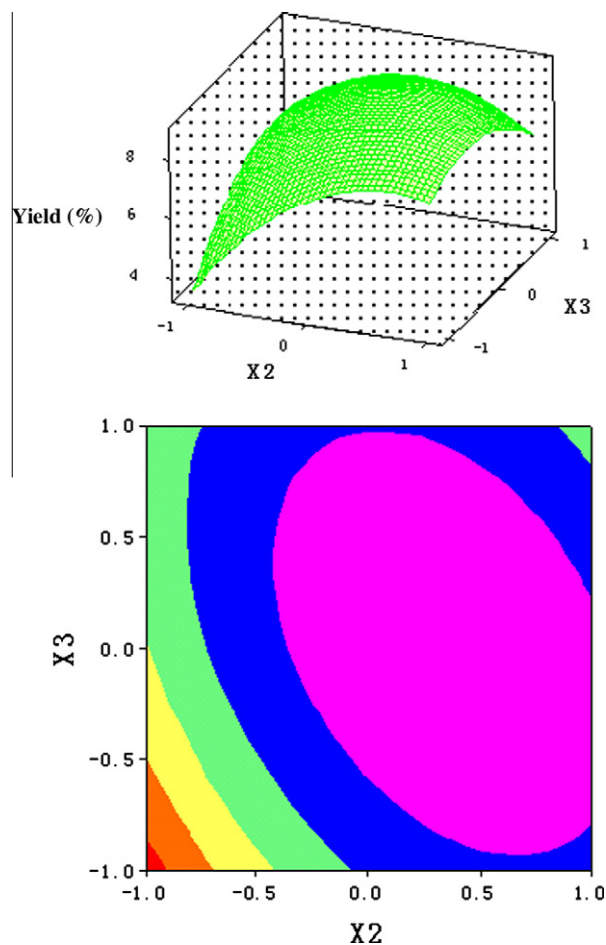


Figure 4. 3D graphic surface optimization of furfural yield versus amount of catalyst and solvent.

catalyst, SBA-15 (1–3 g), were placed in the autoclave, and toluene (50–150 mL), as a mixed solvent, was added simultaneously. The autoclave was closed and then heated. After the reaction, the residue was filtered and the liquid was collected for the determination of furfural yield.

4.3. Optimization of furfural production

4.3.1. Optimization of hydrolysis using an orthogonal test design

Factors such as reaction temperature, acid concentration, reaction time, and *L/S* ratio can greatly influence the degree of xylan hydrolysis. Therefore, the influence of these four factors on hydrolysis was investigated. However, single-factor experiments neither determined the optimal combination of the four factors, nor did they determine which factor had the greatest influence on xylose yield. Therefore, an orthogonal test design was employed to solve this problem. Independent variables with three variation levels, A (reaction temperature), B (sulfuric acid concentration), C (reaction time), and D (*L/S* ratio) are listed in Table 1. In the present study, all selected factors were examined using an orthogonal L₉(3)⁴ test design. The total evaluation index was analyzed by statistical methods.

4.3.2. Optimization of the dehydration process by RSM

RSM is an efficient tool for establishing the relationship of variables of interest (at least two) with the obtained responses. The experimental data were fitted to a smooth curve, which was

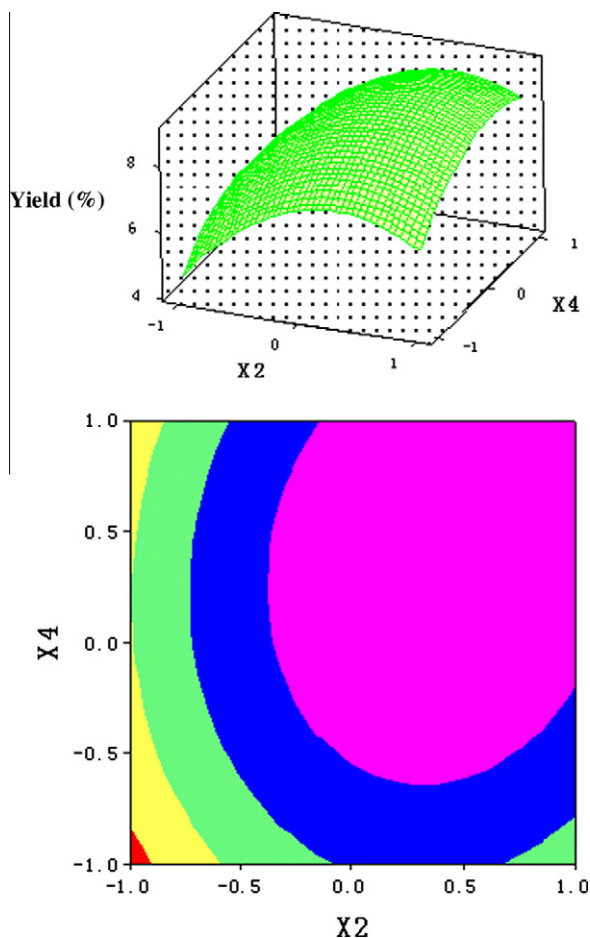


Figure 5. 3D graphic surface optimization of furfural yield versus time and amount of solvent.

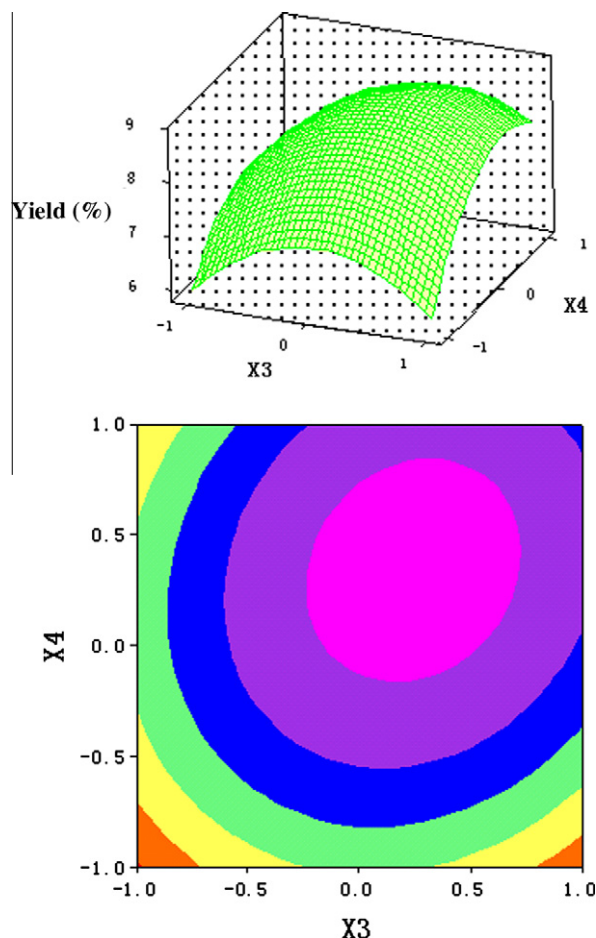


Figure 6. 3D graphic surface optimization of furfural yield versus time and amount of catalyst.

plotted by calculating the specific predicted response. Therefore, RSM established a relationship between the variables and responses more professionally than did traditional design. A Box–Behnken experimental design, with four variables, was used to study the response pattern and to determine the optimum combination of variables. The range of each parameter was: temperature (X_1) 160–200 °C (central value = 180 °C), solvent volume (X_2) 50–150 mL (central value = 100 mL), amount of catalyst (X_3) 1–3 g (central value = 2 g), and time (X_4) 2–6 h (central value = 4 h). For statistical calculations, the variables were coded according to Eq. 2:

$$x_i = (X_i - X_0) / \Delta X_i \quad i = 1, 2, 3, 4 \quad (2)$$

where x_i was the coded value of the independent variable, X_i was the real value of the independent variable, X_0 was the real value of the independent variable on the center point, and ΔX_i was the step-change value.

The furfural yield was taken as the dependent variables or response, Y_i . The proposed model for the response is:

$$Y_i = k_0 + k_1X_1 + k_2X_2 + k_3X_3 + k_4X_4 + k_{11}X_1^2 + k_{22}X_2^2 + k_{33}X_3^2 + k_{44}X_4^2 + k_{12}X_1X_2 + k_{13}X_1X_3 + k_{14}X_1X_4 + k_{23}X_2X_3 + k_{24}X_2X_4 + k_{34}X_3X_4, \quad (3)$$

where Y_i was predicted response, k_0 was the offset term, k_1 , k_2 and k_3 were linear effect terms, k_{11} , k_{22} , k_{33} , and k_{44} were squared effects, and k_{12} , k_{13} , k_{14} , k_{23} , k_{24} , and k_{34} were interaction effects. The behavior of the surface was investigated for the response

Table 5

Comparison of furfural yield produced from various substrates using a two-stage process

Raw material	Investigator	Yield based on weight of raw material (%)
Rice hull	Mansilla et al. ¹⁴	~10.5
Hemicellulose (xylose) of bagasse	Punsuvon et al. ¹⁵	~10.3
Hemicellulose of dPPF	Wiboon Riansangawong et al. ¹⁶	17.34
Rice husk	This study	8.9

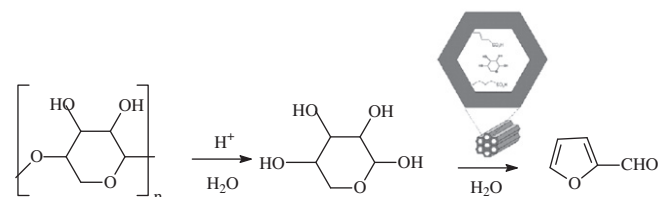


Figure 7. Hydrolysis of rice husk using solid acid catalyst by two-stage process.

function (Y_i), using the regression Eq. 3. The fitted polynomial equation was expressed as a surface plot to visualize the relationship between the response and experimental levels of each factor, and to

deduce the optimum conditions. The computer software used for this study was Minitab 15.

4.4. Analysis

Sugar content was determined by high-performance liquid chromatography under the following conditions: column Aminex HPX-87H (BIO-RAD), eluent sulfuric acid (0.01 N), 65 °C temperature, flow rate of 0.6 mL/min, and detection by the differential refractometer, WATERS 410. Samples (20 µL) were injected into an auto-sampler. In order to depict the degree of the hydrolysis reaction, the yield of xylose was defined as:

$$\text{The yield of xylose} = \frac{M_d}{M_x} \times 100\%,$$

in which M_d represents the mass of xylose in the hydrolyzate, and M_x represents the mass of xylan in the rice husk.

Furfural content was then analyzed by gas chromatography (GC-FID). The flow rate of helium was 1.2 mL/min. Injection and detection port temperatures were 230 °C and 250 °C, respectively. The injection volume was 1 µL. The initial oven temperature was 70 °C for 1 min, followed by a ramp of 20 °C/min to a final temperature of 180 °C, which was held for 2 min. Under these conditions, furfural had a retention time of 5.9 min. The furfural yield from rice husk was calculated as:

$$\text{Yield of Furfural} = \frac{\text{furfural content(g)}}{\text{rice husk content(g)}} \times 100\%$$

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