Furfural production by acid hydrolysis and supercritical carbon dioxide extraction from rice husk

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Abstract−The aim of this research was to study the effect of furfural production from rice husk by hydrolysis accompanying supercritical CO_2 (SC-CO_2) extraction. The two-level fractional factorial design method was used to investigate the production process carried out with respect to furfural yield. The process variables are temperature range of 373-453 K, pressure 9.1-18.2 MPa, CO_2 flow rate 8.3×10^{-5}-1.7×10^{-4} kg/s (5-10 g/min), sulfuric acid concentration 1 to 7 (%wt) and ratio of liquid to solid (L/S) 5 : 1 to 15 : 1 (vol/wt). The results obtained from the experimental design showed that increasing temperature, pressure, CO_2 flow rate and sulfuric acid concentration but decreasing ratio of liquid to solid would improve furfural yield. Moreover, furfural production by two-stage process (pre-hydrolysis and dehydration) can improve furfural yield further to be around 90% of theoretical maximum.

Key words: Furfural Production, Acid Hydrolysis, Rice Husk, Supercritical Carbon Dioxide Extraction

INTRODUCTION

The use of agricultural wastes for energy and intermediary chemicals has economic, ecological and strategic interest. Furfural is produced by acid catalytic dehydration of pentose, which is obtained by acid catalytic hydrolysis of pentosan in biomass. Furfural and its derivatives are strategic chemicals due to several possible applications. Furfural is an important chemical because it is a selective solvent for separating saturated from unsaturated compounds in petroleum refining gas, oil and diesel fuel and for the high demand for its derivatives, particularly furfuryl alcohol, which is used as a basic component for furan resin [1,2].

Industrial technology for furfural production relies on batch or continuous reactors where the pentosan fraction of the lignocellulosic is converted into monosaccharides (pentoses) by acid hydrolysis. Further dehydration reactions of the pentoses yield furfural. Yield loss reactions occur while the furfural is in the liquid phase, by polymerization and by reaction with the precursor pentose [2,3].

Steam distillation is often used to recover furfural from the reaction mixture. This is inefficient because the diffusion of furfural through the liquid surrounding the solid substrate into the stripping steam is slow and because of the high-energy consumption [2,4,5]. Alternatively, the use of supercritical fluid in chemical reactions has the potential advantage of increasing the selectivity of the reaction while maintaining high conversion [6]. A typical application is in a successive reaction where the main product is loss by side reactions. In this case, a supercritical fluid can quickly separate the highly reactive product from a reactor to suppress the side reactions [7-11]. For example, Sako et al. [7] investigated the effect of the extraction of furfural by supercritical CO_2 on the selectivity and yield of furfural. Furthermore, based on kinetic data they proposed a reaction model from furfural formation with or without supercrit-

ical CO_2 extraction. The experimental results showed that the recovery of furfural from the reaction mixture by supercritical CO_2 extraction greatly improved the selectivity and yield of the furfural owing to the suppression of its side reactions. A simple reaction model could represent satisfactorily the change in furfural selectivity and yield with the xylose conversion for the reaction without supercritical CO_2 extraction, while the model could explain fairly well the reaction accompanying supercritical CO_2 extraction.

In this work we investigated the optimum condition for furfural production from rice husk by hydrolysis accompanying supercritical CO_2 extraction using two-level fractional factorial design method.

MATERIALS AND METHODS

1. Materials

5 kg of rice husk from a rice-mill in central Thailand was experimented in a batch reactor. On reception, the moisture of the material was under 8%. It was ground and sieved to a maximum size of 250 μm and the sieved material was stored in the autodesiccator. The chemical composition was determined according to standard methods for analyzing wood and related materials: ASTM D1102 for ash content, ASTM D1107 for ethanol-benzene extractives, ASTM D1106 for lignin, chlorite delignification for holocellulose, and ASTM D1103 for cellulose. The amount of pentosan was estimated from TAPPI T 223 cm-84. Other chemicals used for the experiments were carbon dioxide 99.5%, sulfuric acid 98%, furfural 99%, aniline 99%, acetic acid 99.9%, hydrochloric acid 35.4%, ethanol 95% and stannous chloride.

2. Reactor System and Experimental Procedure

This study was carried out in a semi-batch reactor system shown in Fig. 1. The apparatus was consisted of four main parts: a device to supply a continuous SC-CO_2 flow, a reactor with an inlet for SC-CO_2, an automatic back-pressure regulator and devices to measure temperature, pressure and flow rate.

The SC-CO_2 supply device provided SC-CO_2 at constant tem-
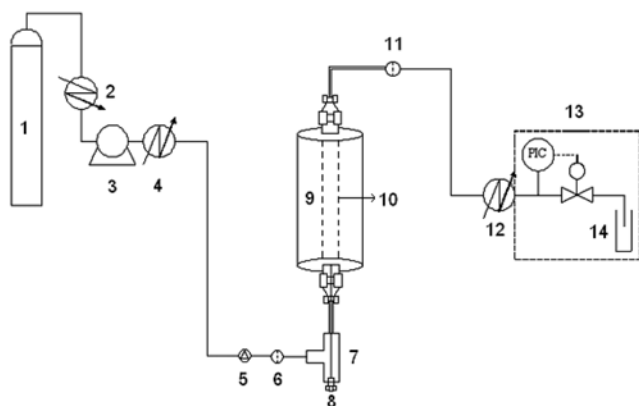
Fig. 1. Schematic diagram of experimental apparatus.
1. Liquid CO_2 cylinder   8. Thermocouple
2. Cooling bath   9. Tube furnace
3. High-pressure pump   10. Reactor
4. Pre-heater   11. Inline filter (0.5 micron)
5. Check valve   12. Co-axial tube cooler
6. All-welded filter   13. Back-pressure regulator
   (0.5 micron)   14. Sample tube
7. Tee connector

perature and pressure. The CO_2 was liquefied by a cooling bath and compressed by a high-pressure pump (Thar, Model P-50-2). Next, liquid CO_2 was heated in a pre-heater and reached supercritical condition. The SC-CO_2 pressure was controlled by an automatic back-pressure regulator, and its flow rate was maintained by software, which controlled the high pressure pump.

The reactor was a 0.065-in I.D. and 3/4-in O.D. Stainless-steel vessel with a volume of 80 ml. The reactor was attached vertically and designed for maximum working temperature and pressure of 550 K and 21.7 MPa, respectively. A tube furnace controlled the reactor temperature and a 1/16-in K-type thermocouple was attached inside the reactor to measure the reaction temperature.

In each experiment the reactor was put with 5 g or 20 g of ground rice husks (depend on ratio of sulfuric acid to rice husk) and sulfuric acid solution proportionally. The reactor was placed in a tube furnace for preheating to the desired reaction temperature. After that, the SC-CO_2 was introduced from the bottom of the reactor and began to extract the aqueous furfural solution. The fluid emitted from the reactor was promptly cooled by a co-axial tube cooler using water as a cooling fluid, depressurized with an automatic back-pressure regulator (Jasco, Model BP 1580-81). The liquid product was separated from CO_2 in a sample tube and the accumulated weight was measured every 30 minutes. The extraction lasted 3 hours. At the end of the run, a UV-VIS spectrophotometer was used for determining the furfural concentration.

3. Product Analysis

Furfural was determined by using a colorimetric method [12]. The analysis is based on the Stenhouse color reaction of furfural with aniline in acetic acid and stannous chloride to stabilize the color. Color was developed in 2 ml distillate or calibration standard by adding 2 ml of 95% ethanol and 1 ml of aniline-acetic acid reagent. After the liquid product was mixed with these chemicals, the sample was analyzed by using a UV-VIS spectrophotometer at 515 nm and the result was compared with a calibration curve of pure fur-

fural.

The furfural yield was defined as a ratio of the weight of furfural extracted to the theoretical furfural that can be converted from pentosan. Stoichiometric yield of furfural is 72.72 g per 100 g of pentosan [2].

4. Statistical Analysis

All experiments were conducted by a 2-level fractional factorial design which allowed fitting of first order models with interaction among the variables. Five variables, which are temperature, pressure, CO_2 flow rate, H_2SO_4 concentration and liquid/solid ratio, were selected to study their effects on furfural yield. ANOVA was applied to detect statistically significant changes on furfural yield with 95% level of confidence ($p < 0.05$). The experiments were carried out at a temperature range of 373-453 K, pressure 9.1-18.2 MPa, CO_2 flow rate 8.3×10^{-5}-1.7×10^{-4} kg/s (5-10 g/min), sulfuric acid concentration range of 1-7%wt and ratio of acid to rice husk 5 : 1 to 15 : 1 vol/wt.

In order to investigate the influence of five variables on furfural yield, a simple regression analysis was applied and Design-Expert 6.0.10 Trial program was used throughout.

RESULTS AND DISCUSSION

1. Composition of rice husk

The main composition of rice husk as shown in Table 1, in dry basis, is composed of 44.32%wt of cellulose, 16.02%wt of lignin, 15.60%wt of Pentosan, 1.35%wt of Ethanol-benzene extractives and 22.74%wt of ash. These data provide the maximum yield of furfural that can be obtained from rice husk.

2. Determination of Studied Variables on Furfural Yield

The experiments were performed on furfural production from rice husk accompanying SC-CO_2 extraction. Table 2 shows the experimental conditions applied for each treatment combination. 16 runs of experiment and their results were obtained as shown in Table 3.

Fig. 2 is the normal probability plot which pronounces the effects of variables on the furfural yield. It is shown that there are five prominent variables and one interaction between variables influ-

**Table 1. Chemical composition of rice husk (dry basis)**

Description	%wt
Ethanol-benzene extractives	1.35
Cellulose	44.32
Lignin	16.02
Ash	22.74
Pentosan	15.60
	100

Table 2. Two-level factorial experimental design

Variables	Low level (−)	High level (+)
Temperature (A), K	373	453
Pressure (B), MPa	9.1	18.2
Flow rate (C), kg/s	8.3×10^{-5}	1.7×10^{-4}
H_2SO_4 concentration (D), %wt	1	7
Liquid/solid ratio (E), ml/g	5	15

Table 3. Experimental design and furfural yield of furfural production from rice husk by acid hydrolysis accompanying supercritical carbon dioxide extraction

Run number	Variables					Yield%
	T (K) (A)	P (MPa) (B)	Flow rate (kg/s) (C)	Concentration (%wt) (D)	Ratio (ml/g) (E)	
1	373	18.2	0.00017	1	15	10.61
2	453	9.1	0.000083	7	15	11.59
3	373	18.2	0.00017	7	5	25.84
4	373	18.2	0.000083	7	15	13.21
5	453	9.1	0.00017	7	5	21.15
6	453	9.1	0.000083	1	5	10.81
7	373	9.1	0.000083	1	15	5.51
8	373	9.1	0.000083	7	5	8.12
9	453	18.2	0.00017	1	5	50.25
10	453	9.1	0.00017	1	15	11.36
11	453	18.2	0.000083	1	15	35.11
12	373	9.1	0.00017	1	5	11.54
13	373	18.2	0.000083	1	5	21.36
14	453	18.2	0.00017	7	15	45.21
15	373	9.1	0.00017	7	15	16.81
16	453	18.2	0.000083	7	5	45.86
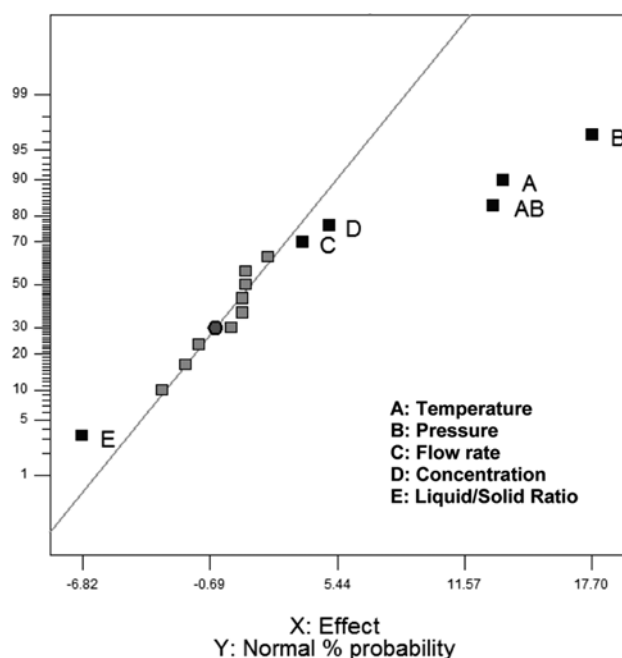
Fig. 2. Normal probability plot of furfural yield for furfural production from rice husk by hydrolysis accompanying SC-CO$_2$ extraction.

Fig. 3. Relation of residuals and normal % probability.

encing furfural yield. These are temperature (A), pressure (B), CO$_2$ flow rate (C), sulfuric acid concentration (D), ratio of acid to rice husk (E), interaction of temperature and pressure (AB). Table 3 is the analysis of variance (ANOVA) with 95% confidence level. The results show the same conclusion as observed from Fig. 2. In order to improve the hydrolysis reaction of pentosan and to increase solubility of furfural in SC-CO$_2$, these variables should be adjusted appropriately.

3. Statistical Modeling

After the 2^4 fractional factorial design was performed, a regression model was developed based on the main variables observed from the last section. The model was a linear model with interaction variables. The equation was expressed in the terms of coded variables as follows:

$$\%Yield = +22.08 + (6.71 * A) + (8.85 * B) + (1.89 * C) + (2.52 * D) - (3.41 * E) + (6.74 * A * B) \qquad (1)$$

where A, B, C, D, and E are temperature, pressure, CO$_2$ flow rate,

sulfuric acid concentration, ratio of acid to rice husk, respectively. It implied that pressure is the variable that has the highest positive effect on %yield, while temperature and interaction between temperature and pressure also have high positive effect on %yield. However, the ratio of acid to rice husk has moderate negative effect on %yield.

Residual analysis was conducted to validate the adequacy of the regression equation, Eq. (1). The residual is the difference between the actual value obtained from the experiment and the predicted value obtained from Eq. (1). Fig. 3 shows the relation of residuals
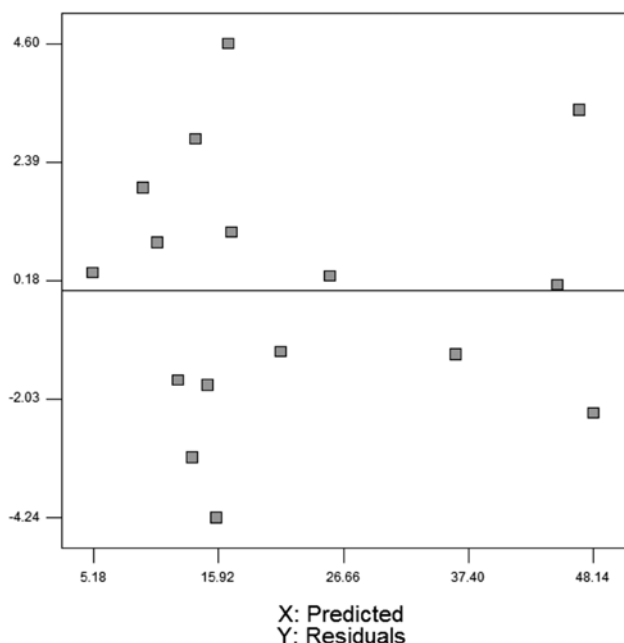

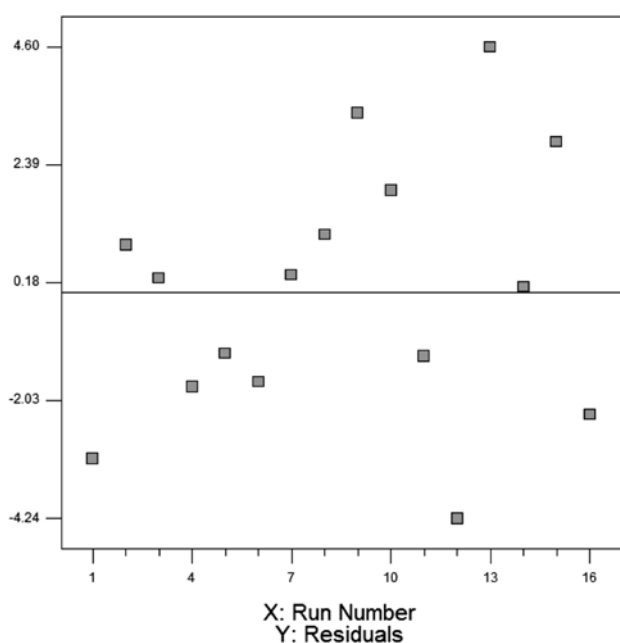**Fig. 4. Relation of residuals and predicted value.**

Fig. 5. Relation of residuals and run number.

with % probability. The line was straight, which implied the residuals followed a normal distribution. Fig. 4 shows residuals have non-format variation and almost constant variation. It implies the linear regression equation with interaction term, Eq. (1), is adequate. Fig. 5, the plot between residual and run number, shows that the residuals are structureless. It implies that residuals were independent of run numbers. Both Fig. 4 and 5 are to validate the assumptions of the residuals being normally and independently distributed with constant variance.

According to the coefficients of variables in Eq. (1), to increase furfural yield one should increase A, B, C and D, but decrease E. These effects of A, B, D and E conformed to the results of Mansilla [4]. A, B and interaction of A and B affected the furfural extraction because the properties of SC-CO_2 (density, diffusivity) change dramatically with A and B [13].

4. Improvement of Furfural Production
4-1. Changing the Major Variables to Improve Yield

From Table 3, one can observe that run number 9 gave the highest yield of furfural. In order to improve the yield, a number of experiments were conducted by varying the related variables in the direction that would promote the product yield. First, the experiment was performed by increasing temperature (A) and decreasing the ratio of acid to rice husk (E). While other variables were kept as conducted in run number 9, the temperature was increased from 453 to 473 K, and the liquid/solid ratio was decreased from 5 : 1 to 1 : 1. The result was drastically improved from 50% to 80% as shown in Fig. 6. This result coincided with the predicted value from Eq. (1), which is 89%, although the numerical value was not the same.

After that, another experiment was performed by increasing pressure (B) and also keeping the ratio of acid to rice husk (E) to 1 : 1, while the rest of the variables were kept at the same condition as run number 9. The pressure was increased from 18.2 to 20.3 MPa. Subsequently, the result followed the same trend as the first attempt. That is, the yield was improved from 50% to 82%. The predicted yield by the regression model was 89.4%. Since the standard deviation of the experiment was about 3.1, both attempts were not
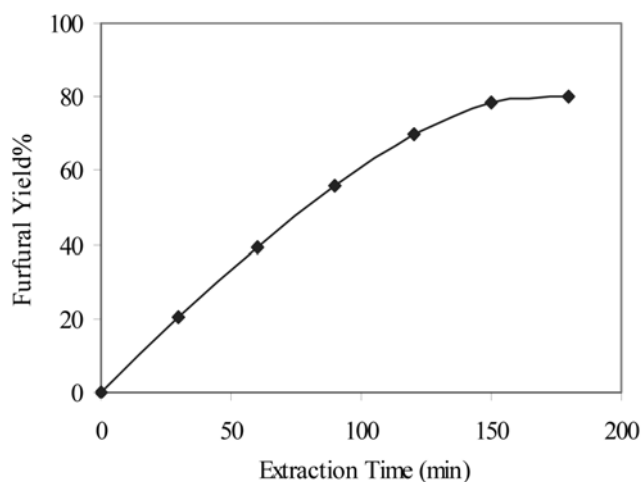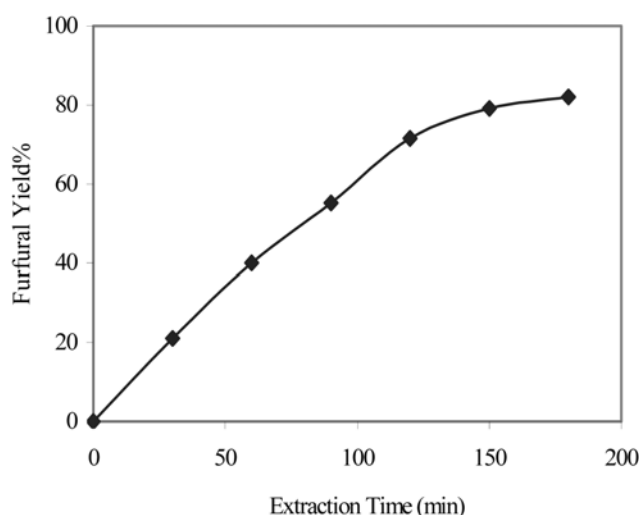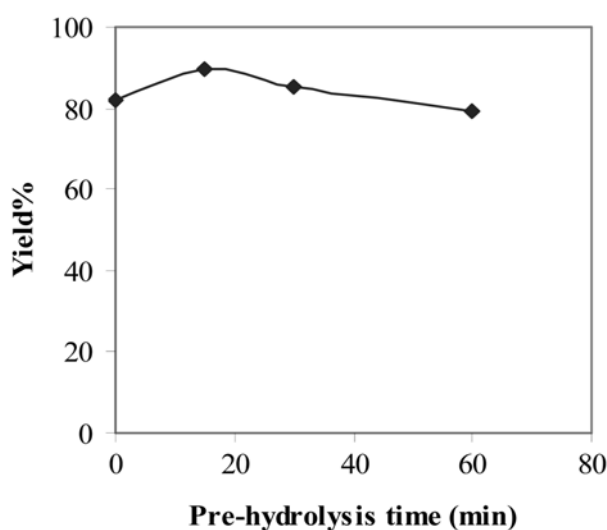

Fig. 6. Influence of main variables on the furfural yield 473 K, 18.2 MPa, CO_2 flow rate: 1.7×10^{-4} kg/s, [H_2SO_4]: 7%wt, L/S ratio: 1 : 1 (vol/wt), time to dissolve rice husk in sulfuric acid solution: 60 min.

Table 4. Analysis of variance table of furfural yield

Source		Sum of squares	Degree of freedom	Mean square	F Value	Prob.>F
Model		2,985.81	6	497.63	51.06	<0.0001
	A	720.12	1	720.12	73.89	<0.0001
	B	1,252.45	1	1,252.45	128.52	<0.0001
	C	57.00	1	57.00	5.85	0.0387
	D	101.20	1	101.20	10.38	0.0104
	E	185.78	1	185.70	19.06	0.0018
	AB	669.26	1	669.26	68.68	<0.0001
Residual		87.71	9	9.75		
Total		3,073.52	15			

Fig. 7. Influence of main variables on the furfural yield 453 K, 20.3 MPa, CO_2 flow rate: 1.7×10^{-4} kg/s, [H_2SO_4]: 7%wt, L/S ratio: 1 : 1 (vol/wt), time to dissolve rice husk in sulfuric acid solution: 60 min.

Fig. 8. Influence of pre-hydrolysis time on furfural yield 453 K, 20.3 MPa, CO_2 flow rate: 1.7×10^{-4} kg/s, [H_2SO_4]: 7%wt, L/S ratio: 1 : 1 (vol/wt), time to dissolve rice husk in sulfuric acid solution: 60 min, extraction time: 3 hours.

statistically different.

4-2. Improving the Process by Introducing a Pre-hydrolysis Step

A two-stage process was adopted [4] for the furfural production. Pentoses were separated from lignocellulosic matrix in a pre-hydrolysis step and cyclization and dehydration of pentoses took place in the second step. The process was carried out by means of boiling the sample in 7% H_2SO_4. The time for pre-hydrolysis was investigated by being recorded immediately after the reaction temperature reached the set point. Then, SC-CO_2 extraction of furfural was performed after the pre-hydrolysis step was finished.

The influence of pre-hydrolysis time on furfural yield is shown in Fig. 8. The figure suggests that there is an optimal time for pre-hydrolysis, because after a long period of pretreatment time the production was decreased. The highest yields around 90% were achieved around 15 min of pre-hydrolysis. After that, the furfural production was decreased as a result of decomposition during the pre-hydrolysis step.

5. Engineering Consideration

Furfural production from rice husk by acid hydrolysis accompanying supercritical carbon dioxide extraction has been shown to be more effective compared with steam distillation. However, the process requires high pressure which leads to higher equipment cost. According to the CO_2 flow rate of 1.7×10^{-4} kg/s (10 g/min) for 20 g of rice husks, extraction time 3 hrs, the CO_2 usage was around 700 tons per tons of furfural. To minimize the CO_2 usage, a recycle unit of CO_2 should be installed. The product from the reactor should be depressurized to an optimum pressure for partial separation of furfural and then recycled and mixed with new CO_2.

In general, the typical operating cost of this process is low since CO_2 is inexpensive and can be recycled. The operating cost, together with the equipment cost, can be reduced to a minimum by proper process design. Therefore, furfural production from rice husk or other biomass by acid hydrolysis accompanying supercritical carbon dioxide extraction should be possibly feasible in an agricultural country where there are enormous amounts of biomass. Further work should be undertaken on CO_2 recycling and to evaluate the overall economics of the process.

CONCLUSIONS

SC-CO_2 is a good solvent for the extraction of furfural from the reaction mixture. It could suppress the side reactions. The parameters that influence furfural yield from rice husk accompanying SC-

CO_2 are the temperature, pressure, sulfuric acid concentration and the ratio of acid to feed stock. Higher yield could be obtained when increasing CO_2 flow rate, because the higher the amount of CO_2, the higher furfural from reaction mixture could be dissolved. Pre-hydrolysis is a determinant step in pentose release from lignocellulosic matrix of rice husk and subsequently increases the furfural yield. In this study furfural yield of 90% was achieved by using a two-stage process accompanying SC-CO_2.

ACKNOWLEDGMENTS

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