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Research Article

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Furfural produced from bamboo by a 2-step method at atmospheric pressure

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ABSTRACT

Process conditions of furfural produced from bamboo by a 2-step method at atmospheric pressure were studied. The first hydrolysis step of bamboo hemicellulose was researched by the experimental factors such as liquid-solid ratio, reaction time, and volume fraction of organic solvent, volume fraction of sulfuric acid and so on. In the optimum conditions: liquid-solid ratio of 14mL • g^{-1}, reaction time 4h, volume fraction of organic solvent 60%, volume fraction of sulfuric acid 5%, hemicellulose hydrolysis rate was 78.68% and xylose yield was 51.93%. Experimental factors, initial xylose concentration, initial acidity, reaction time, and co-catalyst species were studied in the second step of the process. When the conditions of initial xylose concentration, initial acidity and reaction time were 15g/L, 10% and 2h, respectively, with NaCl as co-catalyst specie, furfural yield can reached 90.63%.

Key words: bamboo, atmospheric pressure, two-step method, furfural.

INTRODUCTION

Currently, the world's fossil fuels are drying up and the environment is gradual deteriorating. It's urgent to looking for a renewable, environmental friendly and alternative energy. Biomass, replacing fossil energy, is wide distribution, large volume, low pollution, renewable and can be sustainable used. What's more, it is good for the environment. At present, biomass accounts for about 14% of the world's final energy consumption, which is higher than the proportion of coal energy (12%) [1]. Because the use of biomass energy will not add the amount of surface CO_2 cycle, it is considered to be a very promising new alternative energy source[2-3].

Bamboo has many advantages, such as high output, fast growth, and strong adaptability. The bamboo forest area existing about 540,000 hm^2, accounting for 2.8% of Chinese forest area [4], is a kind of abundant and renewable biomass resource. Bamboo is widely used, such as pulp and paper, preparation, processing and manufacturing handicrafts, fiber extraction [5]. Bamboo fiber is mainly composed of cellulose, hemicelluloses and lignin [6]. Although the use of bamboo fiber has already a lot of achievements, there is a problem that only the utilization of a single component is high, and the raw materials' utilization is low. Cellulose has been widely used, but the use of hemicelluloses and lignin is usually ignored. Therefore, our team explored a way to making bio-based chemicals furfural using bamboo hemicelluloses under ordinary conditions of two-step, and studied the process of separation of bamboo fiber component by extracted lignin to improve the comprehensive utilization of bamboo fiber[7-10].

EXPERIMENTAL SECTION

Materials, reagents and instruments

Sichuan local affinis, raw fiber composition based on dry matter: the mass fraction of cellulose 51.13%, hemicellulose content of 26.46%, 18.23% mass fraction of lignin, ash content of 3.01%. Water boiled dry bamboo with predetermined time, drying to constant weight, crushing, and sieved to 10- 60 mesh residue back bamboo.

Sodium dodecyl sulfate, sodium tetraborate, disodium edetate, disodium hydrogen phosphate, ethylene glycol diethyl ether, cetyl trimethyl ammonium bromide, sulfuric acid, concentrated hydrochloric acid, ferric chloride, 95% ethanol, furfural, etc., were analytical grade; orcinol, chemically pure; D-xylose, biochemical reagent.

Multifunctional high-speed grinder, multi-use recycled water pumps, electric oven thermostat blast, analytical balance, electronic thermostat electric sets, pH meter, constant temperature water bath, UV-visible spectrophotometer, horizontal refrigeration boxes.

Analysis methods
Bamboo fiber components were measured by Van Soest method [11-12] determination; xylose concentration was measured with phenol-hydrochloric acid method [13]. Concentration of furfural was measured by a single wavelength at 278 nm through standard curve with UV-visible spectrophotometer. Acidity of liquid hydrolyzate and reaction was measured with the acid-base titration. Calculated as follows:

Cellulose retention rate= $\frac{m_2}{m_1} \times 100\%$

Hemicellulose hydrolysis rate= $\frac{m_3 - m_4}{m_3} \times 100\%$

Lignin removal rate= $\frac{m_5 - m_6}{m_5} \times 100\%$

Xylose yield based on the weight of hemicellulose in raw material = $\frac{m_7}{m_3} \times 100\%$

Furfural yield= $\frac{m_{10}}{m_8 + \frac{96}{150} \times m_9} \times 100\%$

Where m_1, m_3, m_5 represent the quality of the raw material of cellulose, hemicellulose, lignin, g; m_2, m_4, m_6, respectively, are the quality of the hydrolysis of the residue of cellulose, hemicellulose, lignin, g; m_7, is the mass of xylose hydrolysis solution, g; m_8, m_9, represent the mass of furfural, xylose before reacting, g; m_{10} is furfural distillate, g; 96,150 are the molecular weight of furfural and xylose.

Bamboo hemicellulose hydrolyzate
30.0g prepared bamboo was taken into a three-necked flask and organic solvent - acid - water mixed solution in a certain solid-liquid ratio was added. The solution was shaken and heated to reflux a certain time, and then was filtered by double cloth vacuum filtration and collected the filtration. Residue was washed with 90 ℃ hot water until the filtrate was neutral. Then residue was dried to constant weight in oven, weighed and sampled for analysis of the fiber component.

Four factors of liquid to solid ratio, reaction time, volume fraction of the organic solvent, volume fraction of the sulfate were investigated the influence of bamboo hemicellulose hydrolysis rate an yield of xylose. It could find optimal conditions for the hydrolysis of hemicellulose bamboo.

Bamboo hemicellulose hydrolyzate furfural
Under the optimal conditions of bamboo hemicellulose hydrolysis, hydrolyzate was prepared; the solution was distilled to recover the organic solvent. When solid-liquid was separated, precipitate was collected and filtrate was concentrated. Xylose concentration, furfural concentration and acidity (sulfuric acid volume fraction) in the concentrated were determined, after which the reaction liquid was obtained by adding sulfuric acid in the set conditions. 300mL reaction liquid was taken in a three-necked flask, and then heated to micro-boiling. Furfural was collected by water vapor.

The influence of initial xylose concentration, initial acidity (sulfuric acid volume fraction), reaction time, cocatalyst were investigated to furfural yield and explored the optimum process conditions of furfural produced by bamboo hemicellulose hydrolyzate.

RESULTS AND DISCUSSION

Bamboo hemicellulose hydrolyzate

The orthogonal test results of bamboo hemicellulose hydrolyzate in organic solvents - acid - water mixed system were shown in Table 1.

Table 1 bamboo hemicellulose hydrolyzate orthogonal test results

No.		Liquid-solid ratio/（$mL \cdot g^{-1}$）	Liquid-solid ratio /h	Organic solvent volume fraction /%	Sulfuric acid volume fraction /%	Hemicellulose hydrolysis rate /%	Xylose yield /%
1		6	4	60	3	64.23	29.04
2		10	6	60	5	72.22	50.26
3		14	8	60	7	95.48	74.34
4		10	8	70	3	93.53	44.69
5		14	4	70	5	69.70	52.42
6		6	6	70	7	46.02	41.12
7		14	6	80	3	85.00	42.89
8		6	8	80	5	91.23	39.35
9		10	4	80	7	71.61	58.03
Hemicellulose hydrolysis rate	*K*1	67.160	68.513	77.310	80.920		
	*K*2	79.120	67.747	69.750	77.717		
	*K*3	83.393	93.413	82.613	71.037		
	R	16.233	25.666	12.863	9.883		
Xylose yield	K1	36.503	46.497	51.213	38.873		
	K2	50.993	44.757	46.077	47.343		
	K3	56.550	52.793	46.757	57.830		
	R	20.047	8.036	5.136	18.957		

It can be seen from the value of R in Table 1, the factors that affect the hemicellulose hydrolysis rate were in the order of reaction time> liquid to solid ratio> organic solvent volume fraction> volume fraction of sulfuric acid; thus, factors, affecting the yield of xylose, were in the order of liquid-solid ratio> sulfuric acid volume fraction> time> volume fraction of organic solvent.

The range analysis unfolded the liquid-solid ratio had a great impact on hemicellulose hydrolysis rate and xylose yield. When liquid-solid ratio was increased, the rate of hydrolysis of hemicellulose and the yield of xylose rate were increased. Liquid-solid ratio was varied from 6 $mL \cdot g^{-1}$ to 14 $mL \cdot g^{-1}$, which lead to hemicellulose hydrolysis rate increased rapidly from 67.160% to 83.393% and xylose yields increased from 36.503% to 56.550%. Select the liquid-solid ratio of 14 $mL \cdot g^{-1}$ to maximize the rate of hydrolysis of hemicellulose and xylose yield, as the condition of the second step where xylose solution was prepared by using bio-based chemicals – furfural.

Reaction time had a significant influence on hemicellulose hydrolysis rate. Along with the time, hydrolysis rate was increased, but it had little effect on xylose yield. When the reaction time was extended from 4h to 8h, hemicellulose hydrolysis rate was increased rapidly from 68.513% to 93.413%, while the yield of xylose was slowly gained from 46.497% to 52.793%. It is possibly because that the decomposition rate of xylose is greater than the rate of hydrolysis of hemicellulose. Further, xylose yield was increased slowly in a long reaction time, because of side reactions such as the resin of xylose and polymerization. In order to maximize the xylose yield, reduce energy consumption and improve economic efficiency, reaction time was considered to be 4h.

Organic solvent volume fraction had no influence on the rate of hydrolysis of hemicellulose, xylose yield. Taking costs and economic efficiency into account, organic solvent volume fraction was selected 60% to obtain the highest xylose yield.

On the contrary, sulfuric acid volume fraction had greater impact on xylose yield and less impact on hemicellulose hydrolysis rate. If volume fraction of sulfuric acid was too big, it could be consumed by cellulose hydrolysis and side reaction in the reaction system, and lead to produce more coke composition. Meanwhile, concentrated sulfuric acid would corrode reaction instrument, which could increase the cost of acid consumption and cause serious pollution to the environment. Therefore, considering 5% sulfuric acid was appropriate.

From table 1, the optimum conditions of bamboo hemicellulose hydrolyzate were: liquid to solid ratio of 14mL • g-1, the reaction time was 4h, the organic solvent volume fraction of 60%, sulfuric acid volume fraction of 5%. Under these conditions, the rate of hemicellulose hydrolysis was 78.68%, yield of xylose was 51.93%. The rate of retention of cellulose and lignin removal rate were also higher, respectively, 90.69%, 53.57%.

Preparation of furfural from hydrolysis liquor of bamboo hemicellulose

The hydrolysis liquor, obtained from the hydrolysis of bamboo hemicellulose at optimum conditions, underwent the isolation of lignin. Then, the hydrolysis liquor was concentrated under vacuum. The obtained condensate was collected to determine each factor on the influence of furfural yield.

The effect of initial xylose concentration on furfural yield

In this study, the initial acidity (measured by sulfuric acid volume) was 10%. And different initial concentrations of xylose (5.1705g/L, 8.415g/L, 10.2986 g/L, 14.7429 g/L, and 19.6504 g/L) were chosen. The mixture was hydrolyzed under reflux for 2 h. The reactants were stripped with water vapor, to investigate their effect on the yield of furfural. The result is shown in Figure 1. It was obvious that the yield of furfural dramatically increased, when the concentration was increased from 5.1705g/L to 14.7429 g/L. However, its yield climbed slightly when the concentration was increased to 14.7429 g/L. When the xylose concentration is relatively low, the concentration of H^+ in reaction system is increasing with the rise of xylose concentration. It results in the effective collision between xylose molecules and H^+. Thus, the furfural yield was improved. Nevertheless, when the concentration of xylose is too high, the concentration of H^+ in reaction system does not increase. Therefore, there is no significant increasing in the yield of furfural. In addition, side effects came up in reaction system at an excessively high concentration of xylose, which influenced the yield of furfural. According to the above mentioned, 15 g/L was chosen to contribute to the high yield of furfural.

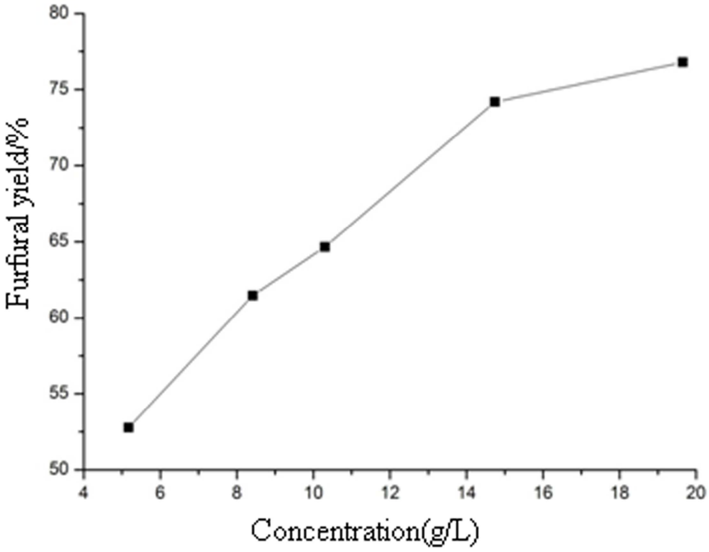

Figure 1 the effect of initial xylose concentration on furfural yield

The effect of initial acidity (measured by sulfuric acid volume) on furfural yield

To investigate the effect of the initial acidity on the yield of furfural, comparative experiments were carried out at 4%, 7%, 10%, 13%, and 16%, respectively. The mixture was hydrolyzed under reflux for 2 h. The reactants were stripped with water vapor, to investigate their effect on the yield of furfural. As shown in Figure 2, it indicates that initial acidity plays an important role in furfural yield. The yield of furfural was obviously increased with the yield jump from 22.17% up to 56.12% when the initial acidity increased from 4% to 10%. When the initial acidity is larger than 10%, the furfural yield will increase slowly. It is easy to know that the reaction rate of xylose degradation may be attributed to concentration of H+ in reaction system. The furfural yield was improved when the concentration of H+ in reaction system is increasing. However, when the initial acidity is too high, the reaction rates of xylose resinification and polymerization is accelerated, which results in high content of coking. Therefore, 10% of initial acidity was selected as the optimal concentration.

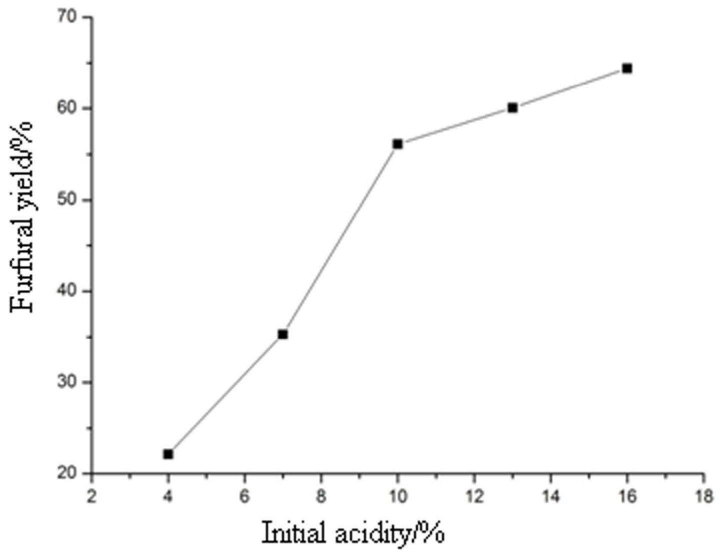

Figure 2 the effect of initial acidity (measured by sulfuric acid volume) on furfural yield

Effect of time on furfural yield

To optimize the time, comparative experiments were also carried out with. The reactants were stripped with water vapor, to investigate the effect of time on the yield of furfural. The result is shown in Figure 3. The yield of furfural increased sharply within 120 min, while after 120 min, its yield began to keep constant. This could be due to the fact that furfural was unstable in the acid solution for a very long time. This will generate many side effects. Therefore, 2 h was chosen to contribute to the high yield of furfural.

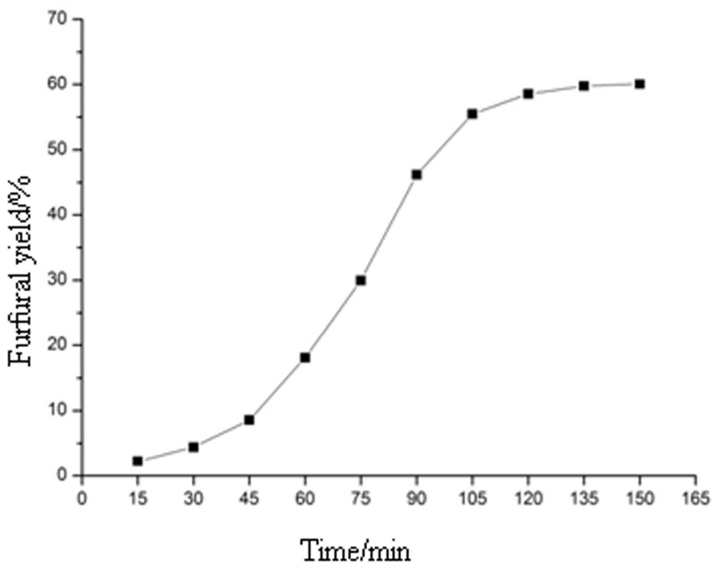

Figure 3 the effect of time on furfural yield

The effect of promoters on the furfural yield

The initial acidity (by volume) of the xylose solution was 10%, and the initial xylose concentration was 7 g/L, promoters such as NaCl, $(NH_4)_2SO_4$, $NaNO_3$, Al_2 $(SO_4)_3$, Na_2SO_4 was added individually, the addition was 50% of the mass of xylose. Furfual product was separated by steam distillation, and the changes of the furfural yields were presented in Figure 4.

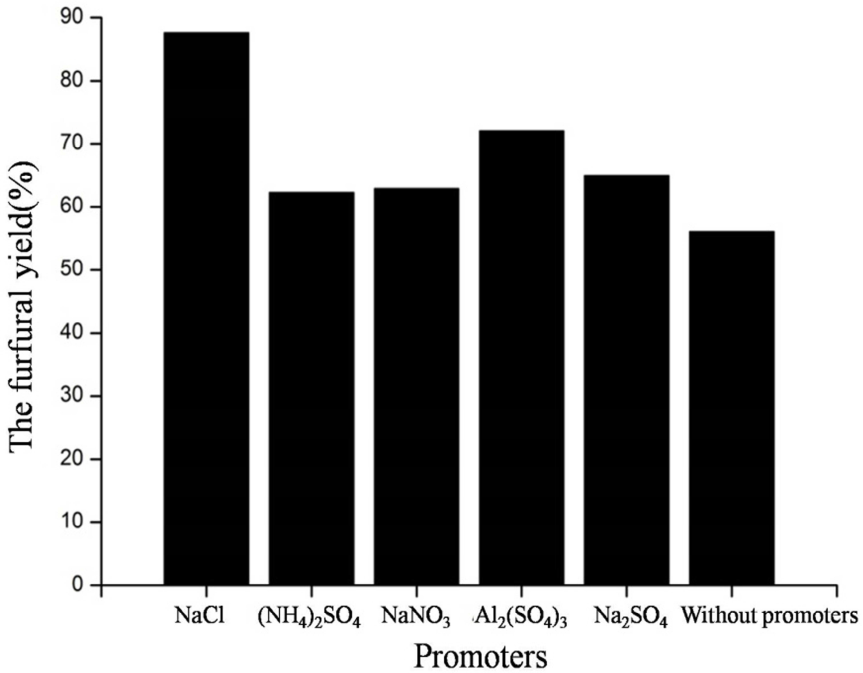

Figure 4 the effect of promoters on the furfural yield

The concentration of H^+ could be improved by common metal salt, and the acidity was strengthened gradually by the increase of the concentration of metal salt until satured[14]. Besides the inorganic acid, some salts of strong acids and weak bases can also be used as a catalyst, which contains ammonium salt, nitrate and aluminum salt, for they can produced H+ by hydrolysis. These salts may act as lewis acid to promote the dehydration and cyclization reaction. NaCl, $(NH_4)_2SO_4$, $NaNO_3$, $Al_2(SO_4)_3$ and Na_2SO_4 were selected as promoters in furfural production in this experimental.

It can be seen that under the same reaction conditions, i.e. same initial acidity, same initial xylose concentration and same reaction time, the furfural yield were improved by the addition of promoters. While NaCl was added as a promoter, the furfural yield was obviously improved to 87.55%, increased by 56.12% than the case without promoter. However, the furfural yield didn’t improve much. It is mainly because that not only the acidity was enhanced by NaCl, but also the solubility of furfural was decreased [15], as a result, the furfural yield was obviously improved. Yemis *et al*. [16] had inferred that Cl^- was good for the generation of furfural; the exact mechanism remains further investigation. As metal salts are cheap with an abundant source, easily recovered and feasible in industrial application, NaCl was suitable to be chosen as the promoter.

From the analysis above, the optimized conditions for the production of furfural by the hydrolysate of hemicelluloses in bamboo were as follows: the initial xylose concentration was 15 g/L, the initial acidity was 10%, the time for reaction was 2 h, and NaCl was added as the promoter; under which the furfural yield was 90.63%.

CONCLUSION

In the first step of bamboo hemicellulose hydrolysis process, liquid to solid ratio, reaction time, the volume fraction of organic solvents, sulfuric acid volume fraction of experimental factors were studied to obtain optimum conditions: liquid to solid ratio of $14mL \cdot g^{-1}$ reaction time of 4h, the organic solvent fraction of 60%, the volume fraction of 5% sulfuric acid. Under these conditions, the rate of hydrolysis of hemicellulose was 78.68%, yield of xylose was 51.93%. Cellulose retention and lignin removal rate were also higher, respectively, 90.69%, 53.57%.

The experimental factors: initial xylose concentration, initial pH, reaction time and cocatalyst were studied in the second step of hydrolysis process of furfural. The yield was 90.63% furfural on the conditions: the initial xylose concentration was 15g / L; the initial pH of 10%, the reaction time was 2h, and NaCl as co-catalyst.

This two-step method furfural process has the following characteristics:
(1) At the first step of the hydrolysis process, the hydrolysis of hemicellulose bamboo provides raw materials for the preparation of furfural and extracts lignin to separate cellulose, which creates conditions to improve the comprehensive utilization of bamboo biomass resources.

(2) At the second step of the reaction, the reactants are maintained micro-boiling until a small amount of furfural was generated in the vapor phase. Since hydrogen ions are not existed in the vapor phase and xylose and the intermediate products are stored in the liquid phase, it can increase the yield of furfural by avoiding side reactions of furfural polymerization.

(3) In this process, there are many advantages: high stability of the reaction system, moderate reaction and low equipment requirements. In addition, the organic solvent is recyclable, which effectively reduces the cost.

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