

Optimization of formic acid hydrolysis of corn cob in xylose production

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Abstract—Dilute acid pretreatment of lignocellulosic material is one of the significant steps in a biorefinery. We used response surface methodology to determine the important factors of formic acid concentration (2%-6% wt%), treatment time (30-150 min), reaction temperature (120-160 °C), and liquid to solid ratio (3-11 mL/g) on dilute acid hydrolysis of corn cob to produce xylose. A xylose yield of 81.6% and selectivity of 15.1 g/g were achieved under the optimal conditions (5% acid concentration, 150 min, 135 °C, and 7 mL/g liquid to solid ratio). The addition of trivalent salts (FeCl₃, Fe(NO₃)₃, and Fe₂(SO₄)₃) to the reaction system enhanced the xylose yield but decreased selectivity. The FeCl₃ concentration over 0.75 mol/L had a negative effect on xylose production.

Keywords: Xylose, Formic Acid, Corn Cob, Trivalent Salts, Optimization

INTRODUCTION

We are stepping into an era of diminishing availability of petroleum resource and increasing concern about global climate change. Renewable biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates through the biorefinery process [1].

Lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin. Hemicellulose, which is mainly composed of xylans, is the second most common polysaccharide in nature [2]. Xylose, the monomeric xylan, can be used as an intermediate to produce a variety of compounds or fuels by chemical or biotechnological processes. One such compound is xylitol, a five-carbon sugar alcohol that is widely used in food and pharmaceuticals [3]. The other is furfural, a high-value and bio-based chemical, that is extensively utilized in oil refining, manufacturing, plastics, pharmaceutical, and agrochemical industries [4].

The pretreatment of lignocellulosic materials is the first key step in conversion of biomass to fuels and chemicals. Various processes including steam pretreatment, organosolv process, acid hydrolysis, and CO₂ explosion, were used to pretreat lignocellulosic materials [5-8]. Among these processes, the dilute acid process proved to be the most efficient and inexpensive method for producing xylose [9]. Pretreatment of different lignocellulosic materials using dilute acid had been studied by many researchers, and hydrochloric acid, sulfuric acid, and nitric acid were generally used as catalysts [10-12]. The employment of mineral acids as catalysts makes their recovery and recycling impractical because the separating of these catalysts is costly and inefficient, leaving large amount of waste water needed to be further neutralized. Problems such as corrosion, safety, and serious sugar degradation may also be encountered. To meet the demand of green chemistry and sustainable technology, the "toxic" acid catalysts should be replaced by the non-toxic, efficient, and

recyclable ones. A promising organic acid, formic acid, could be used in dilute acid hydrolysis of lignocellulosic materials. Though mineral acids are effective catalysts, the utilization of formic acid as catalyst has the following advantages: (1) formic acid, which is a weak acid, is less corrosive than mineral acids to reactors; (2) the use of formic acid would be in favor of xylose production and sugar degradation reaction was milder than that of mineral acids as catalysts; (3) formic acid has the property of being recovered with extractive technology [13]; (4) it can be obtained via the hydrolytic fission of the aldehyde group of hydroxymethylfurfural and furfural, which are biomass-derived industry processes [14,15]. If formic acid is chosen as catalyst to produce xylose, the drawbacks of mineral acid will be avoided to a certain extent. However, because formic acid is a weak acid, the optimal reaction time of formic acid hydrolysis process was longer than that of mineral acids.

In addition to the dilute acid process, inorganic salts have also been used as catalyst to pretreat various lignocellulosic materials [16-19]. Kang et al. [16] indicated the impact of inorganic salts on Miscanthus straw's sugar recovery in the following order: FeCl₃ > ZnCl₂ > CaCl₂ > KCl > NaCl. In pretreatment of silage, trivalent salt shows a stronger catalytic activity than di- or mono-valent salts [18]. So, inorganic salt pretreatment is an attractive method to produce xylose because the catalyst is recoverable and less corrosive.

Corn cob is one of the most abundant agricultural residuals in China. However, it is generally used as fuel without any treatment, which decreases its economic value and causes severe environmental problems. The xylan in the corn cob is able to be easily hydrolyzed by dilute acid to produce xylose. After the dilute acid treatment of corn cob, the solid residue that is porous can be further utilized for production of cellulose, glucose, and ethanol through fermentation [20]. Thus, dilute acid hydrolysis of corn cob is considered as the first stage of integrated strategy for utilization of corn cob.

To the best of our knowledge, there are scarce studies about the hydrolysis of corn cob using dilute formic acid as catalyst. The objective of the present study was to determine the effects of formic acid concentration, treatment time, reaction temperature, and liquid to solid ratio on the production of xylose and byproducts (glucose,

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arabinose, furfural, acetic acid, and hydroxymethylfurfural) using response surface methodology. Moreover, the yield and selectivity of xylose by adding trivalent salts (FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$) into formic acid solutions as promoter were investigated.

EXPERIMENTAL

1. Raw Materials and Chemical

Corn cob samples were bought from Baodi District of Tianjin. D-xylose ($\geq 99\%$), D-cellobiose ($\geq 99\%$), D-glucose ($\geq 99\%$), L-arabinose ($\geq 99\%$), formic acid (HCOOH , $\geq 99\%$), hydroxymethylfurfural ($\geq 99\%$), and acetic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, $\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Furfural (2-furaldehyde, $\geq 99.5\%$), H_2SO_4 ($\geq 98\%$), CaCO_3 ($\geq 99\%$), FeCl_3 ($\geq 99\%$), $\text{Fe}(\text{NO}_3)_3$ ($\geq 99\%$), and $\text{Fe}_2(\text{SO}_4)_3$ ($\geq 99\%$) were kindly provided by Jiangtian Chemical Reagent Co., Ltd. (Tianjin, China). All the chemicals were analytical reagent grade and used without any

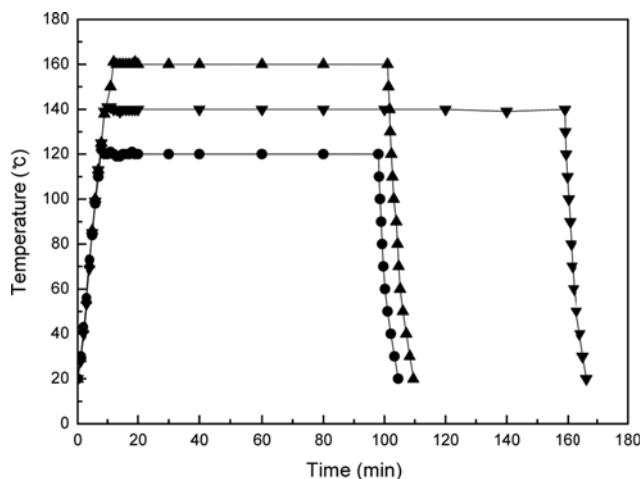


Fig. 1. Temperature profiles of three experiments [CCD 19 (●), CCD 20 (▲), CCD 24 (▼)].

Table 1. Experimental design and results obtained by hydrolysis of corn cob

Standard order	Factor 1 X_1	Factor 2 X_2	Factor 3 X_3	Factor 4 X_4	Responses		By products			
					Y %	S g/g	Arabinose g/L	AA g/L	FF g/L	5-HMF g/L
1	3.0	130	5	60	13.1	8.3	3.5	1.3	0.21	0.28
2	5.0	130	5	60	32.0	10.2	3.9	2.0	0.23	0.31
3	3.0	150	5	60	61.8	17.1	3.2	4.0	2.7	0.80
4	5.0	150	5	60	62.6	16.1	4.9	5.3	4.3	1.0
5	3.0	130	9	60	24.7	8.8	2.1	0.90	0.12	0.37
6	5.0	130	9	60	39.8	12.3	2.3	1.4	0.91	0.40
7	3.0	150	9	60	73.0	14.5	2.8	2.4	1.1	0.42
8	5.0	150	9	60	69.4	12.4	1.7	5.6	2.1	0.48
9	3.0	130	5	120	38.5	13.0	3.8	2.6	0.36	0.79
10	5.0	130	5	120	60.9	14.9	1.9	6.0	0.72	1.4
11	3.0	150	5	120	59.2	12.8	2.1	6.2	6.6	1.3
12	5.0	150	5	120	63.0	9.2	4.6	6.6	8.1	1.5
13	3.0	130	9	120	52.0	17.6	2.0	1.6	0.29	0.37
14	5.0	130	9	120	70.9	18.8	2.3	2.3	0.51	0.39
15	3.0	150	9	120	68.2	12.3	2.1	3.3	3.7	0.55
16	5.0	150	9	120	72.2	8.8	2.4	4.0	8.0	1.2
17	2.0	140	7	90	47.0	14.6	3.2	3.8	0.58	0.59
18	6.0	140	7	90	67.2	16.4	2.9	4.1	2.3	0.92
19	4.0	120	7	90	15.1	6.7	2.3	1.1	0.33	0.01
20	4.0	160	7	90	64.6	6.4	1.0	4.5	9.2	2.2
21	4.0	140	3	90	50.0	15.0	2.2	5.8	3.6	0.86
22	4.0	140	11	90	71.4	18.0	1.8	2.5	0.8	0.28
23	4.0	140	7	30	44.6	12.2	2.9	2.1	0.17	0.47
24	4.0	140	7	150	79.4	12.7	3.4	4.8	1.9	0.90
25	4.0	140	7	90	65.0	16.9	3.2	3.4	1.5	0.61
26	4.0	140	7	90	65.9	16.8	3.2	3.5	1.4	0.63
27	4.0	140	7	90	65.3	16.9	3.2	3.4	1.4	0.60

Y: yield of xylose, S: selectivity of xylose. The yield (Y) and selectivity (S) of xylose were calculated using the following equation: $Y = C_x \times V_{hyd} / m_{x_{max}}$ (1), $S = C_x / C_g$ (2) Where: C_x = mass concentration of xylose in the hydrolysate, g/L; $m_{x_{max}}$ = mass of theoretically converting of xylan content available in corn cob (on a dry weight basis) to xylose, g; V_{hyd} = volume of hydrolysate, L; C_g = mass concentration of glucose in the hydrolysate, g/L. AC: acid concentration, AA: acetic acid, FF: furfural, 5-HMF: hydroxymethylfurfural

further treatment. Deionized water was prepared in our laboratory using a four stage reverse osmosis system.

2. Acid Hydrolysis

Hydrolysis experiments were performed in a 2 L pilot-scale batch reactor. The stainless-steel reactor is equipped with an electric jacket, an intelligent temperature controller with a precision of $\pm 1^\circ\text{C}$, a mechanical stirrer, a manometer, and a cooling coil. Temperature profiles of three experiments are presented in Fig. 1. The reactions were under identified conversion conditions, including acid concentration, treatment time, reaction temperature, and liquid to solid ratio, as outlined in Table 1. According to the liquid-to-solid ratio, corn cob samples were exactly weighed and transferred to the reactor. The prepared formic acid solutions (or formic acid contained trivalent salts) were added to each sample to a constant final volume of 1,000 mL. The reactor was closed and the stirring system was started. After the mixture was homogenized for 5 min, the heating system was begun. When the internal temperature reached the desired point, the timer was started. After the reaction proceeded for a certain time, flowing water was connected to the cooling coil to chill the reaction system to room temperature. After this pretreatment, the solid material was filtered with Whatman filter paper and the filtrate was used for analysis of sugars (xylose, glucose, and arabinose) and by-products (acetic acid, furfural, and hydroxymethylfurfural).

3. Analytical Methods

Corn cob samples were sun-dried, milled and screened into particles with 20-100 mesh. The chemical composition of the corn cob was determined according to the NREL Laboratory Analytical Procedure [21]. Hydrolyzate samples were determined by Agilent 1260 series HPLC equipped with an Aminex HP-87H (Bio-Rad 300×7.8 mm), a cation H Refill Cartridge guard column (Bio-Rad 30×4.6 mm), and a refractive index detector (Agilent G1362A). Before injection, 0.22- μm filters were used to filter the samples. The filtered sample was injected to the HPLC system with a volume of 20 μL . The HPLC was operated at 65°C and eluted with 5 mmol/L H_2SO_4 at a flow rate of 0.6 mL/min. The temperature of refractive index detector was 40°C . A complete analysis was carried out in 55 min.

4. Response Surface Methodology

Response surface methodology was used to determine the optimum condition of dilute formic acid pretreatment of corn cob to produce xylose. Considering the industry practice, four important parameters including acid concentration (2%-6% wt%), treatment time (30-150 min), reaction temperature (120 - 160°C), and liquid to solid ratio (3-11 mL/g) were chosen as process variables. The ranges of the variables were based on the information of the single effect experiment (data not shown). Design-Expert v.8.0.6 (Stat-Ease Inc., Minneapolis, MN) was used to create a central composite design (CCD). The design consisted of 27 sets of experiments, including three central points, as shown in Table 1. Statistical analysis was performed using the software to regress the data obtained. Fischer's test was used to determine the type of model equation, while the Student's t-test was performed to determine the statistical significance of regression coefficients.

RESULTS AND DISCUSSION

1. Composition of Corn Cob

The main composition of the corn cob, on a dry weight basis,

Table 2. Corn cob composition reported by other authors and experimental

	%Glucan	%Xylan	%Arabinan	%Lignin
Garrote (2001)	31.7	30.9	3.77	20.3
Nabarlatz (2007)	38.5 ± 0.3	29.5 ± 0.7	3.3 ± 0.3	18.7 ± 0.4
Experimental	34.2	32.9	3.1	17.9

was glucan 34.2%, xylan 32.9%, arabinan 3.1%, lignin 17.9%. The results were similar to the main component composition of corn cob reported by others, as shown in Table 2 [22,23]. The amount of corn produced per year has been increasing in the major corn producer countries [24]. However, corn cob is considered as agriculture waste without efficiently utilizing. The structural carbohydrates (mainly glucan and xylan) account for more than 65% of corn cob. Corn cob also has low recalcitrance to enzyme and microbial activity [25]. Thus, corn cob is a promising substrate for a biorefinery.

2. Inhibitors and Byproducts during the Process

To better understand the dilute formic hydrolysis of corn cob, a concentration of furfural, 5-HMF, acetic acid, and arabinose is shown in Table 1. Furfural and 5-HMF were formatted from the degradation of pentose and hexose, respectively. Furans have a harmful influence on the bioconversion of xylose. In the runs lower than 140°C , trace amounts of furfural were detected in the reaction solution. When the reaction temperature was above 150°C , the furfural concentration drastically increased. Maximum amount of 9.2 g/L furfural was obtained in run 12 (4%, 160°C , 7 mL/g, and 90 min). It was also interpreted that the increase in reaction temperature, treatment time, and acid concentration increased the concentration of 5-HMF. Thus, to keep the furans at low concentration, the reaction temperature should not exceed 150°C . Because the acetyl group is one of the components in hemicellulose, it is unavoidable to release acetic acid during the acid pretreatment [26]. Maximum acetic acid concentration of 6.6 g/L was dissolved in run 12, indicating a high reaction temperature, elevated formic acid concentration, long reaction time, and low liquid to solid ratio resulted in more acetic acid. In all the experiments, arabinose concentration remained between 1.0 and 4.9 g/L. The high concentration of glucose in the solution affected the bioconversion of xylose into xylitol [27]. Selectivity (the xylose/glucose ratio) is an important parameter for optimizing the hydrolysis conditions for high concentration of xylose and low concentration of glucose. In our study, the selectivity of xylose was higher than 6 g/g, indicating that compared to xylose, glucose was difficult to generate in the reaction conditions.

3. Optimization of the Hydrolysis Process by RSM

3-1. Statistical Modeling

The responses, yield (Y) and selectivity (S) of xylose, obtained by dilute formic acid pretreatment of corn cob are shown in Table 1. Using the designed experimental data, the "fit summary report" of Design-Expert recommended a quadratic model for both xylose yield and selectivity. The quadratic models with actual variables are given in Eqs. (3) and (4), which represent the xylose yield (Y) and selectivity (S) as a function of formic acid concentration (X_1), reaction temperature (X_2), liquid to solid ratio (X_3), and treatment time (X_4).

$$Y = -2085.45214 + 83.83335X_1 + 23.7330X_2 + 11.32414X_3 + 3.68032X_4$$

Table 3. ANOVA for xylose yield and selectivity models

Source	Sum of squares		Df		Mean square		F value		P value	
	Y	S	Y	S	Y	S	Y	S	Y	S
Model	8381	332	14	14	599	23.72	224.6	55.07	<0.0001	<0.0001
Residual	31.99	5.71	12	12	2.67	0.43				
Lack of fit	31.59	5.16	10	10	3.16	0.52	15.71	154	0.0613	0.0064
Pure error	0.40	6.667E-3	2	2	0.20	3.333E-3				
Cor total	8144	337	26	26						
R-Squared	0.99	0.98								

$$\begin{aligned}
 & -0.43961X_1X_2 - 0.36053X_1X_3 + 0.037173X_1X_4 - 0.021365X_2X_3 \\
 & - 0.024337X_2X_4 + 4.56573E-3X_3X_4 - 2.25976X_1^2 - 0.065710X_2^2 \\
 & - 0.33963X_3^2 - 1.14557E-03X_4^2
 \end{aligned} \quad (3)$$

$$\begin{aligned}
 S = & -728.08776 + 20.11979X_1 + 8.77552X_2 + 7.37344X_3 + 1.41281X_4 \\
 & - 0.11687X_1X_2 - 0.013125E-3X_3X_4 - 0.013125X_1X_4 \\
 & - 0.057118X_2X_3 - 8.68750E-03X_2X_4 + 0.011771X_3X_4 - 0.30938X_1^2 \\
 & - 0.025469X_2^2 - 0.014844X_3^2 - 1.19097E-3X_4^2
 \end{aligned} \quad (4)$$

Regression analysis was performed to fit the response function

and experimental data. The models for xylose yield and selectivity were evaluated by the analysis of the variance (ANOVA), which are shown in Table 3. For both responses, the regression was statistically significant at 95%, as an evidence from Fisher's test with a very low probability ($p < 0.0001$). The regression coefficient (R^2) of the first response and the second response was 0.99 and 0.98, explaining 99% and 98% of the variability in the responses.

3-2. Effect of Reaction Temperature on Xylose Yield and Selectivity

Xylose production was significantly affected by reaction tem-

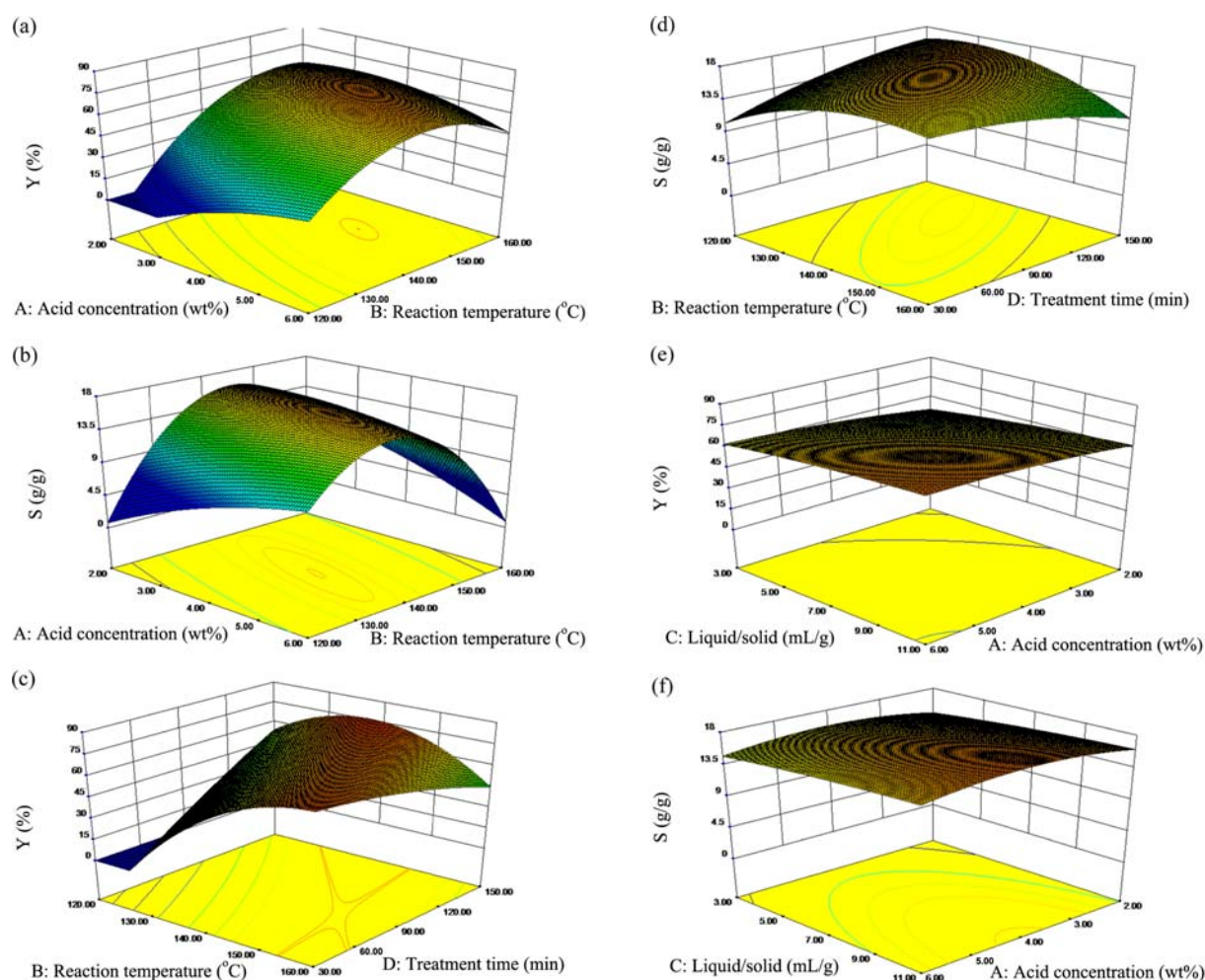


Fig. 2. Effect of reaction temperature, formic acid concentration, treatment time, and liquid to solid ratio on xylose yield and selectivity. (a) And (b) treatment time and liquid to solid ratio were fixed at 90 min and 7 mL/g. (c) And (d) acid concentration and liquid to solid ratio were fixed at 4% and 7 mL/g. (e) And (f) reaction temperature and treatment time were fixed at 140 °C and 90 min.

perature. The effect of temperature (120–160 °C) on xylose formation is depicted in Fig. 2(a) to (d). It is obvious that xylose yield first increased but decreased after the maximum point with increasing temperature. The selectivity of xylose followed a similar trend. It was interpreted that maximum xylose yield was 71% at about 150 °C, and maximum xylose selectivity was 16.8 g/g at about 141 °C when acid concentration was fixed at 4%, liquid to solid ratio at 7 mL/g, and treatment time at 90 min.

The dilute formic acid pretreatment of corn cob could only partly hydrolyze hemicellulose at a lower temperature. Under the circumstance, small amount of xylose was generated. With the increasing of the temperature, the reaction rate of hemicellulose to xylose was accelerated, so the amount of xylose was larger than that of lower temperature. However, the rate of xylose to furfural was also increased so the xylose formed tended to degrade to furfural with the elevating temperature. The filtrate's color changing from yellow to light brown was also found in our study from lower to higher temperature. This was also an evidence of severe degradation of xylose. Compared to xylose, the amount of glucose was small because the crystalline structure of cellulose was partially hydrolyzed from 120 to 160 °C. The amount of glucose increased with the temperature increasing from 120 to 160 °C. So the selectivity of xylose followed the similar trend of the yield of xylose: first increased with enhancing temperature and then decreased.

The activation energy of hemicellulose hydrolysis was lower than that of xylose degradation, indicating that higher temperature was in favor of xylose degradation [28,29]. Canettieri and Rocha [30] found that the increase of temperature provided a higher xylose extraction from *Eucalyptus grandis* residue when the temperature was below 160 °C and the further increase of temperature posed a negative effect on xylose extraction. A similar varying tendency of xylose yield was also reported by Cassales et al. [31]. Hence, exorbitant temperature had a negative effect on xylose production.

3-3. Effect of Acid Concentration on Xylose Yield and Selectivity

The effect of formic acid concentration (2%–6%, pH_{20°C} 2.02–1.76) on xylose yield and selectivity is shown in Fig. 2(a) and (b). The figures indicate that at lower temperature the xylose yield increased with enhancing acid concentration. However, at higher temperature the further increasing of acid concentration had a negative effect on xylose yield. Similar trends of xylose selectivity were obtained with increasing acid concentration. Xylose yield of more than 71% and selectivity of more than 16 g/g were reached in the formic acid concentration ranging from 4% to 5%, when reaction temperature was between 140 and 150 °C, liquid to solid ratio fixed at 7 mL/g, and treatment time set at 90 min.

During dilute acid pretreatment of lignocellulosic material process, H⁺ acts as the role of catalyst. With the increase of formic acid, the H⁺ concentration in the reaction system was also elevated. The elevation of H⁺ concentration had a positive effect on the reaction rate constant of xylan to xylose. The increase of H⁺ concentration also enhanced the xylose to furfural reaction rate. At higher temperature the interactive effect of H⁺ and reaction temperature became the main factor which affected the yield and selectivity of xylose. Under this circumstance, the degradation of xylose was significantly promoted with the increase of formic acid.

Yemis and Mazza [32] reported maximum xylose yield was obtained in the pH range of 2.1–1.6 and xylose yield drastically de-

creased with the further decrease of pH and increase of temperature. Shatalov and Pereira [7] reported that the desirable acid concentration of dilute sulfuric hydrolysis of giant reed was 1–1.5%. They also indicated that the further increase of medium acidity caused drop in xylose yield at higher temperature. Their results follow the same trend as ours. All the works showed that the concentration of acid had an important effect on xylose production and an adverse effect at higher reaction temperature. From the prospect of high xylose yield and low cost of catalyst, the formic acid concentration should be kept not more than 5%.

3-4. Effect of Treatment Time on Xylose Yield and Selectivity

To study the effect of treatment time on xylose yield and selectivity, the treatment time ranged from 30 to 150 min. The xylose yield and selectivity at different reaction times are shown in Fig. 2(c) and (d), when acid concentration and liquid to solid ratio were fixed at 4% and 7 mL/g, respectively. The xylose yield clearly increased with the enhancing of reaction time at low temperature, but the opposite trend occurred at high temperature.

Below 140 °C, the xylose and glucose production rates were low, so the extension of reaction time resulted in high xylose yield and selectivity. However, above 150 °C, the formed xylose tended to convert to furfural at longer reaction time. Especially at 160 °C the maximum xylose yield and selectivity were obtained at about 30 min, which was the shortest reaction time in our study.

Lu and Mosier [29] reported the optimal time of maximum xylose yield was accordingly shortened with the increase of reaction temperature. Same varying tendency of the effect of reaction time on xylose yield was also reported by Akpınar et al. [33] who studied the antioxidant activity during xylose production using H₂SO₄ as catalyst. During the industrial process, a longer reaction time and lower temperature can meet the demand of energy integration because the process can use the steam after other processes which needed higher temperature.

3-5. Effect of Solid to Liquid Ratio on Xylose Yield and Selectivity

Treatments at different liquid to solid ratios (3–11 mL/g) were carried out to investigate the effect of liquid to solid ratio on xylose yield and selectivity. The experimental results are presented in Fig. 2(e) and (f). When the liquid to solid ratio increased from 3 to 7 mL/g, the xylose yield enhanced from about 30% to 63% and the xylose concentration decreased from 34.2 g/L to 30.8 g/L. For the further increase of liquid to solid ratio from 7 to 11 mL/g, the xylose yield slightly increased from about 63% to 69%, indicating that the liquid-to-solid ratio was not a significant factor at higher liquid to solid ratio. In this circumstance, the xylose concentration decreased from 30.8 g/L to 21.3 g/L. The increase of liquid to solid ratio only had a trace effect on xylose selectivity.

With the liquid-to-solid ratio decreasing from 11 to 3 mL/g, the viscosity of the reaction system increased. Hence, the liquidity of the system was decreased. It was difficult for the H⁺ to transfer to the interface of the corncob at the lower liquid to solid ratio. Thus, the hydrolysis reaction became mild compared to high liquid to solid ratio. Therefore, xylose yield increased with the increase of liquid to solid ratio. In the dilute formic treatment of corn cob, only a part of glucan was hydrolyzed. The amount of glucose followed a similar trend of xylose with the increase of liquid-to-solid ratio. Thus, the liquid-to-solid ratio had little effect on xylose selectivity.

Canettieri and Rocha [30] reported maximum xylose extraction

Table 4. Possible solutions for the optimum conditions that maximize xylose yield

Solution	Acid concentration wt%	Temperature °C	Liquid/solid mL/g	Time min	Y (%)	S (%)
1	5.0	134.9	7.0	150.0	82.8	14.9
2	5.0	135.0	7.0	150.0	82.8	14.9
3	5.0	134.6	7.0	150.0	82.8	15.0
4	5.0	135.2	7.0	150.0	82.8	14.8
5	5.0	134.6	7.0	150.0	82.7	15.0
6	5.0	136.7	7.0	150.0	82.6	14.1
7	5.0	135.4	7.0	149.0	82.5	14.8
8	5.0	137.1	7.0	150.0	82.5	13.9
9	5.0	135.1	6.9	150.0	82.4	14.7
10	5.0	131.6	7.0	150.0	82.1	15.9

was obtained at the acid solution-to-solid ratio of 8.6, which was the highest one in their study. Dominguez et al. [34] showed that the highest concentration of xylose was obtained at the lowest liquid to solid ratio. High concentration of xylose had an advantage over low xylose concentration for the purpose of energy saving and further converting of xylose to other chemicals. For example, in a commercial xylose production, reactions at high liquid to solid ratio require larger amount of energy than that of low liquid-to-solid ratio to produce a certain amount of xylose. For the purpose of production of a given quantity of xylitol, a low concentration of xylose means a larger reactor. Although a higher liquid-to-solid ratio obtained higher xylose yield, it was better to set the overall cost of the whole biorefinery process as the criterion.

According to the two models, the optimal working conditions, based on high level of xylose yield and selectivity, were chosen using the following criteria: xylose yield maximize, selectivity >10 g/g, formic acid concentration ≤5%, liquid-to-solid ratio ≤7 mL/g. The best possible solutions which satisfied the requirements are presented in Table 4. From these results, formic acid concentration of 5%, reaction temperature of 135 °C, liquid-to-solid ratio of 7.0 mL/g and 150 min were selected as an optimum point. To confirm the validity of the results obtained from the models, three hydrolysis runs were performed under the optimum point and a mean value of xylose yield of 81.6% and selectivity of 15.1 g/g was attained. The results show that the models adapted well to the experiments.

4. Optimization of the Process when Adding Trivalent Salts in the Reaction System

4-1. Effect of Trivalent Salts on Xylose Yield and Selectivity

To study the impact of trivalent salts on the xylose yield and selectivity, FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$ were added to the dilute formic acid solution, respectively. In each solution, the concentration of the trivalent ion was maintained at 0.05 mol/L. In this set of experiments, formic acid concentration, reaction temperature, and liquid-to-solid ratio were 5%, 135 °C, and 7 mL/g, respectively. The results of trivalent salts on xylose yield and selectivity at different treatment times are shown in Fig. 3. Compared with no trivalent salts, higher xylose yields were obtained, but the selectivities were decreased. The optimal xylose yields for FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$, were 91.4%, 89.4%, and 88.0%, and the corresponding selectivities were 10.1 g/g, 10.9 g/g, and 11.1 g/g, respectively. The reaction times of the corresponding optimal xylose yields for the three

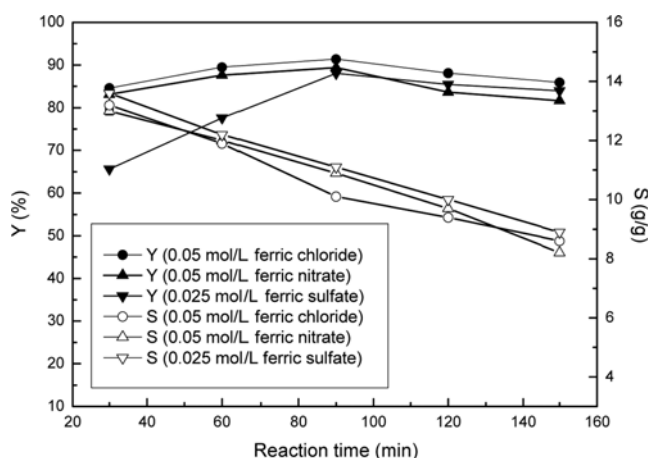


Fig. 3. Effect of trivalent salts on xylose yield and selectivity, when formic acid concentration, reaction temperature, and liquid to solid ratio were fixed at 5%, 135 °C, and 7 mL/g, respectively.

salts were shortened to 90 min.

In the reaction system, trivalent salts acted as the role of promoter. The higher obtained xylose yield, when adding trivalent salts to the formic acid solution, might be the result of the change of reaction mechanism compared with dilute formic acid catalyst process. The mechanism was postulated as follows: (1) the trivalent salts were Lewis acids and acidity of the system was increased when adding the salts; (2) trivalent salts increased the diminishing of the corn cob particles as the evidence of severe crashing of the microscopic structure from the SEM (data shown in Fig. 4); (3) diffusion of H^+ , formic acid, trivalent positive ion and negative ion to the inner surface of corn cob; (4) trivalent positive ion combined with the glycosidic oxygen decreasing the interaction of two sugar unit; (5) H^+ attacked the glycosidic oxygen to cause the broken of C-O bond and H_2O added to the carbon cation; and (6) releasing of xylose, H^+ , and trivalent positive ion. The diminishing of the corn cob size increased the possibility that the catalyst contacted corn cob. The combination of the trivalent ion and glycosidic oxygen might decrease the hydrolysis activation energy. Thus, the adding of trivalent salts accelerated the hydrolysis reaction to a certain extent. Therefore, the optimal reaction time was shortened compared with dilute

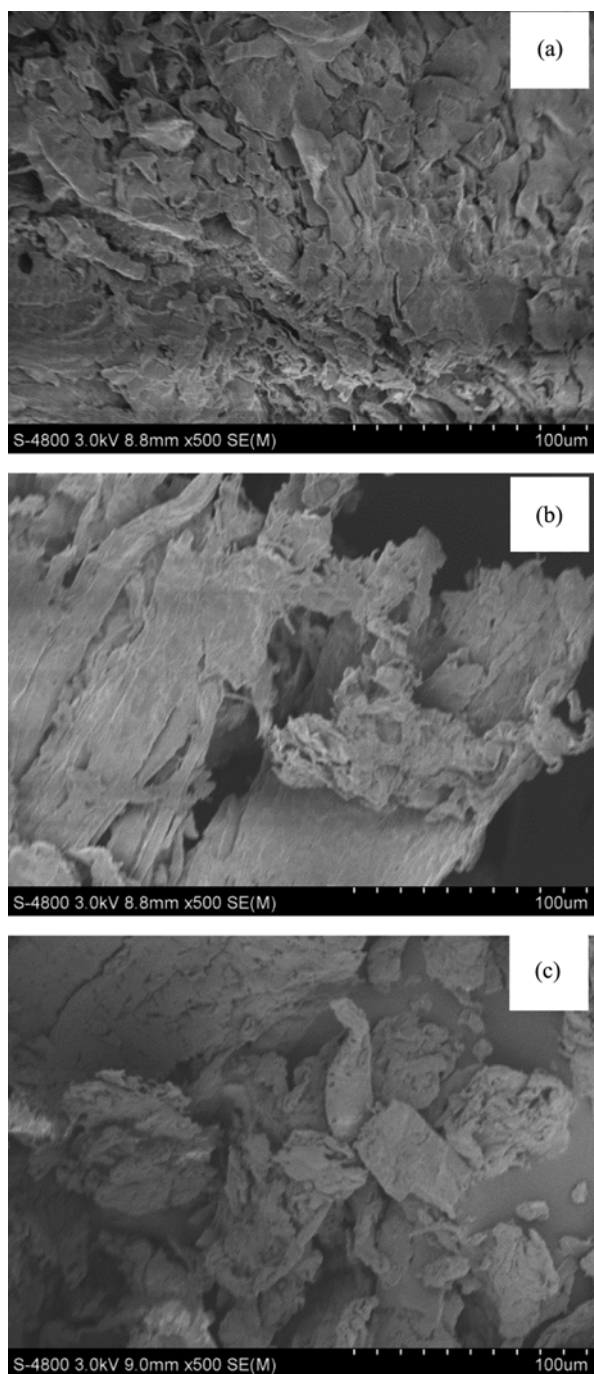


Fig. 4. Microscopic structure of corn cob (a) untreated (b) treated when formic acid concentration, reaction temperature, time, and liquid to solid ratio were at 5%, 135 °C, 150 min, and 7 mL/g, respectively (c) treated with 0.05 mol/L FeCl_3 when formic acid concentration, reaction temperature, time, and liquid to solid ratio were at 5%, 135 °C, 150 min, and 7 mL/g, respectively.

formic acid process. Trivalent salts also had a positive effect on hydrolysis of glucose. Thus, xylose selectivity corresponding to the optimal xylose yield at the present of trivalent salts was lower than that without the trivalent salts.

Liu et al. [17] reported that trivalent salt had the highest capacity to increase the hemicellulose decomposition in pretreatment of corn

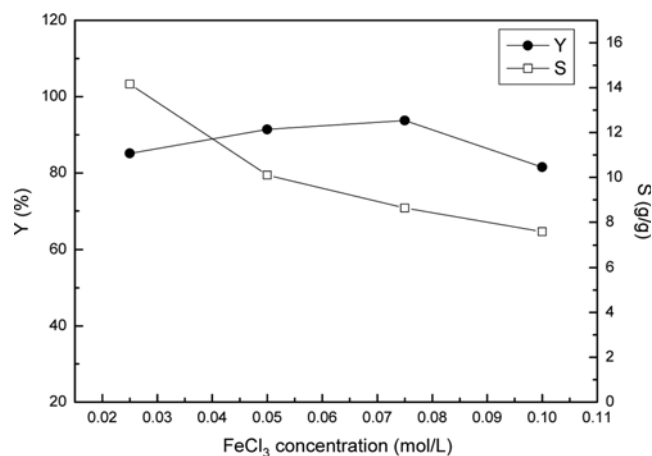


Fig. 5. Effect of FeCl_3 concentration on xylose yield and selectivity, when formic acid concentration, reaction temperature, liquid to solid ratio, and treatment time were maintained at 5%, 135 °C, 7 mL/g, and 90 min.

stover. In wheat straw pretreatment, the hemicellulose removal was significantly increased with 200 mM FeCl_3 solutions at 120 °C [35]. All their work showed that the use of trivalent salt accelerated the hydrolysis of hemicellulose.

4-2. Effect of FeCl_3 Concentration on Xylose Yield and Selectivity

In the pretreatment of corn cob using formic acid and the studied trivalent salts, FeCl_3 showed the potential of highest xylose yield. Thus, the effect of FeCl_3 concentration on the xylose production was determined to maximize the xylose yield. In the experiments, formic acid concentration, reaction temperature, liquid-to-solid ratio, and treatment time were maintained at 5%, 135 °C, 7 mL/g, and 90 min, respectively. The results are presented in Fig. 5. When FeCl_3 concentration increased from 0.025 to 0.1 mol/L, the xylose yield increased slightly first then decreased and xylose selectivity decreased from 14.2 to 7.6 g/g.

The hemicellulose tended to be easily hydrolyzed with increasing the FeCl_3 concentration. However, more FeCl_3 increased not only the generation of xylose but also degradation of xylose to furfural. Thus, the xylose yield had a reduction after the maximum point with the increasing of FeCl_3 concentration from 0.025 to 0.1 mol/L. The increasing of FeCl_3 concentration also had a positive effect on the generation of glucose. Hence, the selectivity of xylose decreased with the increasing of FeCl_3 concentration in the reaction system. From the prospect of maximizing the xylose yield, the optimal concentration of FeCl_3 was 0.075 mol/L under the reaction condition as follows: formic acid concentration, reaction temperature, liquid-to-solid ratio, and treatment time were 5%, 135 °C, 7 mL/g, and 90 min, respectively.

Liu et al. [17] pointed out that the increasing of FeCl_3 from 0.04 to 0.10 mol/L had a positive effect on the hemicellulose removal, but the FeCl_3 concentration of 0.20 mol/L accelerated the xylose into degradation product. From their results, with the increasing of FeCl_3 amount, the same conclusions as ours were obtained.

CONCLUSIONS

We focused on the determination of the optimal condition of pro-

duction of xylose from corn cob using dilute formic acid as catalyst. Through the quadratic models established by RSM, acid concentration of 5%, reaction temperature of 135 °C, liquid-to-solid ratio of 7 g/mL, and reaction time of 150 min were optimal for xylose production. The xylose yield and selectivity were 81.6% and 15.1 g/g under the above conditions, respectively. The addition of trivalent salts to the reaction system had a positive effect on xylose yield but negative on xylose selectivity. Among the studied trivalent salts, FeCl₃ was the best one to promote the xylose yield.

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