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The optimization of formic acid hydrolysis of xylose in furfural production

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ABSTRACT

Formic acid, a byproduct of furfural process, can be an effective catalyst for dehydration of xylose into furfural. Due to the low corrosion resistance, easy to be separated and reused, there is a growing interest in the use of formic acid as catalyst. In this study, response surface methodology (RSM) was used to optimize the hydrolysis process in order to obtain high furfural yield and selectivity. Three important parameters, initial xylose concentration (40–120 g/L), temperature (170–190 °C), formic acid concentration (5–15 g/L) were optimized. The optimum initial xylose concentration, formic concentration, reaction temperature were 40 g/L, 10 g/L, and 180 °C, respectively. Under these conditions, the maximum furfural yield of 74% and selectivity of 78% were achieved.

1. Introduction

Biomass, which is primarily composed of cellulose, hemicellulose, and lignin, is one of the world's most important renewable energy sources.[1,2] As carbohydrates represent 75% of the annually renewable biomass of about 200 billion tons, their utilization for the generation of organic chemicals that eventually replace those derived from petrochemical resources is a major challenge for green chemistry.[3,4] The interest for producing chemicals from renewable resources has increased in the last decade in direct relation to the declining reserves and increasing prices of fossil fuels.

Furfural is a key derivative, readily accessible from renewable biomass and agriculture surpluses, for the production of a wide range of important non-petroleum-derived chemicals.[3] There is a considerable literature on the use of furfural and its increasing demand in different fields, such as oil refining, plastics, and the pharmaceutical and agrochemical industries.[5–7]

So far, there is no synthetic route available for furfural production in the chemical industry. Furfural is exclusively produced from lignocellulosic biomass by dehydrating pentosan (mainly xylan) which is present in significant amounts in the hemicelluloses of some agriculture residues.[8–10] The technical process for furfural production involves the acid catalyzed hydrolysis of hemicellulosic pentose fractions of biomass and consecutive dehydration of the pentose monomers[3] (xylose being the most predominant pentose in most feedbacks). There are two types of technologies to produce furfural. In one-stage technology, depolymerization of pentosans into xylose and dehydration into furfural occur simultaneously. In two-stage technology, a dissolution and depolymerization of pentosans occur under mild conditions, followed by dehydration of pentose into furfural. The first step proceeds rapidly and at high yield. The advantage of two-stage technology is based on the fact that the residual lignocellulose is almost unaltered and can be used for conversion to other chemicals (glucose, ethanol, phenol, etc.) in a subsequent step. Furthermore, the furfural yield will increase remarkably, so two-stage technology represents the developmental tendency of furfural production.[11]

The literature records two alternative hypotheses for the mechanism of dehydration of xylose to furfural, namely (I) a succession of reactions proceeding mainly via open-chain intermediates, and (II) an acid-catalyzed sequence proceeding through a 2,5-anhydride intermediate. Feather et al.[12–14] reasoned that structures **1** and **2** in represent the ring and open chain forms of xylose, which are in equilibrium, then structure **2** convert to structure **3** reversibly, next furfural is formed following the liberation of three water molecules from structure **3** as show in Figure 1. Antal et al.[15] and NimLos et al.[16] deduce that the acid catalyze the reaction of xylose to 2,5-anhydride intermediate, then furfural is formed by losing three water molecules as show in Figure 2. While it has been studied for several decades, the exact mechanism of the furfural forming reaction has not been unequivocally established. But several side reactions lead to the decrease of furfural yield, as shown in Scheme 1, such as fragmentation reactions of xylose, consecutive condensation reactions between furfural and intermediates of the xylose-to-furfural, and resinification of furfural.

In most industrial furfural process, conventional mineral acids, such as sulfuric acid, phosphoric acid, are generally used as catalysts.[17] The cost and inefficiency of separating these catalysts from the products makes their recovery impractical, resulting in large volumes of acid waste, which must be neutralized and disposed

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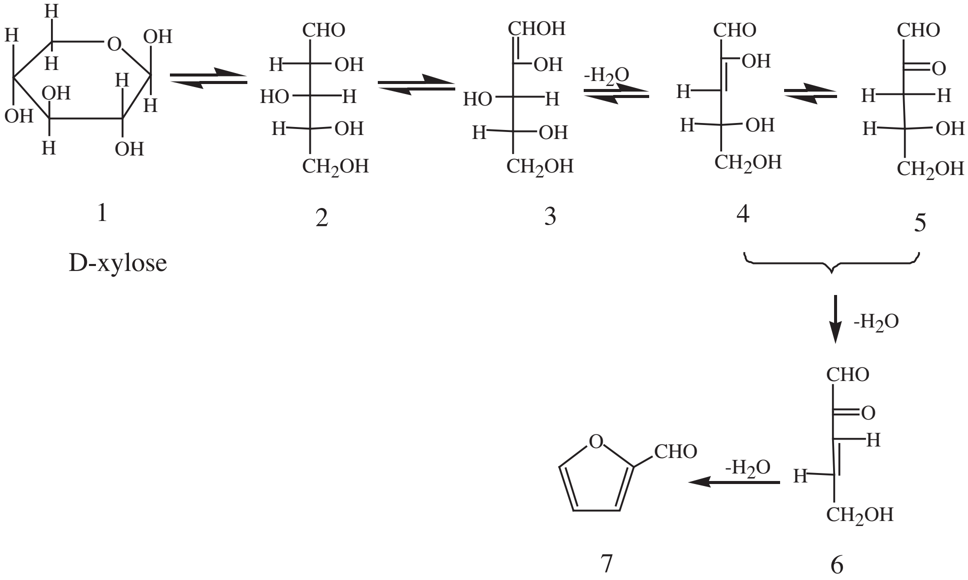


Figure 1. Mechanism (I) of the formation of 2-furfural from D-xylose.[13]

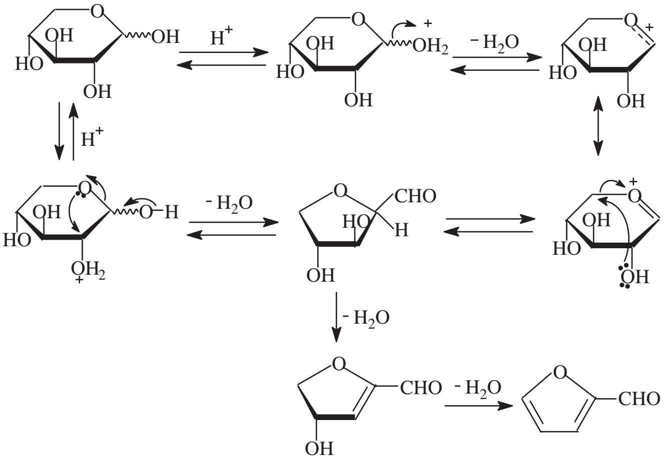
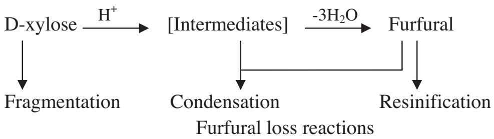


Figure 2. Mechanism (II) of the formation of 2-furfural from D-xylose.[15]



Scheme 1. Simplified scheme of the possible reaction in the xylose-to-furfural process.

off. Other drawbacks include corrosion and safety problems. Due to the compositional complexity of hemicellulose, the hydrolysis reaction is constituted of parallel paths that lead to a complex mixture of sugars (xylose, glucose, arabinose, and mannose) and organic acids (formic acid, acetic acid, levulinic acid).[18] Formic acid results from the cleavage of formyl groups or the hydrolytic fission of the aldehyde group of hydroxymethylfurfural and furfural.[3,19] So furfural waste water contained a lot of formic acid (7.8 g/L, Wuji Furfural Co. of China) which can be reclaimed efficiently with extractive technology.[20,21] If it is chosen as catalyst for furfural production, many drawbacks of mineral acid catalysts will be avoided to a certain extent, and it will realize catalyst system self-production and reduction in production costs. Furthermore, it will reduce industrial pollution emissions and promote the development of furfural process. From a green chemistry perspective, many studies are carried out to evaluate the efficiency of new catalysts (solid acid) on the conversion of xylose.[22,23] In spite of lots of advantages, the solid acid is prone to inaction, which needs more study on its structure and stability.

To our knowledge, there are scarce reports about dehydration of xylose into furfural with formic acid as catalyst. The aim of this work was to evaluate whether formic acid, a byproduct of furfural process, could be an effective catalyst for dehydration of xylose into furfural. Furfural yield was evaluated by varying the initial xylose concentration, reaction temperature, and formic acid concentration. Moreover, the time courses of furfural concentrations of vapor and liquid phases in the reactor were measured. In the present work, dehydration of xylose into furfural was carried out in an autoclave semi-batch mode.

2. Results and discussion

2.1. Formic acid was an effective catalyst

Sulfuric acid and phosphoric acid were widely used as catalysts in industrial furfural process. Our research group had investigated them as catalysts for dehydration of xylose into furfural respectively, and proved that the optimal concentrations of sulfuric acid and phosphoric acid were both about 8 g/L for initial xylose concentration 40–120 g/L. So, just making comparison with formic acid, furfural yield was evaluated using phosphoric acid and sulfuric acid as catalysts with initial xylose concentration 80 g/L by varying reaction temperature, respectively. The experimental results, shown in Figure 3, indicated that furfural yield increased at first, and then decreased with increasing reaction temperature for three different catalysts. The optimal reaction temperatures were 155, 160, and 180 °C for sulfuric acid, phosphoric acid, and formic acid, respectively. And the maximums of furfural yield obtained were 62%, 65%, and 70%, correspondingly. Compared to sulfuric acid and phosphoric acid, a higher furfural yield could be obtained with formic acid as catalyst, but the optimal reaction temperature also rose by about 20 °C. This was easy to understand.

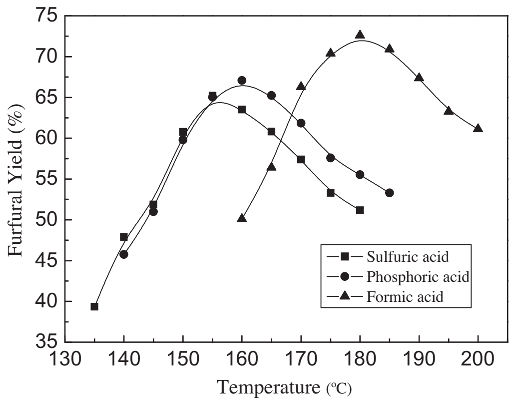


Figure 3. Dependence of furfural yield on reaction temperature with initial xylose concentration 80 g/L for different catalyst.

The catalytic activity of phosphoric acid and sulfuric acid for dehydration of xylose into furfural was higher than formic acid. They made the dehydration of xylose into furfural and accompanied side reactions easier. So the optimal reaction temperature dropped by about 20 °C. In the experiments, it was found that there were more resins adhered to the internal wall of the autoclave with phosphoric acid and sulfuric acid as catalysts compared to formic acid. This indicated furfural formed was more apt to degrade with higher active mineral acid as catalysts. Experimental results indicated that the higher furfural yield could be obtained with formic acid as catalyst for dehydration of xylose into furfural.

Yemiş and Mazza[24] compared the effect of four strong mineral acids (hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid) and two organic acids (acetic acid, and formic acid) on furfural yield. The furfural yields obtained from xylose in the presence of HCl, H_2SO_4, HNO_3, H_3PO_4, CH_3COOH, and HCOOH were 37.5%, 31.9%, 3.5%, 27.6%, 15.8%, and 23.8% at a pH of 1.12, respectively. The result showed that formic acid was an effective catalyst too. The furfural yield reported by I. Agirrezabal-Telleria et al.[22] and Antunes et al.[23] was less than 70%. So, taking into account the higher furfural yield and other advantages, formic acid will be an alternative catalyst in furfural production.

2.2. Reaction time was set as 6.5 h

In the experiments, the furfural formed was removed from the autoclave semi-batch mode as a vapor mixed with steam continuously, the time courses of furfural concentrations of vapor and liquid phases in the autoclave semi-batch mode were measured, and the results were presented in Figure 4. The furfural concentration of vapor phase is higher than liquid phase, and their relationship was determined by vapor liquid equilibrium. The higher the initial xylose concentration was, the higher the furfural concentration of the liquid phase in the reactor was. It can be seen that the furfural concentrations of vapor and liquid phases reached maximum in 2 h at 180 °C, and furfural concentrations varied slightly when reaction time was in the range of 5–7 h. So the furfural yield was optimal when reaction time was 6.5 h in the later experiments.

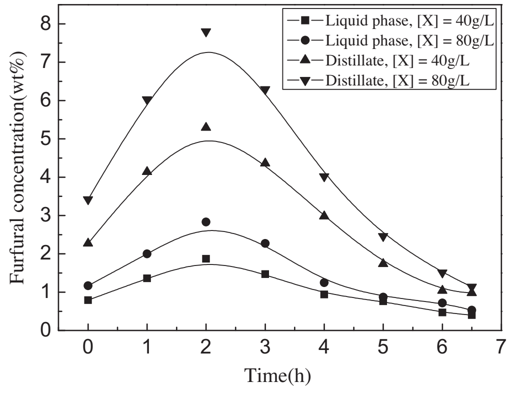


Figure 4. The furfural concentrations of distillate and liquid phases in the autoclave at different time with 15 g/L formic acid.

Table 1
Experimental rang and levels of independent process variables

Independent variables	Symbol	Range and levels		
		−1	0	+1
Initial xylose concentration (g/L)	X_1	40	80	120
Temperature (°C)	X_2	170	180	190
Formic concentration (g/L)	X_3	5	10	15

Table 2
BBD and results obtained by hydrolysis of xylose

Run	Variables			Responses	
	X_1	X_2	X_3	Y_1 (%)	Y_2 (%)
1	−1	1	0	68.87	76.52
2	0	1	−1	69.32	68.97
3	0	1	1	63.05	68.73
4	0	0	0	64.57	75.55
5	0	0	0	66.77	75.34
6	−1	−1	0	70.47	76.20
7	0	−1	1	69.78	72.17
8	−1	0	−1	69.53	76.99
9	1	−1	0	58.00	64.75
10	1	0	1	59.74	63.98
11	0	0	0	68.85	75.83
12	1	1	0	59.24	63.83
13	−1	0	1	70.87	75.55
14	0	−1	−1	64.15	72.39
15	1	0	−1	60.04	65.33

Y_1 (yield) = (Fur/Furmax) × 100; Y_2 (selectivity) = (Yield furfural/Conversion xylose) × 100.
Fur = furfural obtained in the distillate, Fur_{max} = maximum furfural based on the xylose in feed.

2.3. Optimization of the hydrolysis process by RSM

The Design Expert v.8.0.6 (Stat-Ease Inc., Minneapolis, MN) was used to create a Box-Behnken Design (BBD), which is a response surface method. It was also used for regression and graphical analyses of 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. Three important parameters, initial xylose concentration (40–120 g/L), temperature (170–190 °C), formic acid concentration

Table 3
Analysis of variance for furfural yield and selectivity models

Source	Sum of squares		Df		Mean square		*F* value		*P* value	
	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
Model	283.99	352.42	9	9	31.55	39.16	15.83	33.78	0.0036	0.0006
Residual	9.97	5.80	5	5	1.99	1.16				
Lack of fit	0.81	5.68	3	3	0.27	1.89	0.059	31.75	0.9770	0.0307
Pure error	9.16	0.12	2	2	4.58	0.060				
Cor total	293.96	358.22	14	14						
R-squared	0.97	0.98								

(5–15 g/L) were included in the experimental design, as show in Table 1. The design consisted of 15 sets of experiments, including 3 central points, as show in Table 2. The quadratic model was selected for predicting the optimal point and is expressed as

$$Y_1 = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 \quad (1)$$

$$Y_2 = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (2)$$

where Y_1, Y_2 represent response furfural yield, selectivity. a_0,b_0 are the interception coefficients, a_1,b_1, a_2,b_2, and a_3,b_3 are the linear terms, a_{11},b_{11}, a_{22},b_{22}, a_{33},b_{33}, a_{12},b_{12}, a_{13},b_{13}, and a_{23},b_{23} are the quadratic terms, X_1,X_2, and X_3 represent variables studied.

The quadratic models with actual variables are show in Eqs. 3 and 4, which represent the furfural yield (Y_1) and selectivity (Y_2) as a function of initial xylose concentration (X_1), temperature (X_2), formic acid concentration (X_3).

$$Y_1 = -179.20 - 0.23X_1 + 2.33X_2 + 10.59X_3 - 1.29E - 03X_1^2 - 5.28E - 03X_2^2 + 1.49E - 02X_3^2 + 1.78E - 03X_1X_2 - 2.05E - 03X_1X_3 - 5.95E - 02X_2X_3 \quad (3)$$

$$Y_2 = -761.00 + 0.26X_1 + 9.24X_2 + 1.88X_3 - 1.67E - 03X_1^2 - 2.57E - 02X_2^2 - 9.75E - 02X_3^2 - 7.75E - 04X_1X_2 + 1.10E - 047X_1X_3 - 1.37E - 04X_2X_3 \quad (4)$$

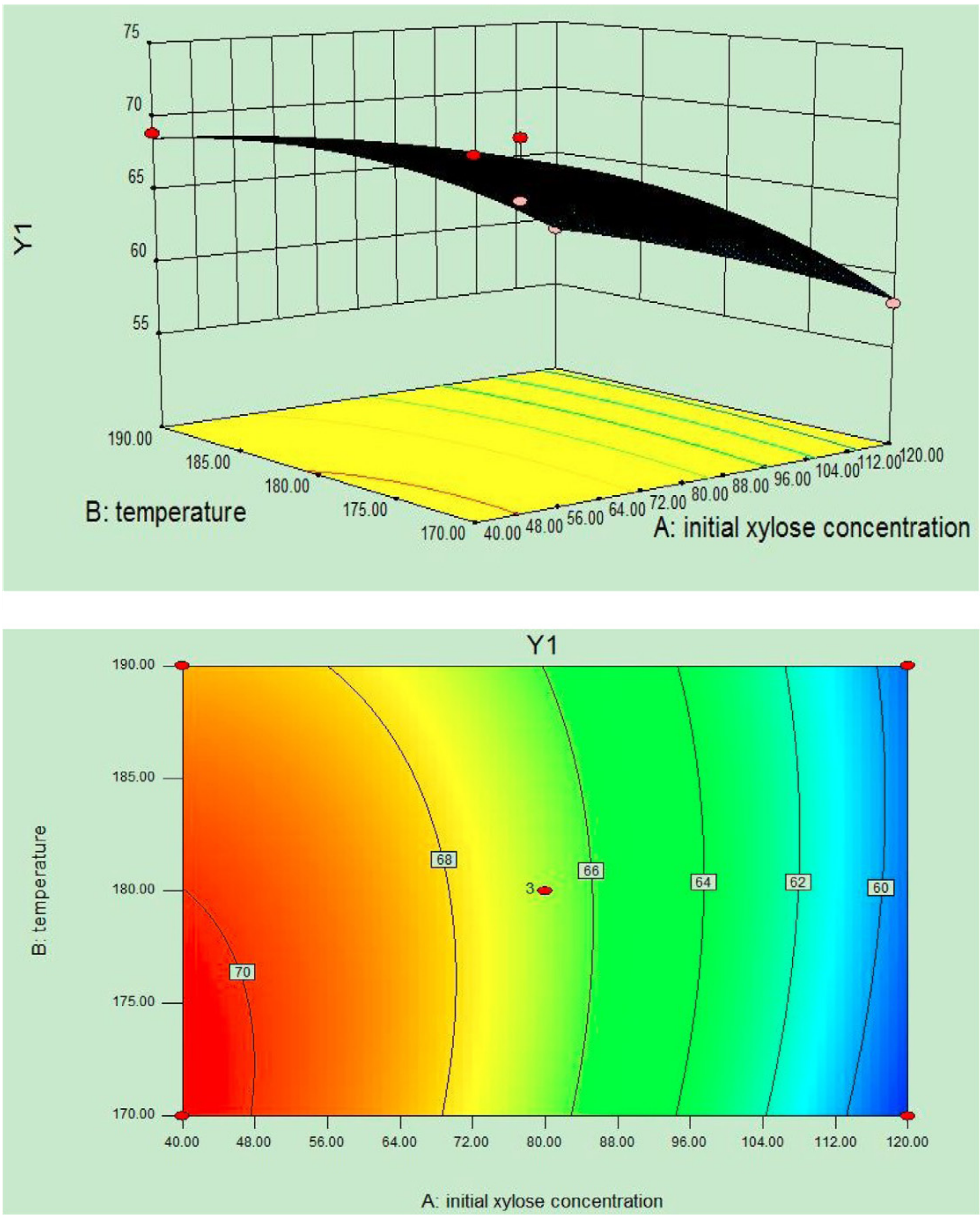


Figure 5. Effect of initial xylose concentration and temperature on furfural yield when formic concentration was set at 10 g/L as the center point.

The second-order model for furfural yield and selectivity was evaluated by ANOVA, which is show in Table 3. For both responses, the regression was statistically significant at the 95% confidence level, as evidenced from the Fisher's F-test with a very low probability (P <0.0036 or 0.0006). The regression coefficient for the first (Y_1) and the second responses (Y_2) was 0.97 and 0.98, respectively, explaining 97% and 98% of the variability in the responses.

2.3.1. Dependence of furfural yield and selectivity on initial xylose concentration

The experimental results presented in Figures 5–8 indicated that the furfural yield and selectivity decreased clearly with increasing initial xylose concentration. As the initial xylose concentration increased from 40 to 120 g/L, the furfural yield and selectivity obtained decreased from about 70% to 60%, about 78% to 65%, respectively.

Formation of furfural is also accompanied by side reactions, such as resinification of the furfural formed, condensation of furfural with xylose-to-furfural intermediates and fragmentation of xylose, all of which would decrease the yield of furfural. According to Dunlop,[25] the initial xylose concentration greatly affects the maximum obtainable yield of furfural in an aqueous solution. The dilute xylose concentrations would serve to reduce the undesirable side reactions between furfural and its precursors, such as the resinification of the furfural produced, condensation of the furfural with xylose-to-furfural intermediates. In the experiments, it was found that the quantity of degradation products of furfural adhered to the internal wall of the autoclave increased with increasing ini-

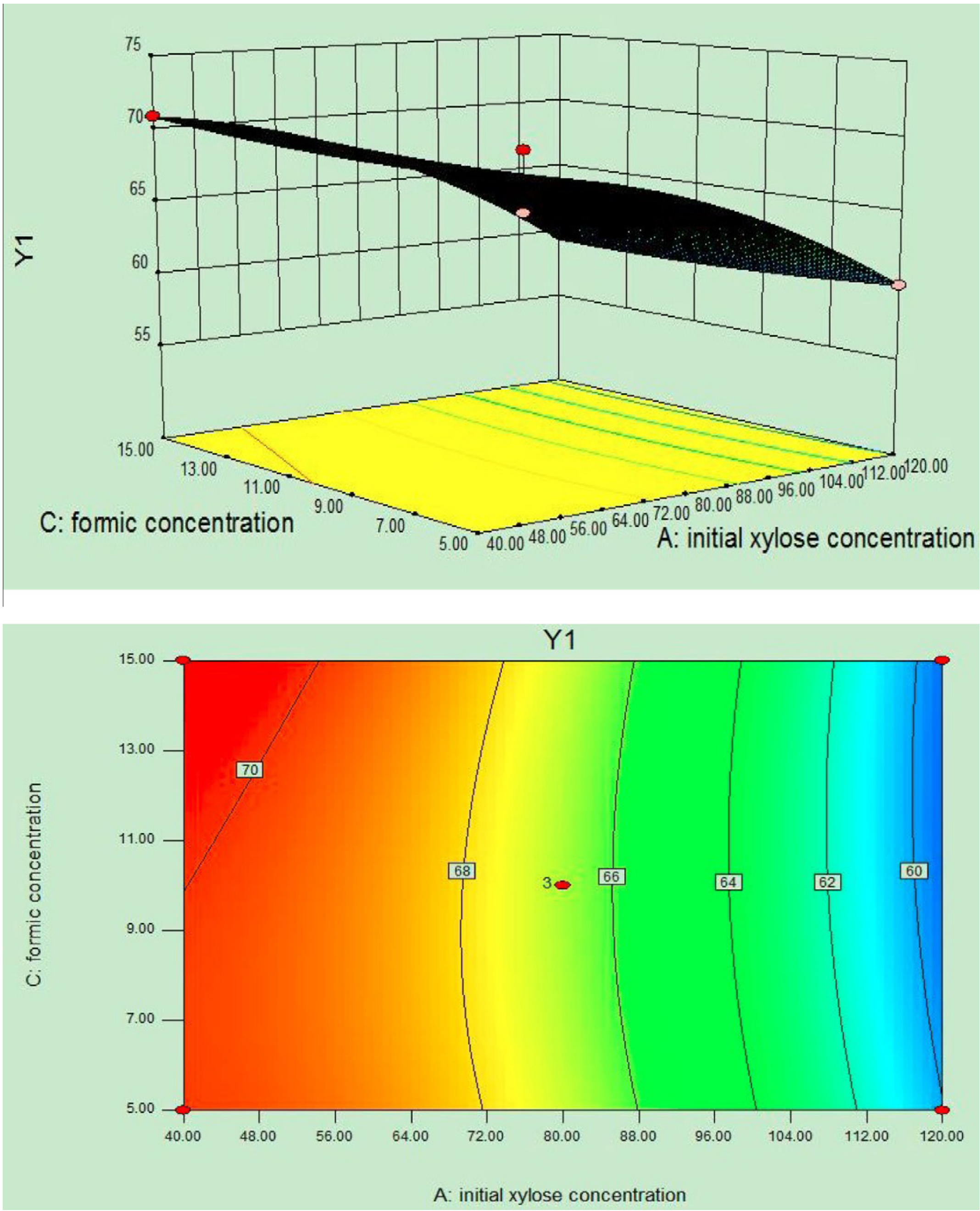


Figure 6. Effect of initial xylose concentration and formic concentration on furfural yield when temperature was set at 180 °C as the center point.

tial xylose concentration. This demonstrated that more and more furfural degraded with increasing initial xylose concentration for not being able to remove from the reaction zone timely.

Antal et al.[15] reported that furfural yield decreased from 53% to 45% when the xylose concentration increased from 20 to 100 mM. A similar trend in the conversion of fructose into 5-hydroxymethylfurfural was reported by Qi et al.[26] and Hansen et al.[27] It could be concluded that the higher the initial xylose concentration was, the lower the furfural yield was.

However, to a commercial process, low initial xylose concentrations require larger reactor and more heat to produce a given quantity of furfural. So, for economical reasons, initial xylose concentration should not be too low. The optimal initial xylose concentration is also decided by furfural yield, operating costs, and the xylose concentration in hydrolysate. Therefore, the overall cost per gallon of furfural produced is a much better criterion for a process design than the achievement of high furfural yields.

2.3.2. Dependence of furfural yield and selectivity on temperature

The experimental results presented in Figures 5 and 7 indicated that the maximum yield and selectivity of furfural were obtained at 180 °C for initial xylose concentration 40 g/L and formic concentration 10 g/L.

Reaction temperature was a crucial factor in furfural process, and it had a greatly influence on furfural yield. Dehydration of xylose into furfural and accompanied side reactions would accelerate with increasing reaction temperature. Moreover, the ratios of the rate constant of dehydration of xylose into furfural to that of accompanied side reactions increased with increasing reaction

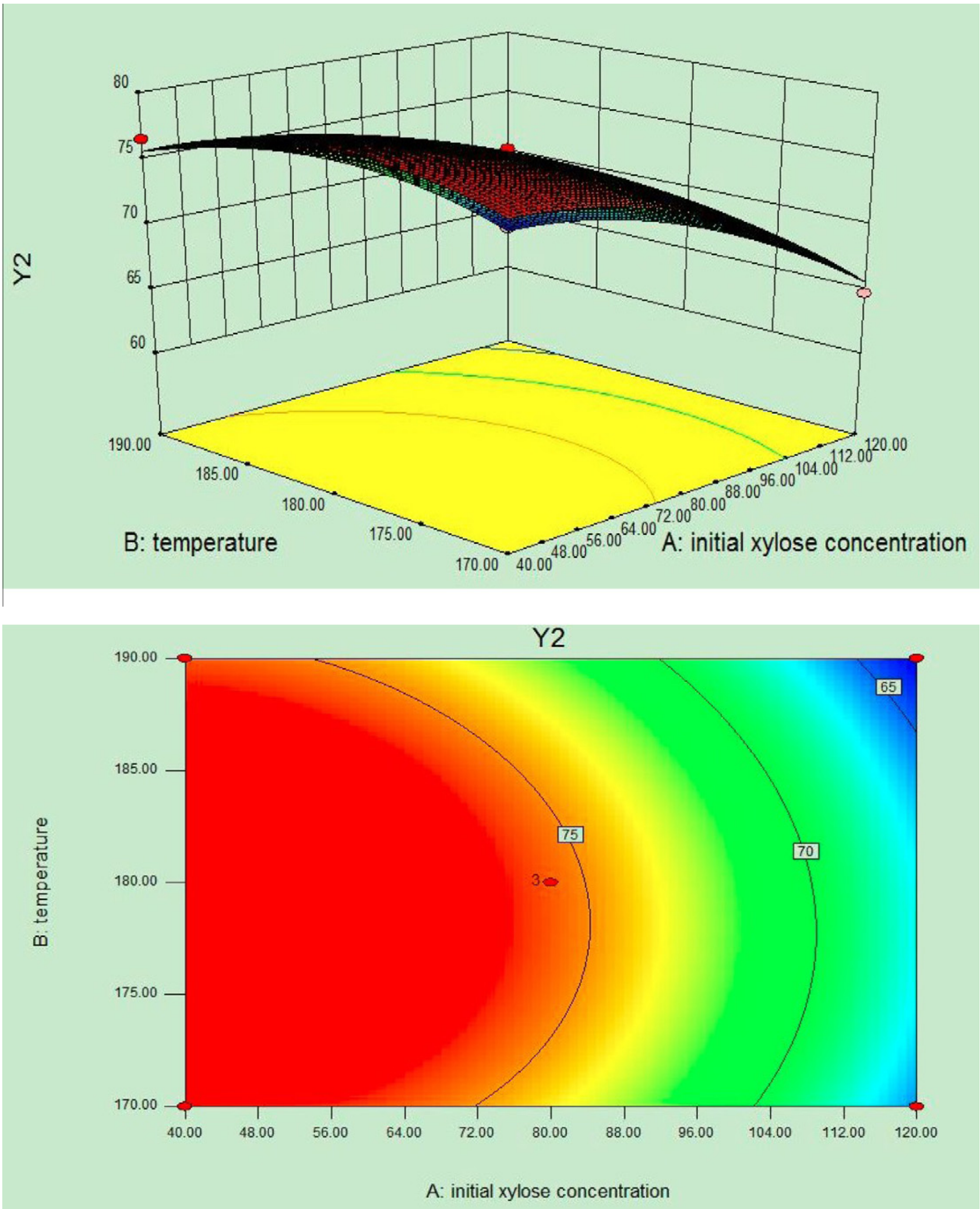


Figure 7. Effect of initial xylose concentration and temperature on furfural selectivity when formic concentration was set at 10 g/L as the center point.

temperature. The rate of dehydration of xylose into furfural is low at lower temperature, and the furfural yield is low. So, furfural yield increased with increasing reaction temperature at first. The furfural concentration of the liquid phase in the reactor would reach maximum faster and faster with increasing reaction temperature. Steam stripping process could not remove the furfural formed from the reaction zone. Under these conditions, more and more furfural formed would degrade because of increasing reaction temperature and higher furfural concentration in the reaction zone. So furfural yield and selectivity increased at first, and then decreased with increasing temperature. It also meant that a higher efficient continuous furfural removal process was required to get higher furfural yield.

Generally, 153–184 °C is used for industrial batch or continuous processes for furfural production.[28] Yemiş and Mazza[24] examined the effect of temperature on the conversion of xylose, xylan, and straw into furfural by microwave-assisted reaction at 140–190 °C. Their results showed that 180 °C was the best temperature for the acid-catalyzed conversion of xylose, xylan, and, indirectly, biomass to furfural by microwave-assisted reaction at a solid:liquid ratio of 1:100, a pH value of 1.12 (0.1 M HCl) and a residence time of 30 min. They also revealed that the decrease in furfural yield obtained from xylan at 190 °C paralleled the increase in solid char yield. Similarly, we found that furfural yield was lower at 160 °C, but there was little resin adhered to the internal wall of the autoclave. The quantity of resin adhered to the internal wall

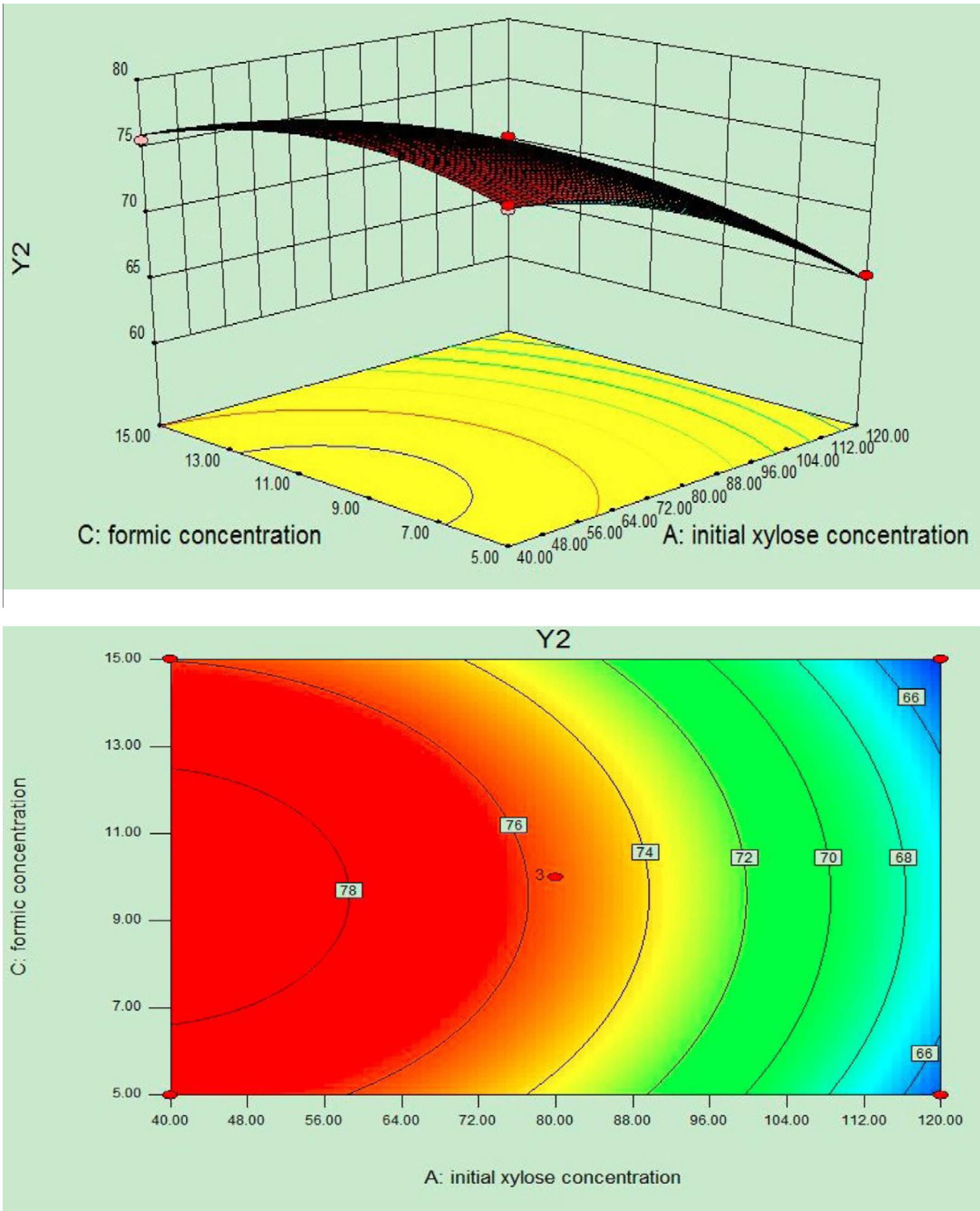


Figure 8. Effect of initial xylose concentration and formic concentration on furfural selectivity when temperature was set at 180 °C as the center point.

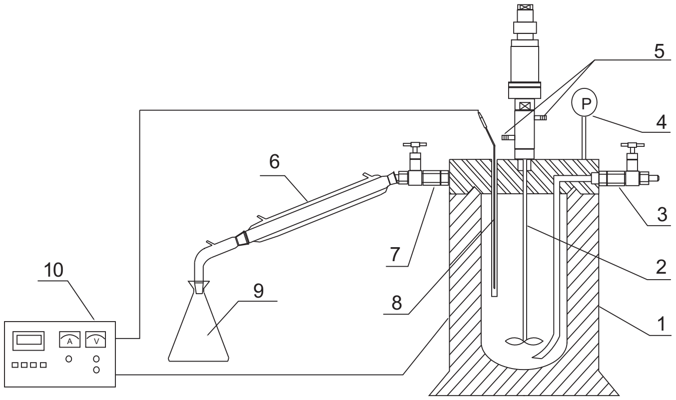


Figure 9. The schematic diagram of the experimental setup. (1) Stainless steel autoclave; (2) magnetic stirrer; (3) liquid bleed valve; (4) pressure gauge; (5 and 6) condenser; (7) vapor bleed valve; (8) thermocouple; (9) measuring receiver; (10) intelligent temperature controller.

of the autoclave increased significantly with increasing reaction temperature from 190 °C.

2.3.3. Dependence of furfural yield and selectivity on formic acid concentration

The results shown in Figures 4 and 6 also indicated that the maximum yield and selectivity of furfural were obtained at 15 g/L and 10 g/L for initial xylose concentration 40 g/L and temperature 180 °C.

In the experiments, it was found that both the rate of furfural formed and the quantity of resinous tar adhered to the internal wall of the autoclave increased with increasing formic acid concentration. This demonstrated that formic acid as catalyst was not only able to accelerate the dehydration of xylose into furfural but also able to accelerate furfural loss reactions.[15] The rate constant of furfural formed is much higher than that of accompanied side reactions. When the concentration of formic acid is lower, its increase will improve the furfural yield. Formic acid as catalyst promotes the rate of furfural formed, and the furfural concentration of liquid phase in the reactor reached maximum faster and faster with increasing acid concentration. Under these conditions, more and more furfural formed would degrade promoted by increasing acid concentration after furfural concentration reached maximum. Therefore, the furfural yield increased at first, and then decreased with increasing formic acid concentration.

Recently, Yemiş and Mazza[24] reported that the furfural yields obtained from xylose increased from 9.3 to 36.1 g/100 g when the HCl concentration increased from 0.01 to 0.1 M while a significant decline in furfural yield when the HCl concentration increased from 0.1 to 0.5 M. Rong et al.[29] reported that the yield of furfural was higher in high concentration of sulfuric acid systems compared to that in low concentration and the best furfural yield was 75% achieved with 10% (w/w) acid, but the yield reduced to 51% when the concentration of sulfuric acid became 12.5% (w/w). So, their results follow the same trend with ours. All the results show that the acidity more than the optimum concentration has an adverse effect on the conversion of xylose to furfural. Our results emphasize the importance of the optimization of formic acid hydrolysis of xylose. The strategies of formic acid recycling will be studied in the future.

According to the two models, the optimal working conditions, based on high level of furfural yield and selectivity, were chosen using the following criteria: furfural yield >70% and selectivity maximize. As an optimum point, 40 g/L initial xylose concentration, 178.8 °C temperature, 9.6 g/L formic acid concentration were selected, the furfural yield and selectivity were 70% and 79%, respectively. To confirm these results, set initial xylose concentration 40 g/L, temperature 180 °C, formic concentration 10 g/L, and the furfural yield and selectivity were 74% and 78%, respectively.

2.4. Conclusion

From the results reported in this work, it can be concluded that formic acid as a byproduct of furfural process, can be an effective catalyst for dehydration of xylose into furfural, and it is superior to phosphoric acid and sulfuric acid as higher furfural yield and selectivity, the low corrosion resistance, easy to be separated and reused. The yield of furfural decreases remarkably with increasing initial xylose concentration and the optimal initial xylose concentration will be determined by economic analysis. The optimal reaction temperature and formic acid concentration were 180 °C and 10 g/L, respectively. Under these conditions, the maximum furfural yield and selectivity were 74% and 78%, respectively, for initial xylose concentration 40 g/L. Steam stripping process was not able to remove the furfural formed from the reaction zone timely in this semi-batch mode, and a higher efficient furfural removal process was required if wanting to get higher furfural yield.

3. Experimental

3.1. Materials

The D-xylose, formic acid, sulfuric acid, phosphoric acid, and ethanol (all purchased from Tianjin Kewei Co. of China) employed in the experiments were analytical reagents and used without further purification. Their mass fractions were better than 99.5%. The water used in the experiments is deionized water (purchased from Tianjin Kewei Co. of China). The furfural waste water was obtained from Wuji Furfural Co. of China.

3.2. Methods

The components of the experimental system include a stainless steel autoclave (2 L, 110 mm inner diameter × 220 mm height)-with an electric jacket, an intelligent temperature controller with a precision of ±1 °C, a magnetic stirrer, two condenser and a measuring receiver as show in Figure 9.

A typical procedure of the experiment is listed as followed: Pour xylose (80 g), formic acid (10 g), water (1000 mL) into the autoclave. Turn on the electric jacket and fix the speed of the stirrer to 150 rpm. Slightly open the valve for sampling vapor phase for a few minutes to release the residual air in the autoclave after the temperature reached 110 °C. Zero time is taken to be when the temperature reaches desired value. Then open the valve for sampling vapor phase to liberate vapor phase continuously and collect all the distillate in a measuring receiver. Meanwhile, reaction system was maintained in a state of boiling by gradually lowering the pressure so as to keep it below the vapor pressure. Be sure to collect no less than 800 mL distillate over the first four hours at a constant flow rate and another 150 mL over the later two hours at a constant flow rate in order to remove almost all the furfural formed in the reactor. Weigh the total distillate and measure the furfural concentration accurately.

Furfural yield is the moles of furfural produced divided by the theoretical moles of furfural based on the amount of xylose in feed. The furfural yield can be calculated by the following formula:

$$Y\% = \frac{c \times m_1 \times 150}{m_0 \times 96} \times 100\%$$

where: c—furfural mass concentration of total distillate; m_1—the total mass of distillate; m_0—the mass of xylose in feed; 150—the mole mass of xylose; 96—the mole mass of furfural.

The furfural in the distillate was monitored by gas chromatography (FULI 9790II, FID detector, China) using capillary packed column (FFAP, 30 m × 0.32 mm × 0.25 mm). Flow rate for nitrogen was 80 ml·min^{-1}. Detector, injector, and column temperatures were 230, 230, and 220 °C, respectively. Ethanol was internal standard substance. Under these conditions, the retention times for ethanol and furfural were 2.3 and 3.1 min, respectively. The furfural in the liquid sampled from the liquid phase in the reactor was monitored by Agilent 1100 HPLC equipment. The column was a Sugar SH1011 (Shodex, 8mmID × 300 mm). The HPLC was operated at the temperature 60 °C and eluted with 0.5 ml·min^{-1} flow of sulfuric (0.5 mmol L^{-1} in water). The temperature of Refractive Index Detector was set at 40 °C. The reaction times for D-xylose and furfural were 15 and 59 min, respectively.

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