

Kinetics of Furfural Production from Corn Cob in γ -Valerolactone Using Dilute Sulfuric Acid as Catalyst

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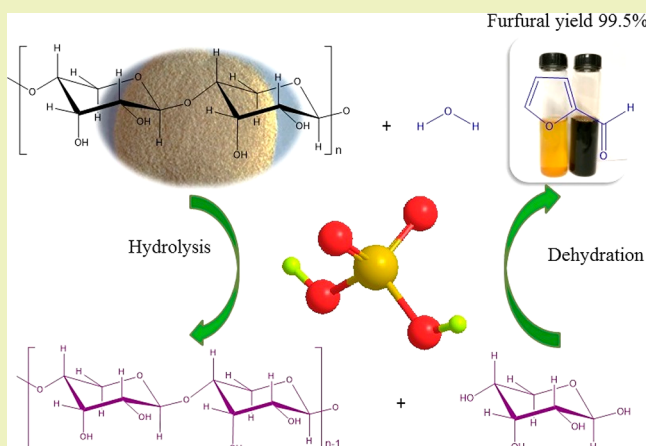
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ABSTRACT: Conversion of corn cob to furfural was investigated using γ -valerolactone as the solvent with a dilute sulfuric acid catalyst. A maximum furfural yield of 99.50% was obtained at 190 °C for 20 min with 0.10% sulfuric acid. A well-evaluated kinetic model was used for this reaction, and its activation energy was calculated. The model agreed closely with the experimental data and kinetics parameters, indicating that γ -valerolactone accelerated furfural formation and decreased the degradation rate as compared to water. Moreover, using γ -valerolactone as a solvent changed the energetics of the conversion reaction of hemicellulose to improve the formation of furfural. The response surface plots of the furfural concentration with respect to the temperature and dilute sulfuric acid density improved our understanding of the furfural production reaction from corn cob in γ -valerolactone solvents.

KEYWORDS: Corn cob, Furfural, Dilute sulfuric acid, Kinetics, γ -Valerolactone



INTRODUCTION

Because of its great amount, cheapness, and environmental advantage, lignocellulosic biomass, such as the waste produced in agriculture, has become an especially suitable bioenergy raw material.¹ The highly functionalized carbohydrate moieties (primarily C5 and C6 sugars) of lignocellulosic biomass, which can be used to produce platform compounds that finally replace those refined from petrochemical materials, are essential to enhancing the energy structure and alleviating environmental problems.² The main components of cellulosic biomass are hemicelluloses, cellulose, and lignin. The oligomer (primarily C5 sugars) can be used for furfural output, which is attracting much interest from researchers. As a promising biobased platform chemical, numerous valuable chemicals can be created from furfural, such as levulinic acid, 2-methylfuran, furfuryl alcohol, cyclopentanone,³ and γ -valerolactone (GVL).⁴ Moreover, plastics, adhesives, and lubricating oil can be produced from furfural instead of petroleum fuels, and furfural can be used as a fuel additive.^{5–7}

The commercial furfural production process is usually conducted using water as the solvent,⁸ which leads to low furfural yields (<50%) because furfural degrades in side reactions such as esterification and condensation reactions. On the other hand, the separation of furfural from water is an energy-intensive process. Therefore, it is necessary to develop

novel greener solvents to improve the furfural yields. As alternative solvents to water, many liquids have been studied to increase furfural yields, such as ILs,^{9–11} organic solvents,¹² and biphasic systems.^{13,14} Peleteiro et al. studied the conversion of eucalyptus globulus wood into furfural in [bmim]HSO₄ acidic ionic liquid at 120–170 °C, and they observed that the highest furfural conversion was 59.1% at 160 °C for 4 h.¹¹ Ionic liquids can improve furfural yields at a lower temperature and are easily separated. However, the preparation process of ILs is complex and the cost is expensive, which limits its large-scale application. Biphasic systems are frequently applied in the conversion of lignocelluloses into furfural. They can improve the furfural yield because the furfural was continuously extracted into the organic phase. High furfural yields (>90%) from lignocelluloses were obtained by Campos Molina et al. over sulfuric acid using cyclopentyl-methyl-ether as the extraction layer, which indicates that cyclopentyl-methyl-ether addition favors high furfural selectivity and prevents furfural degradation.¹⁴ Biphasic systems have benefits in furfural selectivity and yields. However, organic solvents are inherently toxic, and their recovery is difficult, which poses environmental concerns. Hence, there is a need for

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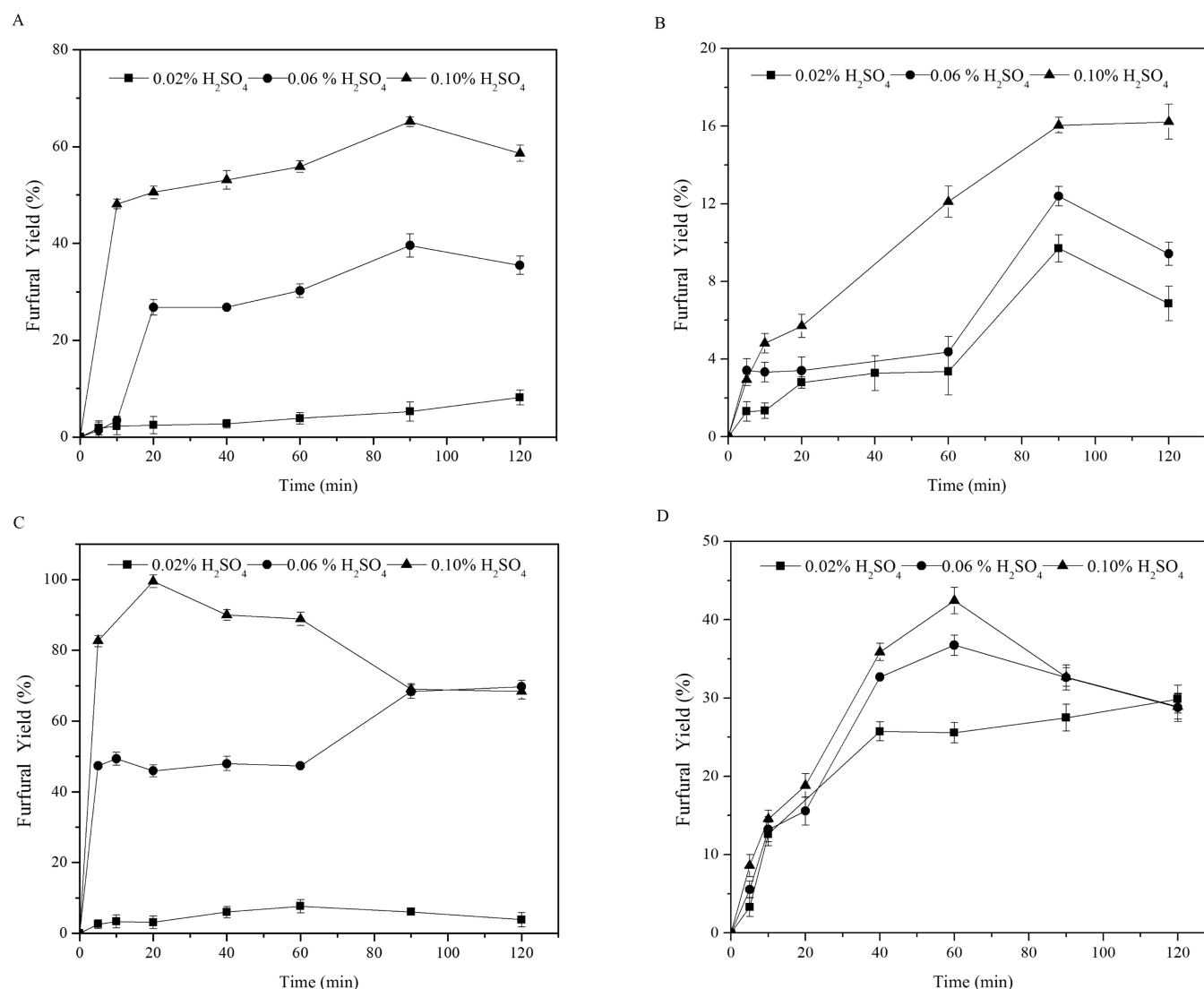


Figure 1. Furfural yield (A) in GVL solvent containing 20% water at 170 °C, (B) in water at 170 °C, (C) in GVL solvent containing 20% water at 190 °C, and (D) in water at 190 °C using sulfuric acid as catalyst.

a green and economical solvent for the efficient increase of furfural yields.

The application of GVL as solvent is noteworthy in biomass transformation processing with a monophasic approach. GVL is generated from lignocellulosic biomass and shows a great increase in the reactivity of the biomass conversion reaction compared to aqueous media. For example, GVL can improve catalytic activity and selectivity to the target chemicals.^{15–17}

Recently, several studies have applied γ -valerolactone (GVL) as a reaction solvent in biomass transformation. Furfural yields of approximately 80% were observed by Gürbüz et al. and Alonso et al. (2013), and they indicated that the furfural production from xylose was efficiently improved.^{6,18} Zhang et al. studied furfural produced from xylose, xylan, and corn cob over FeCl₃ as catalyst in GVL solvent. The furfural yield obtained from corn cob was 79.60% after 100 min at 185 °C.¹⁹ Using GVL as the reaction medium obviously improved the dehydration rate of xylose and reduced the degradation rate of furfural.⁶ Furthermore, γ -valerolactone is a nontoxic and green solvent that has great potential for use in furfural production. After completion of the reaction, furfural can be easily separated from GVL solvents through distillation.²⁰

In this study, GVL was used as a solvent for converting corn cob to furfural with dilute sulfuric acid. Using GVL as a solvent to produce furfural from hemicellulose is well-known, and sulfuric acid is a common Brønsted acid used for furfural production. However, there are few reports about the conversion kinetics of corn cob to furfural in GVL solvents. In our opinion, developing a well-assessed kinetic model is beneficial for understanding furfural production from corn cob with dilute sulfuric acid as catalyst in GVL solvents. A common kinetic model was established to predict the kinetic parameters on the basis of analytical experimental data and calculate the maximum yield of furfural.

MATERIALS AND METHODS

Raw Material. The raw material in our experiment was corn cob from a local farm (Tianjin, China). Corn cob was ground, oven-dried, screened with a 0.85 mm sieve, and selected for the small particle size, and then placed in a self-sealing pouch before use. The determination of corn cob composition was conducted using the laboratory analytical procedure provided by the National Renewable Energy Laboratory.²¹

Furfural Production Process with Dilute Sulfuric Acid as Catalyst. Furfural production from corn cob over a dilute sulfuric acid catalyst was conducted in a 25 mL autoclave using electronic heating

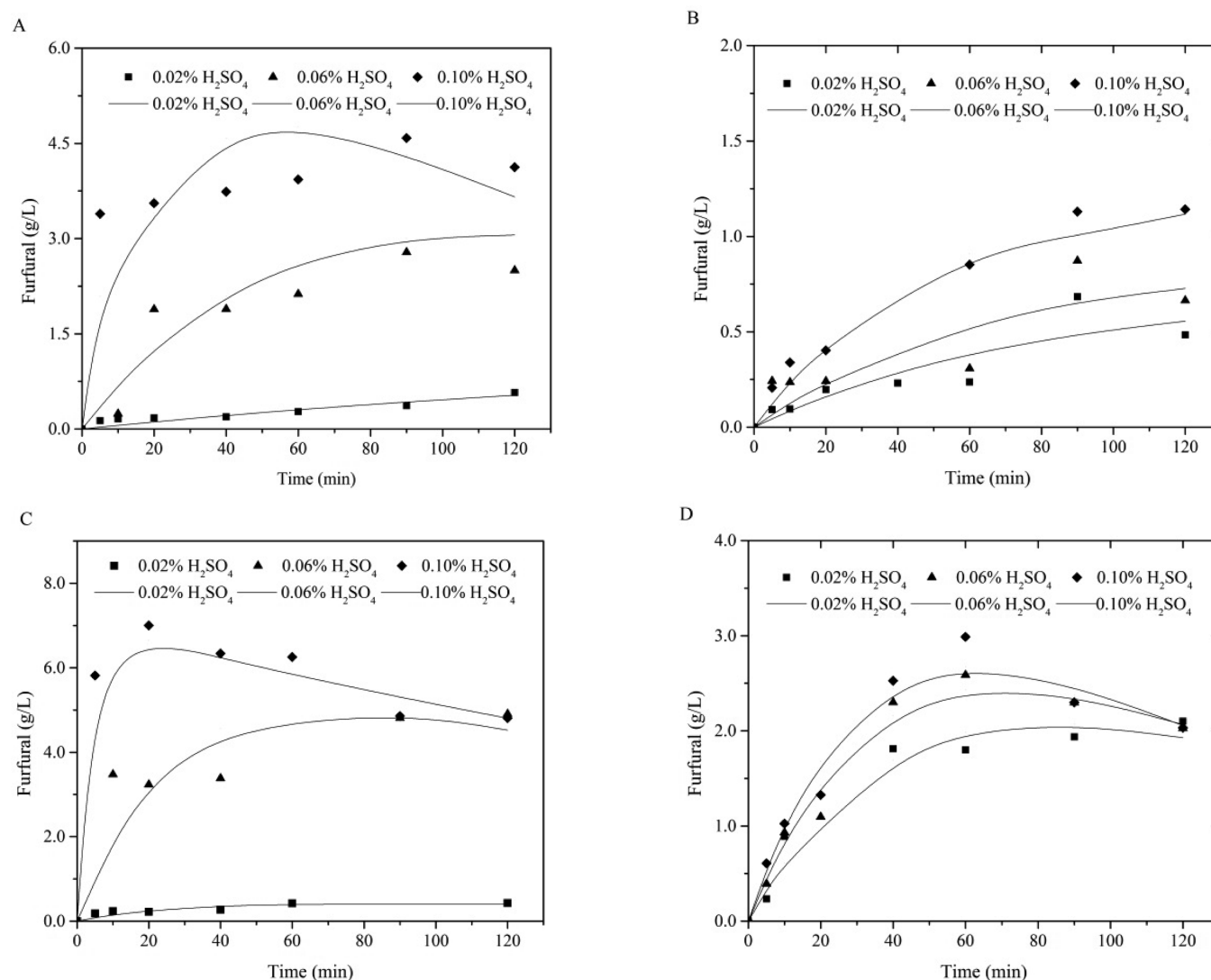


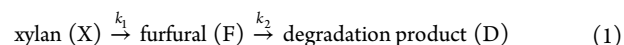
Figure 2. Comparison of experimental values and kinetic models. Points represent experimental data, and solid lines represent kinetic models: (A) in GVL solvent containing 20% water at 170 °C, (B) in water at 170 °C, (C) in GVL solvent containing 20% water at 190 °C, and (D) in water at 190 °C using sulfuric acid as catalyst.

with a magnetic stirrer. In a typical experiment, 0.4 g of corn cob mixed with 15 mL of solvent (mixture of 12 mL of GVL and 3 mL of water) was loaded into the autoclave, and 30, 90, and 150 μ L of 10% sulfuric acid was added to adjust the concentration of catalyst from 0.02 to 0.10 wt %. The control experiment used 15 mL of water instead of the mixture of GVL and water. The mixture was stirred at 500 rpm and heated to the desired reaction temperature (170 or 190 °C) starting from room temperature. The starting time was when the reaction temperature reached the target temperature. The reactor was placed in an ice bath to suspend the reaction at the required reaction time. Finally, the mixture in the reactor was separated by filter paper into a liquid phase and solid phase for further analysis.

Analytical Methods. The composition of the liquid phase was analyzed for furfural using an HPLC system (LabAlliance) with a Bio-Rad Aminex HPX-87H column at 65 °C and 5 mM aqueous sulfuric acid as the mobile phase flowing at 0.6 mL/min. Furfural concentrations were analyzed by Bio-Rad high performance liquid chromatography using a UV detector at a wavelength of 254 nm.²²

Kinetic Models. The Saeman model was used for the production of furfural from corn cob in GVL. In our study, a simplified model was used that ignored the production of intermediates and primarily considered the furfural production. As a uniform first-order irreversible reaction, a two-step reaction was established, in which xylan was first

hydrolyzed to furfural, and furfural was later degraded into byproducts. The proposed model is



On the basis of this model, the concentration of xylose [X], furfural [F], and degradation product [D] at time t (min) was described by eqs 2, 3, and 4, respectively.

$$\frac{d[X]}{dt} = -k_1[X] \quad t = 0, [X] = [X]_0 \quad (2)$$

$$\frac{d[F]}{dt} = k_1[X] - k_2[F] \quad t = 0, [F] = 0 \quad (3)$$

$$\frac{d[D]}{dt} = k_2[F] \quad t = 0, [D] = 0 \quad (4)$$

where $[X]_0$ is the primary concentration of xylan in corn cob in g/L. k_1 and k_2 are rate constants (min^{-1}). The degradation product was mainly humin, which was from the condensation reaction of furfural and xylose.^{8,10} The linear differential method was used to solve the reaction rate equation as follows:

Table 1. Kinetic Rate Constants for the Catalyst Hydrolysis of Corn Cob

T/°C and solvent	H ₂ SO ₄ (wt %)	k ₁ /min ⁻¹	k ₂ /min ⁻¹	k ₁ /k ₂	X ₀ (g/L)	R ²
170	0.02	0.000831	0.003966	0.2096	7.04	0.9475
GVL	0.06	0.010713	0.007480	1.4322	7.04	0.9402
	0.10	0.036973	0.006971	5.3036	7.04	0.8976
170	0.02	0.001293	0.010902	0.1186	7.04	0.8943
water	0.06	0.001918	0.012551	0.1528	7.04	0.8712
	0.10	0.003617	0.014272	0.2534	7.04	0.9885
190	0.02	0.002500	0.034434	0.0726	7.04	0.9143
GVL	0.06	0.032264	0.004684	6.8888	7.04	0.8871
	0.10	0.359228	0.003256	110.32	7.04	0.9588
190	0.02	0.009794	0.014728	0.6650	7.04	0.9804
water	0.06	0.013559	0.015018	0.9029	7.04	0.9868
	0.10	0.016446	0.015417	1.0667	7.04	0.9814

$$[F] = \frac{k_1[X]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \quad (5)$$

A modified Arrhenius equation, eq 6, was applied to calculate the activation energy and evaluate the effect of catalyst concentration and temperature on the rate constants in eq 5:

$$k_i = A e^{[-E_i/RT]} [C]^{m_i} \quad i = X, F, D \quad (6)$$

where R is the universal gas constant and equal to 8.314×10^{-3} kJ/(mol·K). A corresponds to the frequency factor (min⁻¹), E_i is the apparent activation energy (kJ/mol), and m_i is the reaction order.

The Newton method (Solver, Microsoft Excel 2010) using nonlinear least-squares regression analysis was used to calculate the kinetic parameters in the conversion of corn cob to furfural.

The furfural yield is described as

$$\text{furfural yield} = \frac{\text{furfural concentration (g/L)} \times \text{xylen molecular weight}}{\text{primary xylen concentration (g/L)} \times \text{furfural molecular weight}} \times 100\% \quad (7)$$

Applying $dF/dt = 0$ to eq 5, the time t_{\max} to reach the maximum furfural yield in GVL solvents (at a fixed temperature and concentration of dilute sulfuric acid solution) is found to be

$$t_{\max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} \quad (8)$$

RESULTS AND DISCUSSION

Composition of Raw Material. The composition of corn cob is 36.3% hemicelluloses, 29.9% cellulose, 13.0% Klason lignin, 2.1% ash, and 18.7% other components including proteins, ethanol soluble materials, and chemically combined water.

Effects of Temperature and Dilute Sulfuric Acid Concentration on Furfural Yields in GVL. Furfural yield variations with temperature, reaction time, and sulfuric acid concentration in GVL and water solvent are shown in Figure 1A–D, respectively. The results indicate that the furfural yield increased more quickly to a relatively high level in GVL as compared to water. For example, the furfural yield reached 47.37% and 82.64% at 0.06% and 0.10% sulfuric acid for 5 min in GVL at 190 °C, respectively, as compared to the low yields (5.55% and 8.62%) obtained in aqueous solution under the same conditions. This is consistent with Gallo's high furfural yield (>80%) achieved from xylose with short reaction times of approximately 15 min using 0.05 mol/L sulfuric acid in GVL solvent containing 10 wt % water.²³ The results indicate that GVL can improve the rate of furfural production yield over

water.²⁴ In GVL, the furfural yield increased significantly at the same time with the sulfuric acid concentration at a constant temperature, which indicated that a higher concentration of sulfuric acid accelerated the reaction. Figure 1A shows that raising the concentration of sulfuric acid solution from 0.02% to 0.10% at 170 °C results in a relatively large increase of the furfural yield from 2.45% to 50.51% within 20 min in GVL.

The maximum furfural yields were significantly higher in GVL than in water at the same concentration of sulfuric acid and at a fixed temperature: the maximum furfural yield achieved using 0.06% and 0.10% sulfuric acid in GVL was 69.71% at 120 min and 99.50% at 20 min, respectively, as compared to the low furfural yields obtained in water over 0.06% (36.73%) and 0.10% (42.44%) sulfuric acid at 190 °C. In addition, unlike the result in water, the furfural yield would not decrease quickly after reaching the maximum yield, which indicated that GVL could inhibit furfural degradation.^{6,18} This result also occurred in Gallo's study. They found that the reaction was prolonged for an additional 60 min after complete conversion of the monosaccharides with no obvious reduction of furfural concentration at 160 °C using H-Beta in GVL containing 10 wt % water.¹⁷

Kinetic Modeling of Furfural Production with Dilute Sulfuric Acid as Catalyst. Kinetic Parameters of Furfural Production from Corn Cob over Dilute Sulfuric Acid. Figure 2 shows the experimental values and the predicted profiles of furfural concentrations obtained under different reaction conditions for the kinetics experiments in GVL and water. As shown in Figure 2, the predicted values (solid lines) clearly show the variation of the concentration of furfural. The kinetic model profile indicated that the production rate of furfural was faster in GVL than in pure water under the same reaction conditions. For example, the concentration of furfural was 6.65 g/L at 190 °C for 20 min with 0.10% sulfuric acid in GVL, whereas it was only 1.68 g/L in pure water. The variation of the lines from 170 to 190 °C illustrated that the xylose dehydration rate (k_1) in GVL was improved over a fixed concentration of sulfuric acid. For instance, the maximum furfural concentration (6.65 g/L, furfural yield 94.46%) with 0.10% sulfuric acid solution was reached in approximately 20 min at 190 °C in GVL, whereas the maximum furfural concentration (4.77 g/L, furfural yield 67.75%) was reached in 60 min at 170 °C.

Kinetic Model Implications. Table 1 presents the kinetic rate constants for sulfuric acid catalytic conversion of hemicelluloses in corn cob to furfural under different conditions. The estimated kinetic parameters show that using GVL as the solvent instead of water increases the furfural production rate

(k_1) and decreases the furfural degradation rate (k_2) with the same concentration of catalyst. For example, the value of k_1 (furfural production rate constant) showed a 5.59-fold and 10.21-fold increase at 170 °C using 0.06% and 0.10% sulfuric acid in GVL, respectively, as compared to that in water. Furthermore, the value of k_2 (furfural degradation rate constant) in GVL decreased to 59.60% and 48.84% at 170 °C using 0.06% and 0.10% sulfuric acid, respectively, as compared to the values in water. These results are consistent with the previous report that γ -valerolactone improved furfural production reactions and reduced the furfural degradation rate.^{6,18} As compared to water, γ -valerolactone decreased the stabilization of the acidic proton relative to the protonated transition states, which can increase the rate of furfural production from xylose catalyzed by a protonic acid.²⁴ The decelerated furfural degradation rate was reduced in γ -valerolactone because the condensation reactions between pentose intermediates and furfural were inhibited by γ -valerolactone.⁶ The values of k_1 in GVL were shown to improve with the increase of the sulfuric acid concentration. The values of k_1 were much higher than those of k_2 in GVL solvents under all experimental conditions except for 0.02% sulfuric acid, which suggested that the key reaction was furfural production in the conversion reaction. When the temperature increased from 170 to 190 °C, the values of k_1 were increased in GVL at a fixed sulfuric acid concentration, which indicates that temperature can accelerate furfural production. The values of k_2 showed an inverse dependence on sulfuric acid concentration in GVL solvents, which suggests that furfural degradation was inhibited by the increase of sulfuric acid concentration in GVL. The value of k_1/k_2 was used to assess the effect of the reaction conditions. As shown in Table 1, the value of k_1/k_2 was 1.77, 9.37, and 20.93 times larger in GVL as compared to the value in water at 170 °C for sulfuric acid concentrations of 0.02%, 0.06%, and 0.10%, respectively. Furthermore, the value of k_1/k_2 at 0.10% sulfuric acid and 190 °C in GVL exhibited a 103.42-fold increase as compared to that in water, which implies that GVL solvent enhances the reactivity of a homogeneous Brønsted acid catalyst.²⁴ The value of k_1/k_2 in GVL increased with the concentration of dilute sulfuric acid at a fixed temperature, indicating that the selectivity to furfural formation was enhanced by increasing the catalyst concentration in GVL. In addition, the average values of k_1/k_2 were 2.32 and 39.09 at 170 and 190 °C, respectively, which shows that k_1/k_2 was improved with increasing reaction temperature. Moreover, the value of k_1/k_2 (110.32) at 190 °C in GVL was significantly higher with 0.10% sulfuric acid, which implies that this was the best concentration in this experiment for furfural production from corn cob. The kinetic model closely agreed with the experimental data, as the fitting degree R^2 almost always remained high in the model.

To assess the effect of reaction temperature (T) and H_2SO_4 concentration on the rate constants, we used a modified Arrhenius equation to fit the kinetic parameters. The results are shown in Table 2. For k_1 and k_2 , the parameter R^2 indicates a good fit between the experimental and predicted data. The maximum E_i value of furfural production is 101.44 kJ/mol in GVL, which is lower than that in water (154.15 kJ/mol), whereas the maximum E_i value for furfural degradation is 126.72 kJ/mol in GVL, which is higher than that in water (99.42 kJ/mol). These results imply that GVL promotes furfural production and inhibits furfural degradation. Mellmer et al. reported that the activation energy for furfural production

Table 2. Arrhenius Parameters of the Catalyst Conversion of Corn Cob with Dilute Sulfuric Acid

solvent	reaction rate constant	A_i (min)	E_i (kJ/mol)	m_i	R^2
GVL	k_1	9.7×10^{18}	101.44	2.68	0.9684
water	k_1	7.1×10^{16}	154.15	0.41	0.9953
GVL	k_2	6.84×10^7	126.72	-1.35	0.9404
water	k_2	7.1×10^9	99.42	0.22	0.8250

is 114 kJ/mol in γ -valerolactone and 145 kJ/mol in water, whereas the activation energy for furfural degradation is 105 kJ/mol in γ -valerolactone and 85 kJ/mol in water, which is very similar to our results.²⁴ These results indicate that the application of γ -valerolactone as a reaction medium changes the energetics of the hemicellulose conversion reaction to improve formation of furfural. The reaction order (2.68) for furfural production in catalyst concentration in GVL was higher than that in water (0.41), which indicates that the sulfuric acid concentration affected the furfural production rate more deeply in GVL than in water and that the furfural yields were improved by an increase of the sulfuric acid concentration. The k_2 reaction order is negative in GVL, indicating that increasing the sulfuric acid concentration inhibits furfural degradation, possibly due to the accumulation of side products.

Optimization of Furfural Production from Corn Cob Using Kinetic Models. Building kinetic models and defining the best reaction conditions of furfural production from corn cob was the principal aim of our report. Consequently, a simple model for predicting furfural production in GVL was used.²⁵ The correlation between kinetic parameters and catalyst concentration was described by the empirical eq 9. Here, n is 1 or 2, k_0 is the regression coefficient, and m is a power exponent. C (wt %) is the concentration of H_2SO_4 solution.

$$k_n = k_0 C^m \quad (9)$$

Combining eq 9 and the kinetic parameters in Table 1, it is possible to predict the furfural concentration at any time from 0 to 120 min with the concentration of H_2SO_4 from 0.02% to 0.10% and a fixed temperature. As Table 3 shows, k_2 presents a

Table 3. Generalized Models for Estimating Kinetic Parameters of Furfural Production from Corn Cob in GVL Containing 20% Water

temp (°C)	models	R^2
170	$k_1 = 8.2091C^{2.35}$	0.9999
	$k_2 = 0.0189C^{0.39}$	0.8358
190	$k_1 = 230.96C^{2.97}$	0.9641
	$k_2 = 8.2930 \times 10^{-5}(1/C^{1.52})$	0.9706

contrary dependence on H_2SO_4 concentration in GVL at 190 °C, which indicates that furfural degradation was inhibited over high concentrations of sulfuric acid, possibly by the increase of side products.²²

Figure 3 shows the furfural concentration as a function of the concentration of dilute sulfuric acid (0.02–0.10%) and reaction time (0–120 min) at 170 and 190 °C in GVL. The ordinary models for the conversion of corn cob predicted that a higher concentration of dilute sulfuric acid promotes the furfural production rate. The maximum furfural concentration of 4.64 g/L (furfural yield 65.90%) was reached in approximately 50 min at 170 °C with 0.10% sulfuric acid, whereas at 190 °C, a

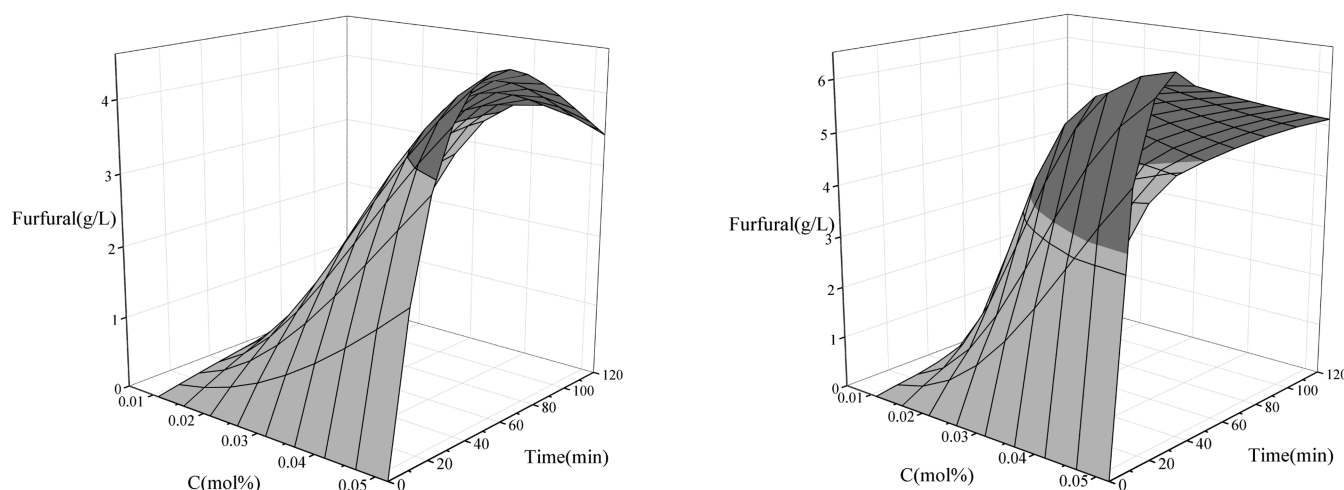


Figure 3. Prediction of the generalized model for the dependence of furfural concentration at 170–190 °C in GVL containing 20% water on the sulfuric acid concentration and reaction time.

similar furfural concentration of 4.96 g/L (furfural yield 70.50%) was reached in 10 min with 0.10% sulfuric acid. This result suggests that the production rate of furfural from corn cob is surprisingly rapid at 190 °C. The dark gray area in the response surface represents the furfural concentration above 3.52 g/L (furfural yield >50%) primarily arising over a higher concentration of dilute sulfuric acid at 170 and 190 °C in GVL. In addition, with the temperature increased from 170 to 190 °C, the dark gray section was progressively enlarged. This result suggested that a higher furfural concentration was achieved over lower concentrations of sulfuric acid and a shorter reaction time at high temperature. This was considering that increasing the reaction temperature and H₂SO₄ concentration can improve the furfural formation. In our experiments, 95.0% of furfural yield was predicted as the maximum concentration (6.69 g/L) through calculation. The furfural yield then decreased slowly over a longer reaction time, due to furfural degrading to side products.

Table 4 shows the maximum furfural yields achieved by the sulfuric acid catalyzed conversion of corn cob in GVL according

Table 4. Optimal Treatment Conditions of Furfural Fomation from Corn Cob According to the Kinetic Model

<i>T</i> (°C)	sulfuric acid (wt %)	time (min)	furfural concentration (g/L)	furfural yield (%)
170	0.02	498.41	0.98	13.85
	0.06	111.11	3.06	43.56
	0.10	55.61	4.78	67.86
190	0.02	82.13	0.42	5.91
	0.06	69.98	5.07	72.06
	0.10	13.21	6.74	95.79

to the determination of t_{\max} values through eq 8. As Table 4 shows, a higher reaction temperature and higher sulfuric acid concentration can greatly shorten t_{\max} . For instance, t_{\max} was 55.61 min at 170 °C with 0.10% sulfuric acid, whereas it was only 13.21 min at 190 °C with the same sulfuric acid concentration. t_{\max} decreased from 82.13 to 13.21 min when the concentration of H₂SO₄ increased from 0.02% to 0.10% in GVL.

CONCLUSIONS

The production of furfural from corn cob using GVL and water as solvent was investigated under different conditions. A maximum yield of furfural of 99.50% was observed at 190 °C for 20 min with 0.10% sulfuric acid. A simplified kinetic model was used to understand the conversion process of corn cob into furfural in GVL solvent. The kinetic parameters indicate that γ -valerolactone can improve furfural production reactions and decelerate the furfural degradation rate. In addition, a modified Arrhenius equation was applied to calculate the activation energy. The use of γ -valerolactone as a reaction medium decreases the activation energy of furfural production and increases the energetics of furfural degradation, which increases the formation of furfural. The response surface plots of the furfural concentration in GVL, including the effect of the catalyst concentration (wt %) and reaction time (min), provided a deeper interpretation of the conversion reaction of corn cob to furfural.

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Notes

The authors declare no competing financial interest.

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