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RESEARCH PAPER

Enhanced production of xylose from corncob hydrolysis with oxalic acid as catalyst

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Abstract The acid-catalyzed treatment was a conventional process for xylose production from corncob. To increase the release of xylose and to reduce the by-products formation and water usage, the oxalic acid was used as catalyst to hydrolyze the corncob and the hydrolytic conditions were investigated. The highest xylose yield of 32.7 g L^{-1}, representing 96.1% of total theoretical xylose yield, was obtained using 1.2% oxalic acid after hydrolysis for 120 min at 130 °C, which was more than 10% higher than that of sulfuric acid-catalyzed hydrolysis. Mixed acids-catalyzed hydrolysis performed a synergistic effect for xylose production and 31.7 g L^{-1} of xylose was reached after reacting for 90 min with oxalic acid and sulfuric acid at a ratio of 1:4 (w/w). A kinetic model was developed to elucidate the competitive reaction between xylose formation and its degradation in the hydrolysis process, and the experimental data obtained in this study were perfectly in agreement with that of predicted from the model. Furthermore, the final xylose yield of 85% was achieved after purification and crystallization. It was demonstrated that xylose production from the corncob hydrolysis with oxalic acid as the catalyst was an effective alternative to the traditional sulfuric acid-based hydrolysis.

Keywords Xylose production · Corncob hydrolysis · Acid-based catalysis · Kinetic model

Introduction

Corncob, the important agricultural residue of the corn processing industry, is receiving increasing attention worldwide because of its high carbohydrate contents and high energy densities [1–5]. It is considered as one of the most suitable biomasses for the production of various high-value-added chemicals such as xylose [4, 6].

Xylose ($C_5H_{10}O_5$) is the most abundant pentose with wide applications in many fields [7–9]. It could be used as raw materials for the production of many chemicals and fuels, such as xylitol and furfural [4, 9–11]. Xylose is mainly existed as the form of xylan in the hemicellulose fraction of biomass, and thus hydrolysis process is required to release it accordingly for further applications. In the process of hydrolysis, hemicellulosic fraction of the biomass was dissolved firstly and xylose was released as the main sugar, and then cellulose and lignin were separated

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subsequently by proper liquid–solid separation method. In recent years, studies on acid-catalyzed hydrolysis of corncob was mainly focused on the production of energy fuels, while little efforts have been made on the direct production of xylose [12–15]. Oxalic acid as the organic dicarboxylic acid is promising and potential for the industry application in hydrolysis of lignocellulosic materials, which was superior in producing monosaccharide compared to mineral acids [16, 17]. However, few studies about the dilute oxalic acid pretreatment of lignocellulosic biomass were investigated and no direct preparation of monosaccharides was involved with oxalic acid. Compared with sulfuric acid, oxalic acid was reported to be more conducive to the increase of xylose yield and the decrease of by-products from the hydrolysis of biomass [16, 18–20]. As such, it is more promising to be used as catalyst for efficient production of xylose from corncob with balanced xylose formation and degradation.

In this study, the sulfuric acid, oxalic acid and mixed acids were, respectively, used as catalyst to produce xylose from corncob and the effects of hydrolysis conditions including acid concentration, reaction temperature and residence time on the xylose yield were investigated. An effective kinetic model was developed to better balance the formation of product and by-products. Furthermore, the purification and crystallization were conducted to recover xylose from the hydrolysate. The results demonstrated oxalic acid as an alternative catalyst for enhanced production of xylose from corncob.

Materials and methods

Materials

The air-dried corncob used in this work was provided by the xylose industry, Jiaozuo Huakang Chemical Co., Ltd., located in Henan Province, China. The dried corncob was grounded into particles with a size of 2–5 mm. All chemicals including xylose, glucose, arabinose, acetic acid (HAC), furfural, sulfuric acid and oxalic acid were purchased from Sigma-Aldrich. All solvents were of HPLC grade.

Experimental design

Corncob samples were characterized using the National Renewable Energy Laboratory's suite of laboratory analytical procedures [21]. The corncob hydrolysis was performed in a 500 mL stainless steel high-pressure reactor (New Era Chemical Machinery Co. Ltd., Weihai, China) equipped with a four-plane blade for stirring and a K-type thermocouple for monitoring the temperature. Silicon carbide electric heating furnace was adopted for heating the reactor.

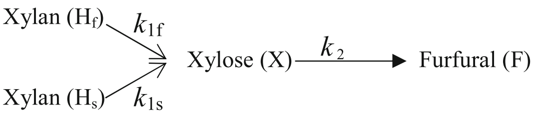
To optimize the hydrolysis conditions for xylose production from corncob, effects of solid–liquid ratio, acid concentration, reaction temperature and reaction time were evaluated [4, 18, 22, 23]. The stirring speed was kept at 50 rpm to maintain uniform mass and heat transfer. At the specified reaction time, the reactor was quenched quickly with ice water bath. The hydrolysate was collected by centrifugation under 12,000 rpm for 10 min and the insoluble residues were washed three times.

Effect of hydrolysis conditions on xylose yield

15.00 ± 0.05 g of corncobs were hydrolyzed in stainless steel reactor at different solid–liquid ratio [1:5, 1:8, 1:10, 1:15, 1:20 and 1:25 (w/v)] with 1.2% (w/w) oxalic acid at 130 °C for 90 min to determine the effect of solid–liquid ratio on xylose yield. After the solid–liquid ratio was determined, the effect of acid concentration on xylose yield was carried out with 30.00 ± 0.05 g corncobs at different concentrations of oxalic acid and sulfuric acid [0.8, 1.2, 1.6, 2.0, 2.4% (w/w)] at 130 °C for 90 min, respectively. Effect of reaction temperature was conducted using respective 1.2% (w/w) oxalic acid and sulfuric acid, containing 30.00 ± 0.05 g corncobs with various temperatures (90, 110, 120, 130 and 150 °C) for 90 min hydrolysis. The residence time was also optimized with corncobs (30.00 ± 0.05 g) hydrolyzed using respective 1.2% (w/w) oxalic acid and sulfuric acid at 130 °C for different residence time (30, 60, 90, 120, 150, 180, 240, 360, 480 and 600 min). The effect of mixed acids on xylose yield was determined under the following condition: corncobs (30.00 ± 0.05 g) were hydrolyzed in stainless steel reactor using mixed acids with various 1.2% (w/w) oxalic acid to sulfuric acid ratio [1:1, 1:2, 1:3, 1:4, 4:1, 3:1 and 2:1 (w/w)] at 130 °C for 90 min.

Kinetic model of acid hydrolysis

Kinetic model could predict the performance of hydrolysis processes and help us understand their role [24–27]. In the present work, the Biphasic model was developed to determine the hydrolysis process of corncob hemicelluloses [24]. As xylan was the major component in corncob hemicellulose, the kinetic study of the acid-catalyzed hydrolysis was based on xylan hydrolysis, which was presented as follows (Scheme 1). For the hydrolysis model, one part of the xylan fraction was hydrolyzed faster than the other part, and the slow and fast hydrolysis fractions were 35 and 65% of total xylan, respectively [24, 27].



Scheme 1 The hydrolysis process of xylan in corncob hemicelluloses

Where H_f and H_s represented fast hydrolysis fraction and slow hydrolysis fraction, k_{1f} (min^{-1}) and k_{1s} (min^{-1}) were the fast and slow reaction rate constants of xylan hydrolysis (equal to xylose formation), respectively, while k_2 (min^{-1}) was the reaction rate constant of xylose degradation. Denoting the concentration of xylan and xylose with H and X, respectively, the differential equations for an isothermal reaction were obtained as follows:

$$\frac{d[H_f]}{dt} = -k_{1f}[H_f], \tag{1}$$

$$\frac{d[H_s]}{dt} = -k_{1s}[H_s], \tag{2}$$

$$\frac{d[F]}{dt} = k_2[X], \tag{3}$$

$$\frac{d[X]}{dt} = k_{1f}[H_f] + k_{1s}[H_s] - k_2[X]. \tag{4}$$

Solving Eqs. (1)–(4), X was given as follows:

$$\begin{aligned}[X] = &\frac{k_{1f}[H_f]_0}{k_2 - k_{1f}}[\exp(-k_{1f}t) - \exp(-k_2 t)] \\ &+ \frac{k_{1s}[H_s]_0}{k_2 - k_{1s}}[\exp(-k_{1s}t) - \exp(-k_2 t)].\end{aligned} \tag{5}$$

Here, t was time and subscript 0 indicated initial conditions. $[H_f]_0$ and $[H_s]_0$ were the concentrations of fast and slow hydrolytic xylan, respectively ($[H_f]_0 + [H_s]_0 = [H]_0$). $[H]_0$ was the theoretical maximum of xylose from xylan without degradation and it represented the value of 34.0 g L^{-1}.

The rate constants of k_{1f} and k_{1s} at different reaction conditions were determined from the experimental data using non-linear regression analysis according to the classic Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right). \tag{6}$$

The experiment diagrams and estimation of kinetic parameters to fit these non-linear models for corncob hydrolysis were conducted with Origin Pro 8.1 (Origin Lab Corporation, MA, USA) and MATLAB R 2014a (The MathWorks, Inc., Natick, MA, USA). Reliability of the estimated parameters was evaluated with the obtained determination coefficient (R^2).

Analysis method

Sugars (xylose, glucose and arabinose), acetic acid and furfural were determined by high performance liquid chromatography (HPLC) using refractive index (RI) and UV/visible detectors (Waters, USA) equipped with a Bio-Rad Aminex HPX-87H (300×7.8 mm) column. 5 mmol L^{-1} H_2SO_4 was employed as the mobile phase with a 0.6 mL min^{-1} flow rate at 60 °C. The hydrolysate was centrifuged, and separated into two aliquots. The two samples acetic acid and furfural were analyzed by HPLC under different wavelength, 210 and 274 nm, respectively. The other aliquot was neutralized to pH 5.0–6.0 with calcium carbonate, filtered and then analyzed for sugars content. All experiments were conducted in triplicate.

Results and discussions

The main compositions of corncob employed here analyzed by quantitative acid hydrolysis with standard reaction system were as follows: 34.74 ± 0.18% cellulose, 35.02 ± 0.26% hemicelluloses (xylan, 29.92 ± 0.16%), 20.20 ± 0.13% lignin, 4.21 ± 0.06% acetyl group and 5.81 ± 0.05% other compositions (ash and protein). The major polymeric fractions of corncob in this study were in agreement with the literatures [14].

Effect of solid–liquid ratio on xylose yield

Effect of the solid–liquid ratio on the xylose yield was investigated. As shown in Fig. 1, the highest xylose yield was achieved with the solid–liquid ratio from 1:8 to 1:10. Generally, higher corncob content was conducive to the

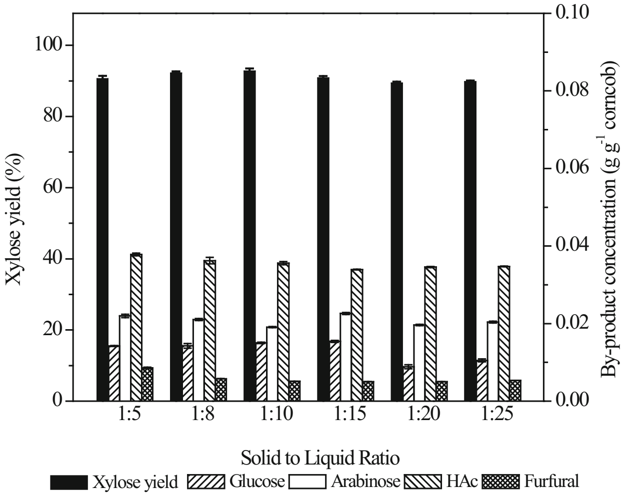


Fig. 1 Effect of solid to liquid ratio on the xylose yield. Yields of xylose (%): the percent of the final xylose concentration (g L^{-1}) divided by the initial corncob mass concentration (g L^{-1})

formation of xylose. When the solid–liquid ratio decreased from 1:10 to 1:25, the xylose yield decreased accordingly, due to the decrease of the hydrolysis rate. Moreover, water usage could be reduced with the increase of corncob percentage. Therefore, it was concluded that the solid–liquid ratio of 1:8 was more acceptable for practical application and only 800 mL of water was required for 100 g of corncob.

Effect of acid concentration on xylose yield

The effect of acid concentration on xylose yield was shown in Fig. 2. The xylose yield increased from 27.7 to 31.6 g L^{-1} with the increase of oxalic acid concentration from 0.8 to 1.2% after 90-min reaction at 130 °C. However, it dropped to 30.4 g L^{-1} when oxalic acid concentration was further increased to 1.6%. This may be caused by the faster reaction rate of by-product formation than that of xylose production at high acid concentration. Compared with oxalic acid as catalyst, the maximum xylose concentration of 28.8 g L^{-1} was obtained with 1.2% sulfuric acid. However, there were no significant changes in xylose yield with sulfuric acid concentration further increased from 1.2 to 2.4%. The xylose yield in sulfuric acid was lower than that obtained in oxalic acid might be due to the degradation of xylose. Results showed that the by-product concentration of furfural 0.5 and 1.8 g L^{-1} was observed with 1.2% oxalic acid and sulfuric acid, respectively. Though the cost of oxalic acid was higher than sulfuric acid, the oxalic acid hydrolysis with higher xylose yield and less furfural was better for downstream compatibility. Especially, oxalic acid is a weaker oxidizers that has lower corrosiveness to equipment. On the basis of these results, oxalic acid was more promising than sulfuric acid for the production of xylose from corncob.

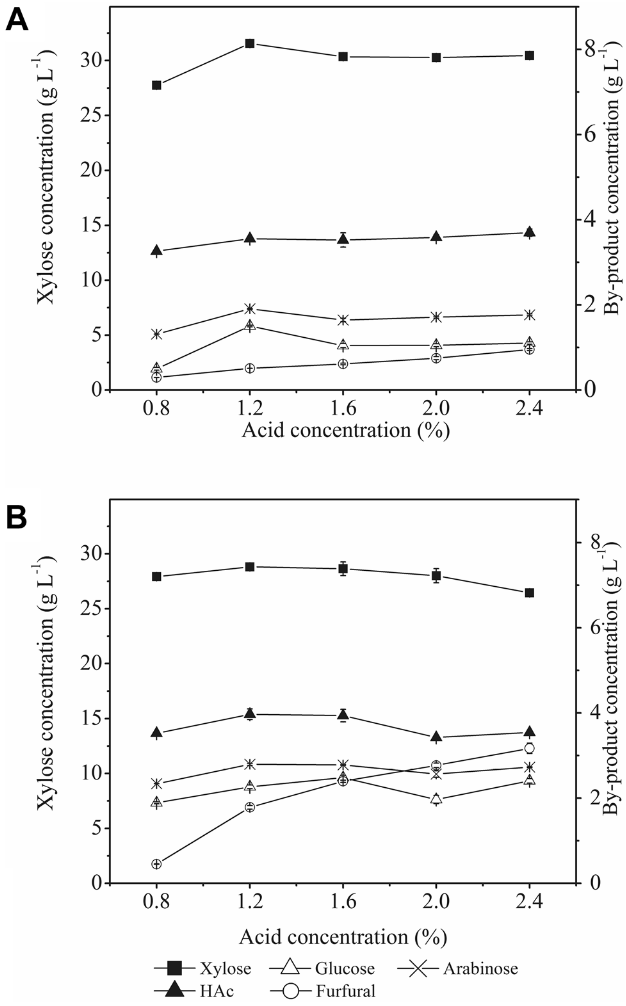


Fig. 2 Effect of acid concentration on the xylose yield with 30.00 ± 0.05 g corncobs and acid concentrations from 0.8 to 2.4% at 130 °C reacted for 90 min. **a** Oxalic acid, **b** sulfuric acid

Effect of hydrolysis temperature on the xylose yield

The effect of hydrolysis temperature on the xylose yield was performed to evaluate the acid hydrolysis conditions for increase the xylose production. As shown in Fig. 3, it showed the xylose yield increased with the increase of hydrolysis temperature from 90 to 130 °C and the maximum xylose yields of 31.6 and 28.8 g L^{-1} were obtained with 1.2% oxalic acid and 1.2% sulfuric acid at 130 °C, respectively. The xylose yield decreased dramatically as temperature was increased from 130 to 150 °C in sulfuric acid, and similarly, it was proposed that higher reaction temperature was conducive to the side-reactions, resulting in the decomposition of xylose. Meanwhile, the obvious uptrend of furfural yield was observed for the sulfuric acid-catalyzed hydrolysis. It demonstrated that sulfuric acid resulted in easier xylose degradation at high temperatures compared to oxalic acid. As such, the temperature of 130 °C was determined as optimal for the followed experiments.

Effect of residence time on xylose yield

The effects of reaction time on xylose yield ranging from 0 to 600 min were investigated. As shown in Fig. 4, the maximum xylose yield of 32.7 and 29.0 g L^{-1} was achieved after reaction for 120 and 60 min with corncobs treated with oxalic acid and sulfuric acid, respectively. Xylose yield of 32.7 g L^{-1} with oxalic acid, to the best of our knowledge, was the highest yield ever reported for acid-catalyzed hydrolysis of corncob to product xylose. Additionally, it showed that the xylose yield changed little by the reaction time was further increased with oxalic acid. However, the xylose yield decreased sharply and the furfural yield increased dramatically by the hydrolysis of

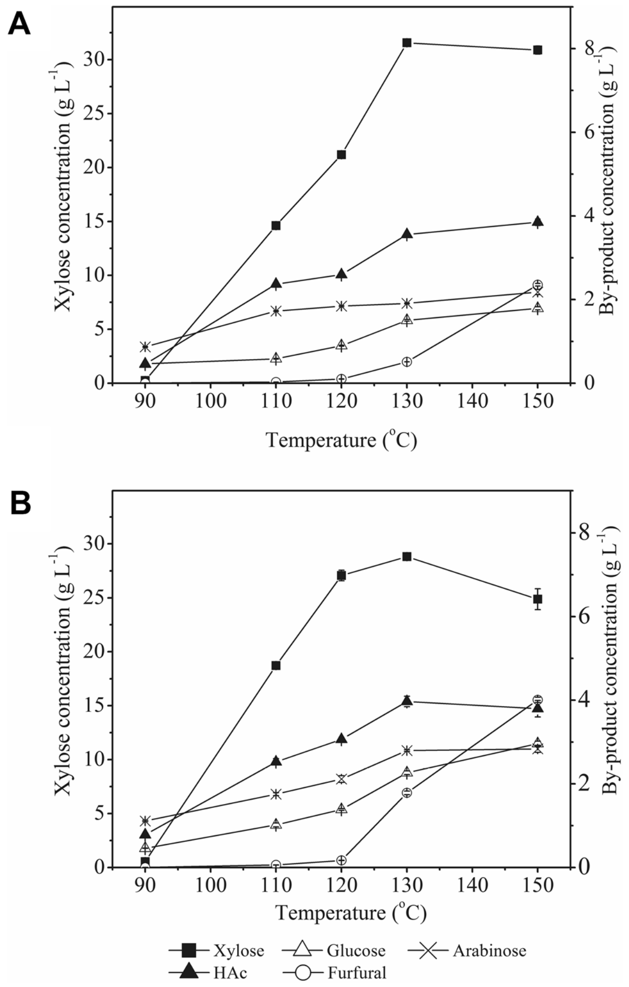


Fig. 3 Effect of hydrolysis temperature on the xylose yield containing 30.00 ± 0.05 g corncobs with temperature from 90 to 150 °C for 90 min. **a** Oxalic acid, **b** sulfuric acid

sulfuric acid with longer residence time, indicating that furfural was strongly dependent on residence time for sulfuric acid.

Effect of combined use of oxalic acid and sulfuric acid on xylose yield

It was observed from the above results that the strong acid of sulfuric acid could promote the corncob hydrolysis to xylose in shorter time compared to oxalic acid. However, the largest drawback to use sulfuric acid is that it could readily degrade xylose in contrast to oxalic acid. Meanwhile, sulfuric acid has a higher neutralization cost and may be accompanied by high capital cost of the equipment and reactor materials of construction for dealing with its corrosive nature [28]. Here, the hydrolysis of corncob treated with combined use of oxalic acid and sulfuric acid was further investigated. As shown in Fig. 5, the maximum xylose yield of 31.7 g L^{-1} was obtained when the ratio of

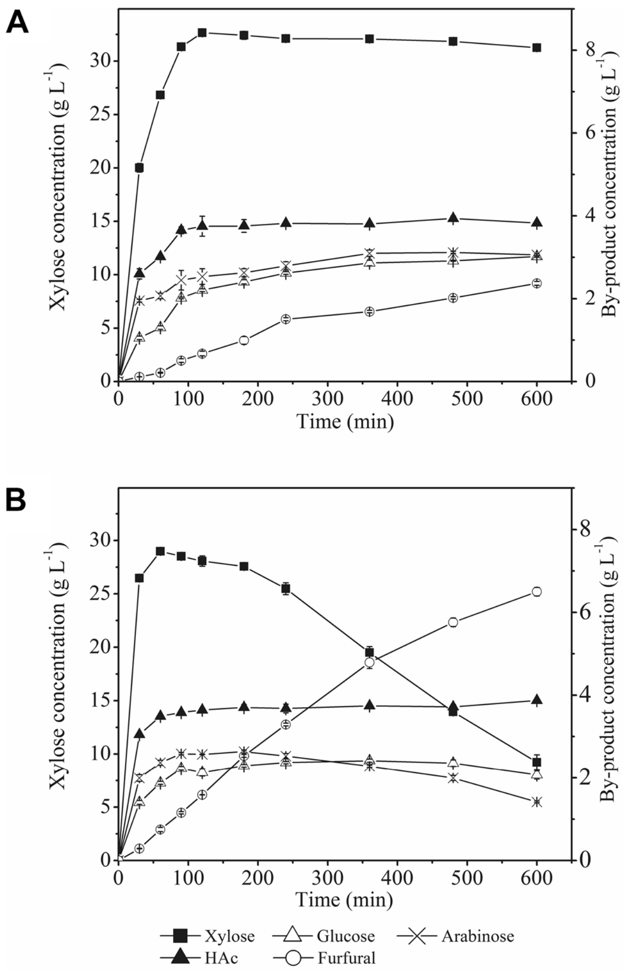


Fig. 4 Effect of acid residence time on the xylose yield with corncobs (30.00 ± 0.05 g) hydrolyzed using respective 1.2% (w/w) oxalic acid and sulfuric acid at 130 °C for residence time from 30 to 600 min. **a** Oxalic acid, **b** sulfuric acid

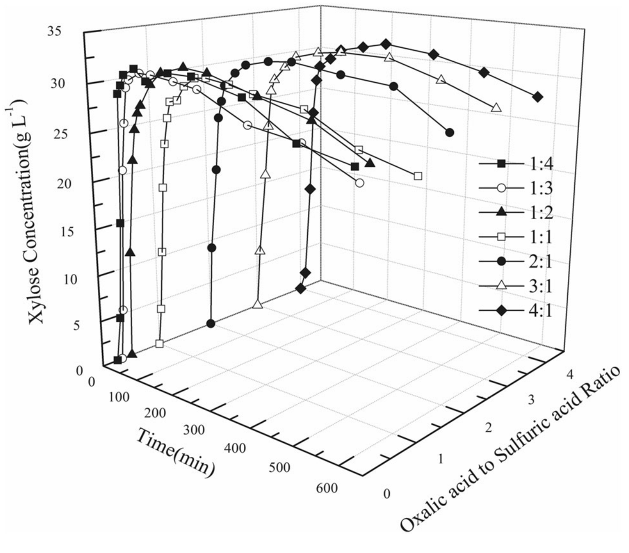


Fig. 5 Variation of xylose yield with the ratio of oxalic acid and sulfuric acid from 1:1 to 4:1 at 130 °C for 90 min

oxalic acid and sulfuric acid ratio was 1:4 after 90-min reaction at 130 °C. It demonstrated that the combined use of oxalic acid and sulfuric acid was conducive to the balance of xylose yield and residence time compared to the use of single acid.

Kinetic model

In this study, the biphasic model was developed to elucidate the competitive reaction of xylose production and degradation during corncob hydrolysis treated with acid. The theoretical values were calculated by Eq. (5) and the experimental data was presented in Fig. 6. The experimental data showed a perfect fit to the theoretical values. The xylose yield was significantly affected by the temperature, residence time and acid concentration. The maximum xylose yield of 32.7, 29.0 and 31.7 g L^{-1} was achieved at 130 °C for 120, 60 and 90 min by oxalic acid, sulfuric acid and the mixed acids, respectively.

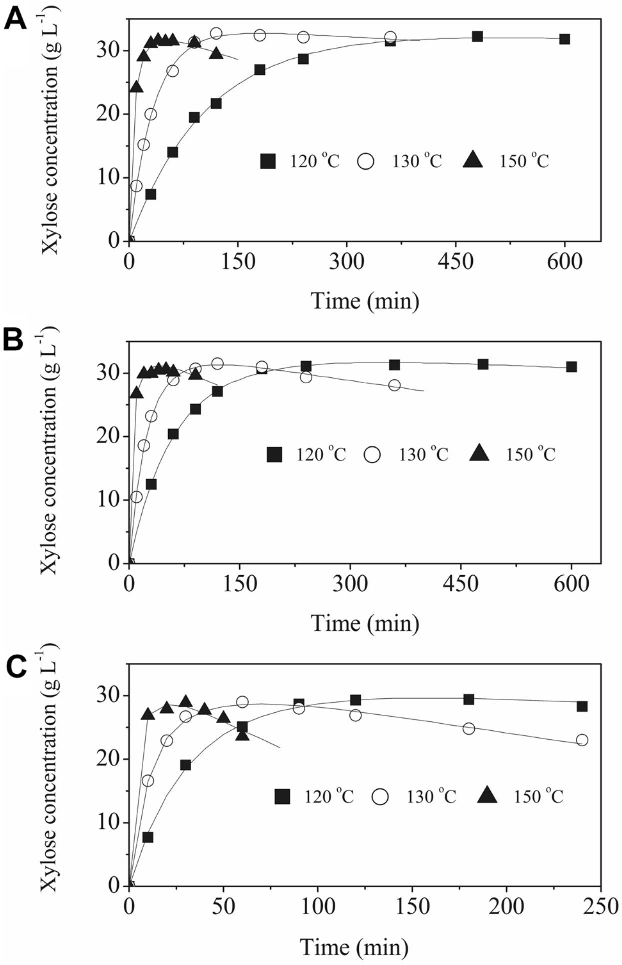


Fig. 6 Experimental and predicted reaction progress for oxalic acid, sulfuric acid and mixed acids hydrolysis at 120,130,150 °C. **a** Oxalic acid, **b** combined use of oxalic acid and sulfuric acid, **c** sulfuric acid. Symbolic labels representing experimental data; line representing prediction data

The reaction rate constants of xylose production (k_{1f} and k_{1s}) and degradation (k_2) at various temperatures were calculated using MATLAB R 2014a and listed in Table 1. It showed that the rate constants increased with reaction temperature elevating and the acidic condition was also conducive to the rate constants. This result was consistent to the experimental data discussed above. It was observed that xylan could be hydrolyzed to xylose easily in sulfuric acid (higher k_{1f} and k_{1s}), but the degradation of xylose was also occurred easily (higher k_2 value). Therefore, high xylose yield could only be obtained with balance of k_{1f}, k_{1s} and k_2. Although using sulfuric acid as catalyst exhibited higher k_1, the lower k_2 in oxalic acid-based hydrolysis resulted in decreased xylose degradation, resulting in much higher xylose yields. According to the classical Arrhenius equation, ln$k$ was plotted against T^{-1} to obtain E_a (activation energies). The Ea for the fast hydrolysis step were determined as 105.2, 133.7 and 135.4 kJ mol^{-1} for sulfuric acid, oxalic acid and mixed acids, respectively. Considering the balance among reaction rate, xylose yield and by-product production, the mixed acids might be potential to produce xylose from corncob.

To further evaluate the applicability of the kinetic models presented in this work, hydrolysis experiments were carried out at temperatures of 140 and 170 °C in 1.2% oxalic acid conditions. Results suggested that xylose concentrations of 31.5 and 31.0 g L^{-1} were obtained at 140 °C for 95 min and 170 °C for 12 min, respectively, which were agreement with the predictions by kinetic model, of which 32.1 and 31.4 g L^{-1} xylose should be obtained for 97.1 min and for 13.6 min, respectively.

Purification and crystallization process of xylose

The xylose purification and crystallization from hydrolysate was conducted and the process was carried out as follows: the ion-exchange treatment to remove acid was conducted after the active carbon discoloration of hydrolysate, then the sugary liquor was concentrated and xylose was further crystallized. 8% (w/v) of activated carbon addition at 80 °C for 20 min was the best condition for decolorization process and it was conducted two times to remove impurity ions with excellent efficiency. The results demonstrated that the ion removal rate reached 94 and 50% after treated by D380 anion exchange resin and D001 cation exchange resin, respectively, with the transmittance of solution greater than 99.9%. The xylose crystallization yield of 85% with the purity of 98.6% was realized after 12 h of crystallization.

Table 1 Rate constants for different acid hydrolysis in corncob at various temperatures

Acid type	Temperature (°C)	k_{1f}	k_{1s}	k_2	R^2
Oxalic acid	120	1.02×10^{-2}	6.83×10^{-3}	1.15×10^{-4}	0.9986
	130	3.41×10^{-2}	2.18×10^{-2}	2.05×10^{-4}	0.9987
	150	2.00×10^{-1}	5.59×10^{-2}	1.22×10^{-3}	0.9995
Combined use of oxalic acid and sulfuric acid	120	1.99×10^{-2}	8.56×10^{-3}	1.81×10^{-4}	0.9992
	130	5.04×10^{-2}	2.27×10^{-2}	6.02×10^{-4}	0.9988
	150	3.56×10^{-1}	6.30×10^{-2}	1.68×10^{-3}	0.9997
Sulfuric acid	120	3.78×10^{-2}	1.29×10^{-2}	7.24×10^{-4}	0.9980
	130	1.02×10^{-1}	2.48×10^{-2}	1.90×10^{-3}	0.9978
	150	3.83×10^{-1}	7.73×10^{-2}	6.00×10^{-3}	0.9965

k_{1f} (min^{-1}) the rate constants of fast xylan hydrolysis; k_{1s} (min^{-1}) the rate constants of slow xylan hydrolysis; k_2 (min^{-1}) the reaction rate constants of xylose degradation; R^2 the determination coefficient

Conclusions

In this study, oxalic acid-catalyzed hydrolysis was conducted for xylose production. The results showed that oxalic acid possessed superior in high yield xylose production from hemicellulose and the advantageous features including low by-products and compatibility down-stream processing was obtained. The combined use of dilute oxalic acid and sulfuric acid provided as a promising strategy applied to hydrolyze hemicellulose to xylose with relatively shorter reaction time and higher xylose yield. The kinetic model developed in this study provided good insight on the production and degradation of xylose in the hydrolysis process, and the theoretical data calculated from the model were perfect fit to the experimental data. The high xylose yield with high purity was achieved after purification and crystallization.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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