Comparative Study of Single Stage and Two-Stage Pretreatments on Corn Stover: A Kinetic Assessment

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The effects of two-stage pretreatment consisting of tepid water (first stage) and $FeCl_3$ (second stage) pretreatments on hemicellulose hydrolysis were investigated. A kinetic comparison between the single stage ($FeCl_3$-only pretreatment) and the two-stage pretreatment was evaluated. Compared with single stage pretreatment, the two-stage pretreatment decreased the activation energy E_a of hemicellulose hydrolysis by 38.3% and decreased the optimal reaction time by 34.8%. Besides, the xylose content increased by 14.9% and the catalyst dosage decreased by 31.9% in the two-stage pretreatment. This study provided an efficient pretreatment process for hemicellulose hydrolysis.

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Keywords: Two-stage pretreatment; Hemicellulose hydrolysis; Kinetics; $FeCl_3$

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INTRODUCTION

Corn stover is a key raw material because of its abundant availability, relatively low cost, and renewable character for the production of high added-value products, such as biofuel. However, corn stover primarily consists of cellulose, hemicellulose, and lignin, which are high polymeric type compounds. Besides, these three main components form a complex three-dimensional structure, which results in the inefficient utilization of this material by microorganisms (Zheng *et al*. 2014; Sankaran *et al*. 2020). In order to improve the efficient utilization of corn stover by microorganisms, disruption of the cellulose and hemicellulose polymeric chains into monosaccharides *via* pretreatment is needed. Former researchers have investigated many pretreatment methods, such as dilute acid (Mafe *et al*. 2015; Zang *et al*. 2015; Saha *et al*. 2016; Sivagurunathan *et al*. 2017; Morais *et al*. 2020), alkali (Nargotra *et al*. 2018; Yang *et al*. 2019), steam explosion (Kataria *et al*. 2016; Theuretzbacher *et al*. 2016), ammonia (Sakuragi *et al*. 2017; Joy *et al*. 2020), enzymatic pretreatment (Yeo-Myeong *et al*. 2014; Bhushan *et al*. 2021), and other methods (Zakaria *et al*. 2015; Zhang *et al*. 2016; Fu *et al*. 2021; Rana and Prajapati 2021; Yiin *et al*. 2021). However, these pretreatments still have several problems, such as low efficiency, high cost, and environmental pollution (Liu *et al*. 2009).

Compared to these pretreatment methods, inorganic salt pretreatment has shown some advantages of high efficiency, less corrosion, and recoverability. Moreover, there are research findings that the Fe^{3+} ion could catalyze the hydrolysis process well, especially the hemicellulose hydrolysis. Sun *et al*. (2011) reported that the maximum xylose yields reached 92.72% of initial xylan when the hemicellulose was hydrolyzed using $Fe(NO_3)_3$. Liu *et al*. (2009) reported that the $FeCl_3$ exhibited a particularly strong catalytic capacity on hydrolyzing hemicellulose, and 90% xylose yield was obtained. However, in terms of price, $FeCl_3$ is cheaper than $Fe(NO_3)_3$; therefore, $FeCl_3$ is a more viable alternative for hemicellulose hydrolysis.

However, ferric salt is less effective than dilute acid pretreatment. In order to achieve the same effect as dilute acid treatment, a large amount of ferric salt is required, which will greatly increase the cost of pretreatment. Therefore, to improve competitiveness of ferric salt, a new method such as two-step (two-stage) method (the first stage is low temperature water extraction, the second stage involving catalyst pretreatment) was put forward to improve the catalytic effect and reduce the amount of ferric salt. Wang *et al*. (2012) reported that compared to single stage pretreatment, the total sugar content increased by 23.8% and the amount of catalyst ($Fe(NO_3)_3$) decreased by 28.8% when using two-stage pretreatment. However, the advantages and disadvantages of single stage and two-stage methods had been compared only in terms of sugar yield up to the present, and there are few works to compare their kinetics. In this work, the Saeman model was employed to simulate hemicellulose hydrolysis of corn stover for single stage and two-stage pretreatments. The objective of this work was to obtain an in-depth mechanism for understanding the two-stage pretreatment by analyzing the kinetics, and to predict the maximum sugar yield of two-stage pretreatment.

EXPERIMENTAL

Material

Corn stover was collected from local agricultural fields at Zhu Madian, located in the south-central of Henan province, China; the geographical coordinates are 32°18'-33°35' north latitude, 113°10'-115°12' east longitude. The corn stover was air-dried and milled to uniform particles size of < 0.5 mm. The miller was purchased from local vendor, and its model is BJ-500A. All samples were stored in airtight plastic bags in a desiccator prior to use. The initial chemical composition of corn stover is shown in Table 1. These values were consistent with those reported by other researchers for corn stover (Saha *et al*. 2013; Zhong *et al*. 2018; Yu *et al*. 2020).

Methods

Single stage ($FeCl_3$-only) pretreatment

Pretreatment of corn stover was conducted in a 250 mL stainless steel reactor (Shanghai Jieang, JGF, China). The reactor used has an electric heater with a thermocouple and a magnetic force agitation. Each experiment was carried out using a 1:9 ratio of corn stover (g) and catalyst (g). The pretreatment temperature was set to be 130, 150, and 170 °C, the reaction times were set to be 2, 5, 10, 30, and 60 min, and the $FeCl_3$ concentrations used was 0.1 mol/L. After treatment, the mixture (solid residues + hydrolysate) was filtered in a vacuum system using a Buchner funnel. The solid residues and the hydrolysate were stored for further analysis.

Two-stage pretreatment (Tepid water pretreatment + $FeCl_3$ treatment)

In the first stage, corn stover was pretreated using tepid water in 1 L glass bottles at 60 °C for 4 h. The ratio of corn stover to deionized water was set at 1:9 (w/w). After tepid water pretreatment, the mixture was filtrated by filter cloth to obtain the soaked residue and hydrolysate. The hydrolysate was filtered through a filter film (0.22 μm) for determination of sugars and furfural. The soaked residue was washed and dried at 60 °C for the second stage $FeCl_3$ treatment.

In the second stage, the soaked residue was pretreated by $FeCl_3$. The experiments were conducted in the same reactor and under the same condition as the single stage pretreatment.

Analytical method

The chemical composition of the corn stover and the soaked residue obtained from the first stage was determined according to the National Renewable Energy Laboratory (NREL 2006) analytical methods for biomass.

The composition of the hydrolysate was determined by HPLC (Shimadzu, LC-20A, Kyoto, Japan) using a Bio Rad (Hercules, CA, USA) Aminex HPX-87H (300×7.8 mm column). The operating conditions of HPLC were 65 °C, 5 mM H_2SO_4 as eluent, and 0.6 mL/min flow rate. Two detectors are needed, one is a refractive detector for analyzing sugars and another one is a UV detector for analyzing furfural. HPLC grade (>99.9%) standard sugars (D-(+) glucose, D-(+) xylose, L-(+) arabinose) were purchased from Sigma Aldrich, USA. Furfural (>99.5%) was purchased from Macklin reagent, China.

Kinetic Model Development

The Saeman model was developed to simulate the hemicellulose hydrolysis catalyzed by $FeCl_3$ (Saeman 1945),

$$\text{Hemicellulose (H)} \xrightarrow{k_1} \text{Xylose (X)} \xrightarrow{k_2} \text{Degradation Production (D)} \quad (1)$$

where k_1 (min^{-1}) is kinetic coefficient of xylose release and k_2 (min^{-1}) is kinetic coefficient of xylose degradation. Decomposition products can be furfural. The concentration of xylose could be predicted as follows,

$$X(t) = X_0 e^{-k_2 t} + H_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad (2)$$

where X is the concentrations of xylose (g/L) and H is the concentrations of xylan (g/L), t is time (min), the subscript 0 represents initial conditions, hence $X_0 = 0$ g/L.
Thus

$$X(t) = H_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad (3)$$

The yield of xylose (Y) was calculated as shown in Eq. 4.

$$Y(t) = \frac{X(t)}{H_0} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad (4)$$

The kinetic parameters estimation was achieved by a commercial optimization routing dealing with Newton's method to minimize the sum of squares of deviations between the experimental and calculated data (Sun *et al*. 2011).

When the xylose yield reached the maximum $\frac{dY_{\max}}{dt} = 0$, this was applied to Eq. 4. Then the optimal reaction time when the xylose yield could reach the maximum could be calculated,

$$t_{\max} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \tag{5}$$

where $t_{\max}$ is the optimal reaction time.

The Arrhenius equation was applied to correlate the kinetic coefficients (Zhang *et al*. 2011), as follows,

$$k_i = A_i e^{-\frac{E_a}{RT}} \tag{6}$$

where k_i is the kinetic coefficient (i = 1 or 2), A_i is a pre-exponential factor (same units as k_i), E_a is the activation energy (KJ/ mol), R is the gas constant, 8.3143 × 10^{-3} (KJ/(mol K)), and T is the absolute temperature (K).

RESULTS AND DISCUSSION

Effect of $FeCl_3$ Concentration on the Xylose Yield

To determine the optimal $FeCl_3$ concentration, corn stover was pretreated at 150 °C for 10 min at various $FeCl_3$ concentrations (0.05 mol/ L, 0.1 mol/ L, and 0.2 mol/ L). Figure 1 shows the effect of $FeCl_3$ concentration on the xylose yield from corn stover. As presented in Fig. 1, the xylose yield increased first and then decreased with increasing $FeCl_3$ concentrations to 0.05 mol/L, 0.1 mol/L, and 0.2 mol/L. The maximum yield of xylose (71.8%) was reached with 0.1 mol/L $FeCl_3$, which is consistent with the results related to hemicellulose hydrolysis pretreated by ferric salt (Liu and Wyman 2006; Chen *et al.* 2015; Huang *et al*. 2019). The yield of xylose decreased from 71.8% to 9.6% with increasing $FeCl_3$ concentration.

These results implied that xylose was further degraded into the decomposition products, and the decomposition product is mainly furfural. If the $FeCl_3$ concentration was increased, xylose would continue to be degraded to form more furfural. Therefore, under the present experimental conditions, to obtain a high xylose yield, the optimal $FeCl_3$ concentration of 0.1 M was chosen.

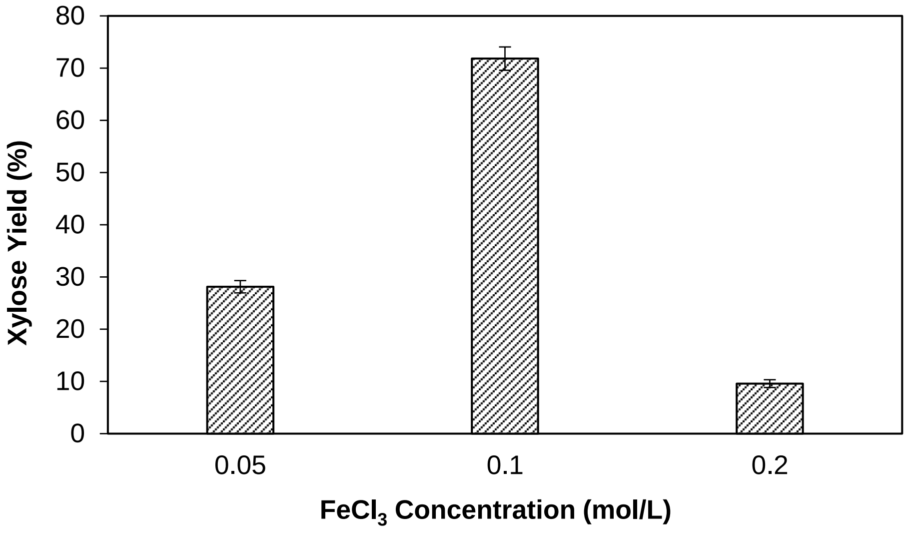

Fig. 1. Yields of xylose in liquid from the pretreatment at 150 °C for 10 min with different $FeCl_3$ concentrations

Single Stage Pretreatment of Corn Stover with $FeCl_3$

Effects of single stage pretreatment

Figure 2 shows the concentrations of xylose obtained under various operational conditions. It showed that xylose concentration was always increasing with time at 130 °C, and the highest concentration of xylose (20.3 g/L) was obtained when the reaction time was 60 min, under this condition, the xylose yield was 88.7%. It was also found that the xylose concentration showed different changing rules when the temperature was varied.

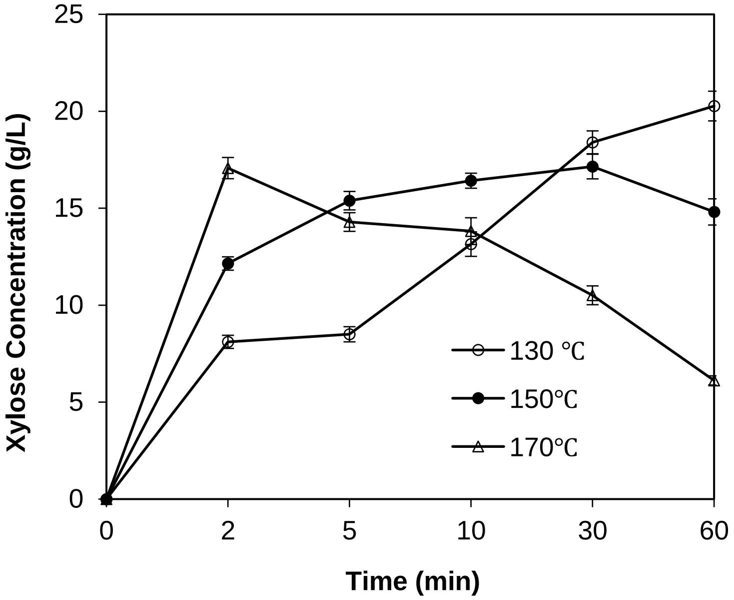

Fig. 2. Effects of temperature and time on the xylose concentration after single stage pretreatment

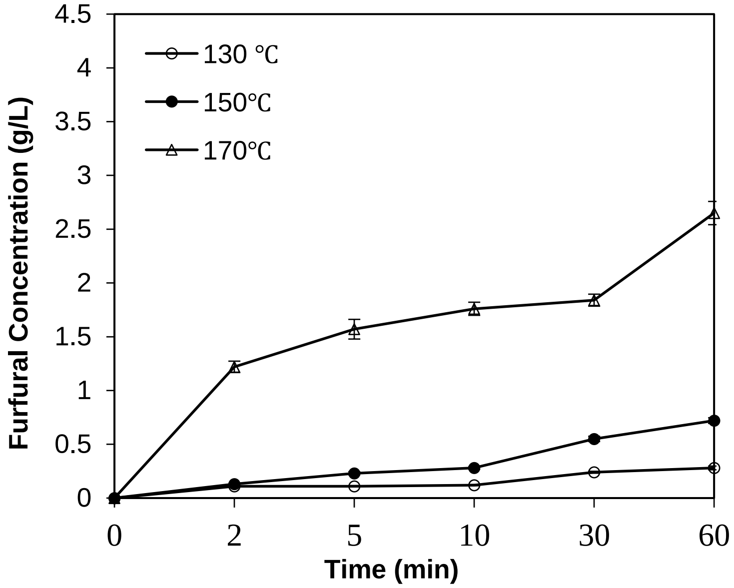

Fig. 3. Effects of temperature and time on the furfural concentration after single stage pretreatment

As presented in Fig. 2, the xylose concentration reached a maximum first and then began to decrease with increasing time when the temperature was raised to 150 °C and 170 °C, and the decreasing rate at 170 °C was faster than that at 150 °C. The xylose yield was lowest (6.12%) at the severest conditions (170 °C, 60 min). These results indicated that xylose was further degraded into the furfural, which was consistent with the trend of furfural concentration (showed in Fig. 3). Figure 3 showed that the furfural concentration increased with the increasing of temperature and time. The maximum furfural concentration obtained was 2.65 g/L from experiment performed at 170 °C for 60 min, which is consistent with the result related to corn stover pretreated by ferric salt (Kamireddy *et al*. 2013).

Kinetic model for hemicellulose hydrolysis of corn stover

Table 2 shows that both k_1 and k_2 increased with temperature, and k_1 was higher than k_2 under all pretreatment conditions. As the temperature reached 170 °C, k_2 increased faster than k_1; thereby the xylose would degrade quickly. The result agreed well with the experimental result that the xylose yield was the lowest at 170 °C. The values of k_1 and k_2 in this study were higher than those obtained from inorganic acid catalysis or $Fe(NO_3)_3$ treatment (Herrera *et al*. 2004; Sun *et al*. 2011).

The Arrhenius kinetic parameters for corn stover hydrolyzed by $FeCl_3$ are shown in Table 3. The pre-exponential factor for hemicellulose hydrolysis in corn stover by $FeCl_3$ was 1.42×10^7. The activation energy E_a was 63.2 KJ/mol, which was lower than those observed for a dilute sulfuric acid pretreatment (E_a = 129.8 KJ/mol), which implied that compared with sulfuric acid, $FeCl_3$ was more efficient to hydrolyze hemicellulose (Esteghlalian *et al*. 1997).

Optimization for xylose yield from corn stover

It is better to obtain hydrolysates with high xylose concentration to be used as fermentation media. Thereby, the operation conditions were optimized by kinetic models. The maximum xylose yields from single stage pretreatment obtained with the determined t_{max} are shown in Table 4. The results revealed that t_{max} would be reduced if the temperature were increased; meanwhile, the xylose yield would decrease accordingly. This is mostly because the xylose would degrade severely at higher temperature. Therefore, the optimal condition for corn stover hydrolysis was considered as 150 °C, 0.1 M $FeCl_3$ for 14.1 min according to Eqs. 4 and 5. Under these conditions, the maximum xylose yield was 91.0%.

Two-stage Pretreatment of Corn Stover

Effects of tepid water pretreatment

Table 1 displays the chemical composition of corn stover and soaked residue obtained from the first stage pretreatment. After the first stage pretreatment (tepid water pretreatment), the total solid recovery was 68.0%, which indicated that 32.0% of the raw material was dissolved in the first stage. The reduction in the total amount of solid content also meant that the catalyst amount to be used for the second stage would decrease. Besides, the xylan content increased after water pretreatment. This was because the solid had dissolved. The high content of xylan in the solid fraction made it valuable for further utilization.

Table 1. Chemical Composition of Corn Stover and Soaked Residue

Composition (% Dry Matter)	Corn Stover	Soaked Residue
Glucan	35.59	38.06
Xylan	18.90	21.01
Araban	3.140	4.360
Acetyl group	3.400	4.250
Klason lignin	14.50	17.80
Ash	4.710	2.750
Others	19.76	11.77

Effects of $FeCl_3$ pretreatment

The effects of the $FeCl_3$ pretreatment on xylose concentrations of the soaked residue hydrolysis are shown in Fig. 4. The results illustrated that there was some notable difference between the single stage and two-stage pretreatments. The xylose concentration reached a maximum value first and then decreased with the increasing of reaction time at all temperatures. The xylose concentration reached the maximum (23.4 g/ L) at 130 °C for 30 min, the conversion yield was 90.3%, which was higher than that (88.7%) obtained in single stage pretreatment (130 °C, 60 min). In addition, compared with the single stage pretreatment, the xylose concentrations in the two-stage pretreatment were all higher than those of the single stage pretreatment at all conditions, which implied that the two-stage pretreatment was a more effective method than single stage pretreatment for hemicellulose hydrolysis. These results were consistent with that reported by Wang *et al*. (2012).

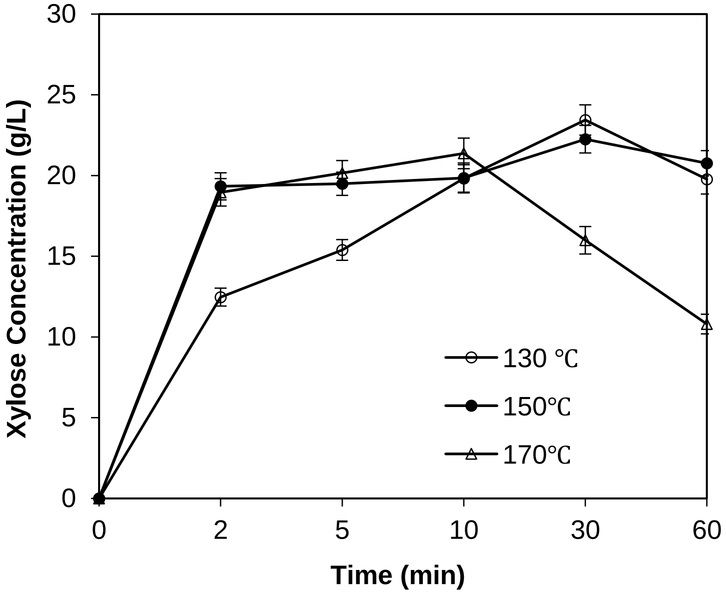

Fig. 4. Effects of $FeCl_3$ concentration, temperature, and time on the xylose concentrations after two-stage pretreatment

Figure 5 shows that the furfural concentration increased with temperature and time. The maximum furfural concentration obtained was 4.14 g/L, which was obtained in the experiment performed at 170 °C for 60 min. In addition, compared with the single stage pretreatment, the furfural concentrations in the two-stage pretreatment were all high at all conditions. This is because the xylose content obtained in two-stage pretreatment was higher than that obtained in single stage pretreatment; therefore, the degradation of xylose in two-stage pretreatment was also higher than that in single stage pretreatment. However, the formation rate of xylose was greater than degradation rate; thereby, the two-stage pretreatment is efficient.

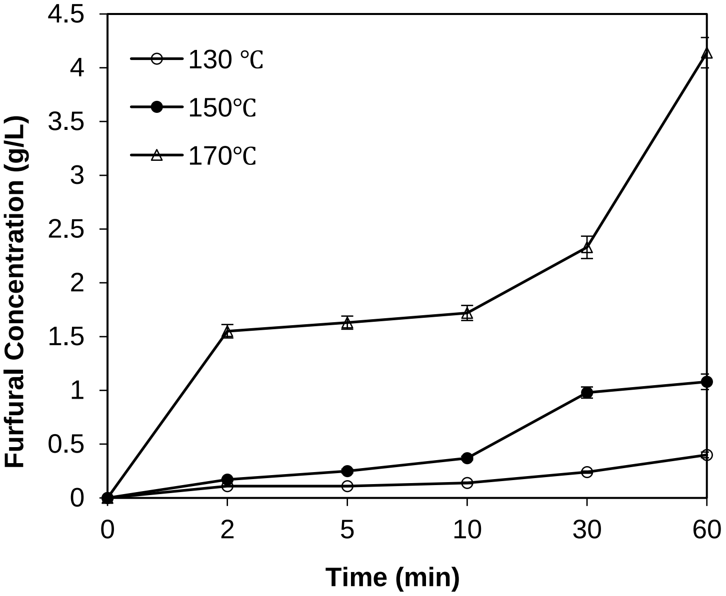

Fig. 5. Effects of $FeCl_3$ concentration, temperature, and time on the furfural concentrations after two-stage pretreatment

Kinetic model for hemicellulose hydrolysis of the soaked residue

The kinetic model for hemicellulose hydrolysis of soaked residue catalyzed by $FeCl_3$ in two-stage pretreatment is shown in Table 2. Table 2 displays that the values of k_1 and k_2 in two-stage pretreatment increased with increasing temperature and the k_1 values were higher than k_2 values under all pretreatment conditions, which implied that the formation rate of xylose was greater than its degradation rate. In addition, the k_1 values of two-stage pretreatment were higher than that of single stage pretreatment at all temperatures, which indicated that the corn stover extracted by tepid water was easier to hydrolyze than raw corn stover.

The correlation of constant k_1 with temperature is shown in Table 3. The activation energy E_a for two-stage pretreatment was 39.0 kJ/mol. This was lower than that for single stage pretreatment (63.2 KJ/mol), which implied that the soaked residue was easier to hydrolyze than raw corn stover.

Table 2. Kinetic Parameters for Hemicellulose Hydrolysis of Corn Stover under Various Pretreatment Conditions

T (°C)	Single stage			Two-stage		
	k_1	k_2	R^2	k_1	k_2	R^2
130	0.08923	0.004543	0.968967	0.200281	0.005478	0.974985
150	0.228317	0.010700	0.948415	0.494425	0.005534	0.939547
170	0.489558	0.033749	0.897182	0.566684	0.017395	0.983406

Table 3. Activation Energies and Pre-Exponential Factors for Hemicellulose Hydrolysis of Corn Stover under Different Pretreatment Conditions

Pretreatment	Pre-exponential Factor, A_i (min^{-1})	Activation Energy E_a (KJ/mol)	Arrhenius Fit R^2
Single stage	1.42×10^7	63.24	0.9988
Two-stage	2.55×10^4	39.00	0.8646

Optimization for xylose yield of soaked residue

The optimal condition and the maximum xylose yield obtained from soaked residue hydrolysis are shown in Table 4. The results revealed that there were similar trends of xylose yield and reaction time with those of raw corn stover hydrolysis. The optimal condition of soaked residue hydrolysis, which was 150 °C, 0.1 M $FeCl_3$ for 9.2 min, and 97.1% xylose yield was obtained under this optimal condition. Compared with raw corn stover hydrolysis, the soaked residue hydrolysis furnished higher xylose yield with less time. These results implied that corn stover pretreated by tepid water was easier to hydrolyze than raw corn stover. Therefore, the two-stage pretreatment was more efficient than single stage pretreatment.

Table 4. Optimal Conditions Obtained from Saeman Model for Single Stage and Two-Stage Pretreatments

T (°C)	Single stage		Two-stage	
	Time (min)	Xylose Yield (%)	Time (min)	Xylose Yield (%)
130	35.2	90.15	18.5	92.37
150	14.1	90.99	9.2	97.14
170	5.9	86.77	6.3	91.53

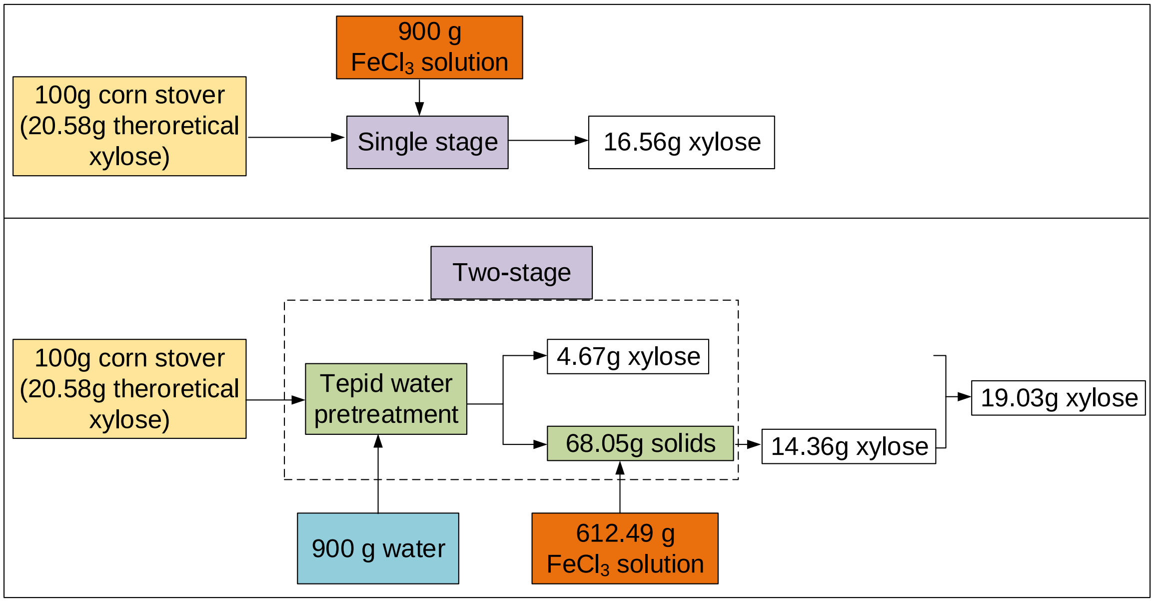

Fig. 6. Material balance chart of single stage and two-stage pretreatment process

Materials Balance Comparison of Single Stage and Two-Stage Pretreatments

Materials balance of single stage and two-stage pretreatments were calculated to compare the two different pretreatments completely and systematically. The results are shown in Fig. 6. In the single stage pretreatment, 900 g catalyst solution was needed to treat 100 g DM of raw corn stover, and 18.7 g xylose was obtained. However, in the two-stage pretreatment, 612.5 g catalyst was needed to treat the soaked residue, and 20.1 g xylose was obtained. This meant that the xylose content increased by 14.9%, and the catalyst dosage decreased by 31.9% when the corn stover was treated by two-stage pretreatment. Therefore, compared with single stage pretreatment, the two-stage pretreatment is more competitive and attractive for biofuels.

CONCLUSIONS

1. The results of this study demonstrated that the two-stage pretreatment (the first stage of tepid water pretreatment, the second stage of $FeCl_3$ pretreatment) is an efficient method for hemicellulose hydrolysis in corn stover.
2. A kinetic comparison between single stage ($FeCl_3$-only pretreatment) and two-stage pretreatment was presented. The results showed that the optimal conditions of hemicellulose hydrolysis were 150 °C, 14.1 min in one-step pretreatment, and 150 °C, 9.2 min in two-step pretreatment, which decreased the reaction time by 34.8%. Under the optimal conditions, the single stage pretreatment yielded the maximum xylose yield (91.0% of initial xylan), the two-stage pretreatment hydrolyzed 97.1% of initial xylan.
3. The activation energy E_a of hemicellulose hydrolysis was 63.2 KJ/mol for single stage pretreatment and 39.0 KJ/mol for two-stage pretreatment, which decreased by 38.3%, which implied that the hemicellulose pretreated by the two-stage pretreatment was easier to hydrolyze.
4. A materials balance was calculated to compare the single stage and two-stage pretreatments. The results illustrated that the xylose increased by 14.92%, meanwhile, the catalyst dosage decreased by 31.9% using two-stage pretreatment, which implied that compare to single stage pretreatment, the two-stage pretreatment was more competitive for hemicellulose hydrolysis.

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