

Modeling and Optimization of the Dilute Sulfuric Acid Treatment on Corn Stover at Low Temperature

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Corn stover was hydrolyzed using dilute sulfuric acid at mass fractions of 2, 4, and 6 % over reaction times up to 300 min at 80 °C. The mass concentrations of sugars (xylose and glucose) and degradation product (furfural) were determined and the kinetic parameters of mathematical models for predicting them in the hydrolysates were obtained. According to the models, an optimal condition for hydrolysis was achieved which was 5 % H₂SO₄ at 80 °C for 240 min and the liquor contained up to 13.21 g L⁻¹ xylose, 5.07 g L⁻¹ glucose and 0.80 g L⁻¹ furfural. The hydrolysates obtained from corn stover can be used to produce hydrogen and methane by anaerobic fermentation process. The models could be used successfully to predict the mass concentrations of xylose, glucose and furfural within 0–300 min under experimental acid mass fractions.

Key words:

Hydrolysis, corn stover, xylose, glucose, furfural, kinetics

Introduction

Corn stover is a renewable, cheap and widely available resource, which is commonly used in the production of energy by combustion. The hydrolysis of corn stover to produce sugars and conversion to fuels and chemicals by biological method could be a good alternative use for this abundant resource.^{1–4} The use of cellulase is a common approach to hydrolyze corn stover and it offers the benefits of mild reaction conditions and selective hydrolysis. In order to achieve useful rates of enzymatic hydrolysis, the lignocellulose must first be pretreated to make the lignocellulosic biomass accessible and reactive to allow high rates and yields on enzymatic hydrolysis.⁵ A number of pretreatment methods have been proposed and investigated by former researchers, including dilute-acid,⁶ alkali,⁷ steam explosion⁸ and ammonia pretreatment.⁹ An effective pretreatment is characterized by several criteria. It avoids the need for reducing the size of biomass particles, preserves the pentose fractions, and limits formation of degradation products that inhibit growth of fermentative microorganisms, minimizes energy demands and limits cost.¹⁰

Dilute-acid at moderate temperatures effectively removes and recovers most of the hemicellulose as dissolved sugars, and glucose yields from cellulose increase with hemicellulose removal to almost 100 %. Although little lignin is dissolved,

data suggest that lignin is disrupted, which increases cellulose susceptibility to enzymes. The most widely used and tested pretreatment approach is based on dilute sulfuric acid.¹¹ However, nitric acid,¹² hydrochloric acid¹³ and phosphoric acid¹⁴ have also been tested. Dilute-acid pretreatment offers good performance in terms of recovering hemicellulose sugars. Wyman reported that the dilute sulfuric acid hydrolysis process was a more economic process than other methods.¹⁵ Alkali pretreatment processes utilize lower temperatures and pressures compared to other pretreatment technologies. Alkali pretreatment may be carried out at ambient conditions, but pretreatment time is measured in terms of hours or days rather than minutes or seconds. Unlike acid-catalyzed pretreatments, a limitation occurs because some of the alkali is converted to irrecoverable salts or incorporated as salts into the biomass by the pretreatment reactions. Compared to dilute-acid pretreatment, steam explosion does not make use of sulfuric acid and is less corrosive to equipment. However, steam explosion yields lower amounts of hemicellulose sugars. Studies suggested an 80 % recovery of 5-carbon sugars with dilute-acid pretreatment while only 65 % in steam explosion.¹⁶ Ammonia fiber/freeze explosion (AFEX) pretreatment yields optimal hydrolysis rates for pretreated lignocelluloses with close to theoretical yields at low enzyme loadings (< 5 FPU per gram of biomass or 20 FPU g⁻¹ cellulose).¹⁷ Herbaceous and agricultural residues are well suited for AFEX. However, this method is

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only moderately effective on hardwoods and is totally ineffective on softwoods.

Most of the xylose and a little amount of glucose can be obtained after pretreatment, and in order to increase the availability of the remaining solids, hydrolyzation of cellulose to glucose must be avoided. Therefore, the selectivity (xylose-glucose ratio) is an important quantity to optimize the hydrolysis conditions.¹⁸ The hydrolysates obtained from corn stover can be used to produce hydrogen and methane by the anaerobic fermentation process.^{19,20} Thus, the hydrolysis process of corn stover using dilute acid can be conceived as the first stage of an integrated strategy for corn stover utilization. Except for xylose and glucose, another byproduct furfural is also present. For the fermentation process, the presence of furfural in the hydrolysates can hinder or prevent a subsequent fermentation step.²¹ The generation of byproducts is increased by increasing the temperature. Therefore, the dilute acid hydrolysis of corn stover at low temperature could be a promising way to use this resource. Furthermore, operating at low temperature is safer and more economic than using higher temperature.²²

Acid hydrolysis releases oligomers and monosaccharides and has already been modeled as a homogeneous reaction in which acid catalyzes the breakdown of hemicellulose to xylose followed by the breakdown of xylose to furfural. Various researchers adapted Saeman's kinetics to describe the hydrolysis of hemicellulose and formation of furfural at high temperatures,²³ but few researchers do it at atmosphere pressure. In this work, the hydrolysis of corn stover using dilute sulfuric acid for obtaining fermentable xylose solutions at low temperature was studied. Through Saeman's model, kinetic parameters of mathematical models for predicting the concentration of xylose, glucose, and furfural were found and used to optimize the process. The experimental results and models were very useful and enabled prediction of the mass concentrations of xylose, glucose and furfural within 0–300 min under experimental acid fractions, as well as selection of several different conditions to achieve the same results. Furthermore, the hydrolysis process of corn stover using dilute acid can be conceived as the first stage of an integrated strategy for corn stover utilization.

Experimental

Raw materials

Corn stover collected in a local farm (Hengshui, China) was used as raw material. The corn stover was air-dried, milled, screened to select the fraction of particles with a size lower than 2.0 mm, and homogenized in a single lot.

Analytical methods

Analysis of the main mass fractions (glucan, xylan and lignin) was carried out by performing a quantitative acid hydrolysis under standard conditions.²⁴

Treatments were performed at 80 °C in media containing 2 g, 4 g and 6 g H₂SO₄ per 100 g liquor using a charge of 1 g corn stover per 10 g liquor. At given reaction times, the liquor was sampled from the reaction media and analyzed. The samples were diluted with water, centrifuged, filtrated with 0.22 μm microvoid filter film, and analyzed by UV/VIS spectroscopy at 280 nm for furfural and by HPLC for glucose and xylose. The HPLC analyses were carried out using a Zorbax Carbohydrate analysis column, the mobile phase was 75 % acetonitrile. Other parameters employed in HPLC analyses were as follow: injection volume, $V = 25 \mu\text{L}$; column temperature, $T = 35 \text{ }^\circ\text{C}$; flow rate, $Q = 1.0 \text{ mL min}^{-1}$.

Statistical analysis

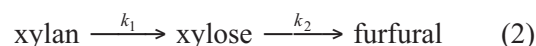
All experiments were carried out in triplicate and data were expressed as average values. Non-linear regression analyses of experimental data were performed with a commercial optimization routine dealing with the Newton's method (Solver, Microsoft Excel 2003) by minimizing the sum of the squares of deviations between experimental and calculated data as reported previously.²⁵

Kinetic models

Due to the difficulty in finding a strict mechanism for hydrolysis of reactions, it is usual to use simplified models to determine the kinetics of the hydrolysis of lignocellulosic materials. The models proposed in the literature use pseudo-homogeneous irreversible first-order reactions. The first model used successfully was proposed by Saeman, as follows:



In this model, Saeman hydrolyzed wood by making use of sulfuric acid. Many researchers also applied it to the hydrolysis of the hemicellulosic fraction.^{22,26} Therefore, it could be generalized for hemicellulosic hydrolysis by eq. (2).



Where k_1 is the rate coefficient of xylose release (min^{-1}) and k_2 is the rate coefficient of xylose decomposition (min^{-1}). Based on this reaction model, eq. (3) expresses xylose mass concentration γ_x as a function of time (t):

$$\gamma_x = \gamma_x^0 e^{-k_2 t} + \gamma_{x,n}^0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

The initial xylan and xylose mass concentrations are defined at time 0 as $\gamma_{x,n}^0$ and γ_x^0 , respectively. Assuming that γ_x^0 is close to 0, a simplified model yields as eq. (4):

$$\gamma_x = \gamma_{x,n}^0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

A similar model can be developed to describe the increase in glucose mass concentration; in this case, the decomposition reactions were negligible and the model can be simplified as eq. (5):



Where k_3 is the rate coefficient of glucose release (min^{-1}). Eq. (6) expresses the glucose mass concentration γ_g as a function of time (t):

$$\gamma_g = \gamma_g^0 (1 - e^{-k_3 t}) \quad (6)$$

γ_g^0 is the potential glucose mass concentration estimated by regression.

Eq. (7) can be used to express furfural mass concentration γ_f as a function of time in the same way:

$$\gamma_f = \gamma_f^0 (1 - e^{-k_4 t}) \quad (7)$$

γ_f^0 is the potential mass concentration of furfural (g L^{-1}) that is determined by regression analysis.

Eqs. (4), (6) and (7) have been applied to model the hydrolysis of corn stover with dilute sulfuric acid. Non-linear regression analyses were performed to obtain the kinetic parameters and coefficients. The results were statistically evaluated with the coefficient of correlation R^2 to establish the significance of the models.

Results and discussion

Sugars and byproducts formation

We chose the ranges of sulfuric acid mass fractions as $w = 2\% - 6\%$ and reaction time as 0–300 min because these values were similar to those used for dilute sulfuric acid hydrolysis of other lignocellulosic substrates.^{12,22,27}

The composition of the main fraction of corn stover was glucan, 43.4 %; xylan, 19.0 %; lignin, 21.2 %. Through material balance, if the conversion of xylan to xylose is quantified, the maximum possible mass concentration of xylose was $\gamma_x = 21.6 \text{ g L}^{-1}$.

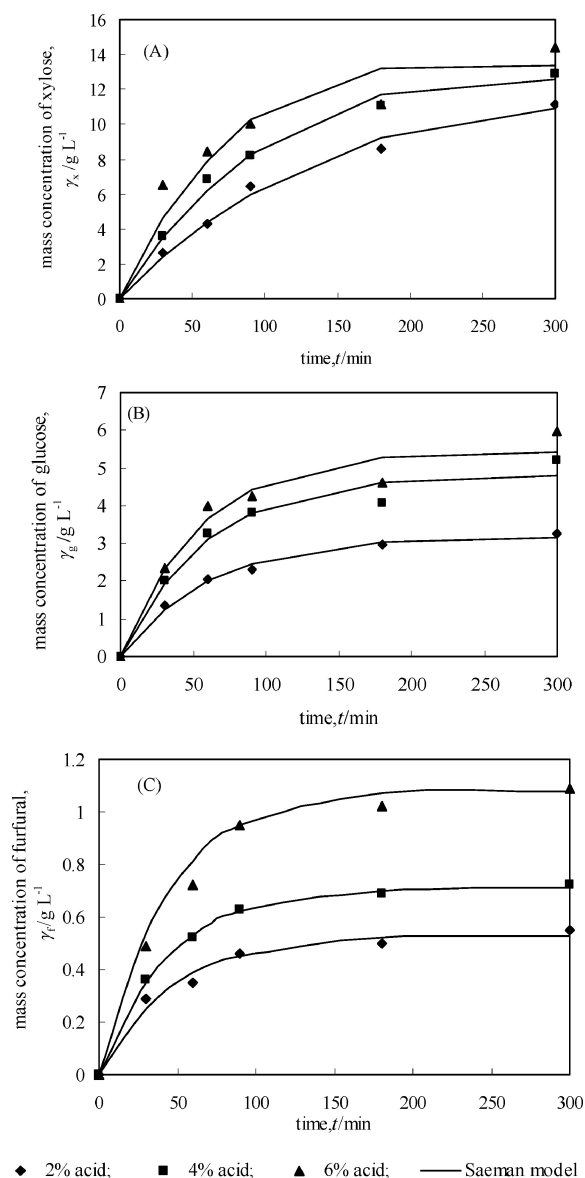


Fig. 1 – Experimental and predicted dependence of the products generated during the hydrolysis at 80 °C

Fig. 1 shows the mass concentrations of xylose, glucose and furfural released during the hydrolysis of corn stover at 80 °C. Xylose mass concentration in Fig. 1 (A) increased with increasing the acid mass fraction and reaction time, and it rose much faster within 180 min. However, xylose concentration increased more slowly after 180 min. The maximum xylose concentration (14.38 g L^{-1}) was achieved at approximately 6 % H_2SO_4 for 300 min, which accounted for about 70 % of the maximum possible mass concentration of xylose. In the hydrolysis, other sugars were released, mainly glucose. Glucose comes from both cellulose and hemicelluloses; however, by using dilute acid, it comes principally from hemicelluloses. Fig. 1 (B) shows that glucose mass concentration increased from 1.35 g L^{-1} to 5.99 g L^{-1} with increasing the acid mass fraction and reaction

time. Fig. 1 (C) shows that the furfural mass concentration increased much faster within 90 min while it increased slowly after 90 min.

The concentrations of xylose, glucose and furfural increased with increasing the acid mass fraction and reaction time entirely, however, the increasing rate was lower after a certain period. It is possible that the speed of generation and decomposition attained equilibrium. The mass concentrations of xylose and glucose increased weakly than furfural with increasing the acid mass fraction. It proved that the high acid fraction negatively influenced the hydrolysis of hemicellulose at 80 °C.

Kinetic modeling of xylose production

Xylose is a main product in the hydrolysis process of corn stover. $\gamma_{x,n}^0$ was fixed at 21.6 g L⁻¹ taking into account the solid/liquid ratio and the stoichiometric ratios. Table 1 shows the kinetic and statistical parameters obtained for the xylose released in the hydrolysis of corn stover at 80 °C.

Comparing the values of k_1 and k_2 obtained in Saeman's model, the rate of xylose generation appeared to be faster than the decomposition rate, even though both accelerated with increased acid fraction. The correlation coefficient R^2 showed a good agreement between experimental and predicted data for all regressions. The models predicted that xylose mass concentration increased with increasing the acid fraction and reaction time, but it increased weakly after 180 min.

A generalized model for predicting xylose produced by the hydrolysis was developed. Kinetic parameters k_1 and k_2 were correlated with the sulfuric

Table 1 – Kinetic and statistical parameters of xylose, glucose and furfural

	w = 2 % acid	w = 4 % acid	w = 6 % acid
xylose			
k_1, min^{-1}	0.004013	0.006098	0.008254
k_2, min^{-1}	0.001886	0.001969	0.002019
R^2	0.9960	0.9961	0.9621
glucose			
k_3, min^{-1}	0.016345	0.017387	0.018547
$\gamma_{g,n}^0, \text{g L}^{-1}$	3.20	4.82	5.46
R^2	0.9966	0.9860	0.9803
furfural			
k_4, min^{-1}	0.016389	0.022823	0.027224
$\gamma_{f,n}^0, \text{g L}^{-1}$	0.60	0.71	1.06
R^2	0.9771	0.9994	0.9981

Table 2 – Generalized models for predicting kinetic parameters of xylose, glucose and furfural

	Model	R^2
xylose	$k_1 = 0.002534 w^{0.65}$ (9)	0.9983
xylose	$k_2 = 0.001807 w^{0.062}$ (10)	0.9999
glucose	$k_3 = 0.01506 w^{0.11}$ (11)	0.9868
furfural	$k_4 = 0.011916 w^{0.46}$ (12)	0.9662

acid fraction (w) by means of the empirical eq. (8), where j is integer in the range 1–4, k_0 , and n are the regression parameters, and w is the acid mass fraction expressed as %.

$$k_j = k_0 w^n \quad (8)$$

In the xylose model, k_1 was correlated with H₂SO₄ fraction as shown in eq. (9) of Table 2 and k_2 can be determined by eq. (10) of the same table. The correlation coefficient R^2 showed good values for all regressions.

By combining eq. (9) and (10) in Table 2 with Saeman's model, it was possible to predict the xylose mass concentration at any experimental conditions. Fig. 2 shows how the generalized models predicted the dependence of xylose mass concentration on the acid mass fraction and time using the parameters found for Saeman's model. This kind of response surface is very useful because it allows selection of several different conditions to achieve the same result.²⁸ For example, Fig. 2 shows that 13.0 g L⁻¹ could be achieved by using 5 % H₂SO₄ for 210 min or 5.5 % H₂SO₄ for 180 min. Therefore, it was possible to select conditions leading to the highest xylose concentration and the minimum degradation product concentrations by comparing response surfaces for different products of the corn stover. The response surface could also be used to

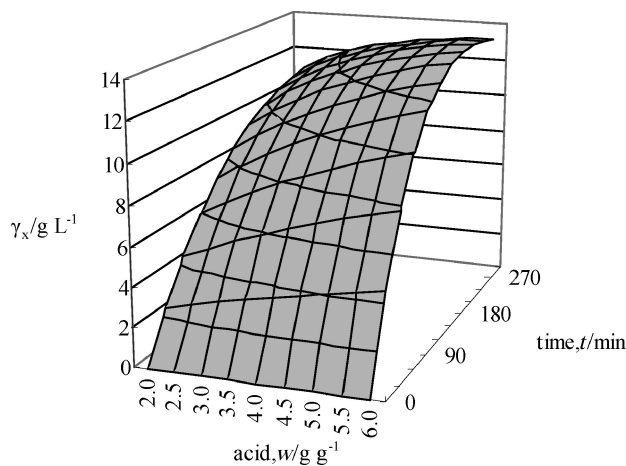


Fig. 2 – Prediction of the generalized model for the dependence of xylose concentration

obtain the optimum xylose concentrations. The model predicted a maximum xylose concentration using 6 % H_2SO_4 for 240 min. In these conditions, 13.54 g L^{-1} was predicted. Higher xylose concentrations could not be obtained even if longer reaction times were used.

Kinetic modeling of glucose production

Glucose is a secondary product obtained in the hydrolysis of corn stover. The kinetic model of glucose mass concentration can be obtained by using the similar equations to those for xylose mass concentration. However, γ_g^0 cannot be obtained experimentally because glucose proceeds from both hemicellulose and cellulose, even though cellulose is not usually hydrolyzed over the range of operational conditions tested; therefore, γ_g^0 has been introduced as a new regression parameter. Table 1 shows both values obtained by regression for γ_g^0 and k_3 increased with the acid concentration. The glucan susceptible to hydrolysis was in the range of $3.20 - 5.46 \text{ g L}^{-1}$, which represented 7.37 – 13.0 % of total glucan in corn stover. This result was lower than sorghum straw at $122 \text{ }^\circ\text{C}$.²⁹ It could be inferred that the treatment at low temperature was more selective, being able to hydrolyze the hemicellulose leaving cellulose and lignin in the solid phase. This was adequate for subsequent processing of the solid residue.

The kinetic parameter k_3 increased with the acid fraction and R^2 showed a good agreement between experimental and predicted data. Fig. 1(B) shows the experimental and predicted data for these hydrolyses at each acid fraction.

A generalized model for predicting glucose released was also developed. Eq. (11) of Table 2 shows the dependence of kinetic parameters on H_2SO_4 fraction. Fig. 3 shows how the generalized model predicted the dependence of glucose concentration on the H_2SO_4 fraction and reaction time. A continuous increase could be observed of k_3 with reaction time and no clear dependence on H_2SO_4 fraction. The models predicted a maximum glucose mass concentration (5.44 g L^{-1}) at the most severe conditions (6 % H_2SO_4 and 300 min), but less than 4.5 g L^{-1} were obtained after $t < 90 \text{ min}$ for any H_2SO_4 fraction. The generalized models proposed here were useful tools for selecting operational conditions that ensured the lower glucose mass concentration and the maximum xylose mass concentration.

Kinetic modeling of furfural production

In the hydrolysis of corn stover, furfural is the main degradation product. Saeman's model can be used empirically to model furfural data, although it was developed for the conversion of lignocellulosic polymers to monomers. In this case, γ_f^0 was the po-

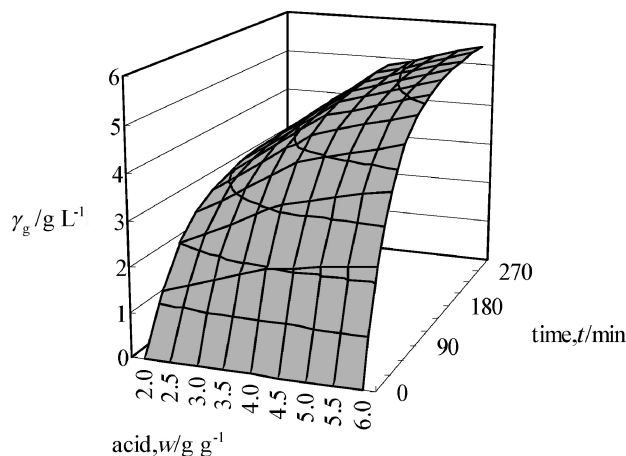


Fig. 3 – Prediction of the generalized model for the dependence of glucose concentration

tential furfural mass concentration and k_4 was the furfural generation rate. Table 1 shows the kinetic and statistical parameters fitting the model for the furfural in the hydrolysis of corn stover at $80 \text{ }^\circ\text{C}$ and Fig. 1(C) shows the experimental and predicted data for furfural in these hydrolyses. γ_f^0 varied slightly in the range $0.60 - 1.06 \text{ g L}^{-1}$, and the average value was 0.83 g L^{-1} . The statistical parameters confirmed that the model fitted very well.

A generalized model for predicting furfural mass concentration was also developed. Eq. (12) in Table 2 shows the dependence of kinetic parameters on H_2SO_4 fraction. Fig. 4 shows how the generalized model predicted the dependence of furfural mass concentration on the H_2SO_4 fraction and reaction time. The model showed that an interaction between acid fraction and time existed. At this temperature, the model predicted a continuous increase in the value of furfural mass concentration and time. Furfural is an inhibitor of microorganism growth.³⁰ Therefore, if the hydrolysates are prepared for fermentation, conditions that minimize the furfural mass concentration should be selected.

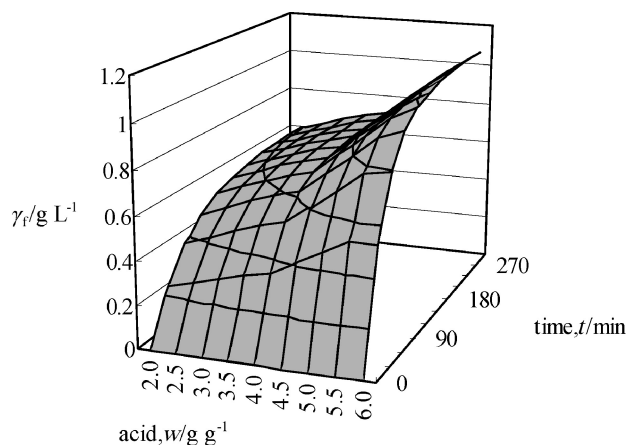


Fig. 4 – Prediction of the generalized model for the dependence of furfural concentration

Overall optimization

If the hydrolysis of corn stover is to be used as fermentation media and the solid residue is to be processed for glucose production, it is important to obtain sugar solutions with low concentration of glucose. Thus, the selectivity (xylose-glucose ratio) is an important parameter to optimize the hydrolysis conditions. The optimal working conditions were defined using the following criteria: (a) xylose yield could not be lower than 13 g L⁻¹; (b) highest selectivity was attained. Based on these conditions, optimal conditions for hydrolysis hemicellulose of corn stover were found. This operational condition was achieved at 5.0 % H₂SO₄ at 80 °C for 240 min and the models predict the highest selectivity 2.60 g g⁻¹. Under the optimal hydrolysis conditions, samples containing up to 13.21 g L⁻¹ xylose, 5.07 g L⁻¹ glucose and 0.80 g L⁻¹ furfural were obtained.

Conclusions

Corn stover is a renewable, cheap and widely available resource. It is a promising source to produce sugars and convert to fuels and chemicals by biological method. Dilute sulfuric acid pretreatment was effective in solubilizing hemicellulose in corn stover. Kinetics of hydrolysates production from corn stover at low temperature was investigated in this study, and the Seaman's model was used to describe the hydrolysates production. Experimental results showed that about 70 % of the maximum possible concentration of xylose could be obtained in the pretreatment process. In order to increase the availability of the corn stover, an optimal condition for hydrolysis was chosen which was 5 % H₂SO₄ at 80 °C for 240 min. Under this condition, 61 % of the maximum possible xylose mass concentration could be achieved, and the glucose and furfural mass concentrations were 5.07 g L⁻¹ and 0.80 g L⁻¹, respectively. The hydrolysates obtained from corn stover can be used to produce hydrogen and methane by anaerobic fermentation process. Therefore, this study can be conceived as the first stage of an integrated strategy for corn stover utilization.

List of symbols

k	– rate coefficient, min ⁻¹
Q	– volume flow rate, mL min ⁻¹
R^2	– correlation coefficient
T	– temperature, °C
t	– time, min
V	– volume, L
w	– mass fraction, %
γ	– mass concentration, g L ⁻¹

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