



Kinetics of Acetic Acid Pretreatment Catalyzed by $\text{Fe}(\text{NO}_3)_3$ of Corn Stover

XIAOYAN YU^{1,*}, JUN QI², SHUTING ZHANG² and XUEBIN LU²

¹Institute of Mining Technology, Liaoning Technical University, Hulu Dao 125105, P.R. China

²School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, P.R. China

*Corresponding author: E-mail: xyy198208@tju.edu.cn

Received: 10 December 2013;

Accepted: 26 March 2014;

Published online: 26 December 2014;

AJC-16534

Corn stover was treated with acetic acid in presence of $\text{Fe}(\text{NO}_3)_3$ as catalyst to enhance its sugar yields in the hydrolysis. Kinetics of acetic acid pretreatment catalyzed by $\text{Fe}(\text{NO}_3)_3$ was investigated in order to verify the feasibility of the catalytic reaction. The results showed that $\text{Fe}(\text{NO}_3)_3$ could effectively improve the hydrolysis rate of hemicelluloses and cellulose. Ferric nitrate not only greatly increase the rate of xylose and glucose formed (k_1), but also decrease the degradation rate of the sugar formed (k_2). When pretreatment catalyzed by $\text{Fe}(\text{NO}_3)_3$, selectivity coefficient S value, that is the ratio of hydrolysis rate k_1 to degradation rate k_2 , are more than 1 and it increases gradually with the increase of acetic acid concentration.

Keywords: Corn stover, Acetic acid, $\text{Fe}(\text{NO}_3)_3$, Kinetics.

INTRODUCTION

A great deal of fossil fuel consumption and the global warming alarms have given rise to an intensified search for sustainable renewable resources. Due to its abundant availability and low-cost, lignocellulosic biomass especially agricultural waste appears to offer a great promise as a feedstock for further bioconversion. Lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin¹. Hemicelluloses as cellulose, is polymers constituted of sugar units, it differs from cellulose by being smaller and branched polymers. Lignin is a complex, crosslinked polymer formed with phenylpropane units². The complex three-dimensional structure assembled leads to remarkably resistance against chemicals and microbial attack that makes it difficult to hydrolyze. Therefore, a pretreatment of lignocellulosic biomass is necessary to obtain higher hydrolysis efficiency and better digestibility.

Many studies in the pretreatment have been carried out, such as hot water^{3,4}, strong inorganic acid under hydrothermal conditions⁵⁻⁹, steam exploded or microwave radiation¹⁰⁻¹², alkaline treatment^{13,14}, etc. Currently pretreatment technology with dilute strong inorganic acid (concentration of 0.5-1 %) such as sulfuric acid, nitric acid and hydrochloric acid has been extensively used because of higher sugar recovery, but their use would lead to the serious environmental concerns. Moreover, it is not suitable for methane production because methane production is inhibited due to the production of H_2S and N_2 from reducing sulphate and nitrate, respectively¹⁵. In

contrast, weak organic acids pretreatment can eliminate these disadvantages. However, there is a lower hydrolysis efficiency compared with dilute strong inorganic acid. Zhao *et al.*¹⁶ treated the rice straw using 0.75 mol/L mixed solution of acetic acid and propionic acid (weight percent of the two acids were 1:1) and found that about 34 % of lignin was removed and 21 % of the hydrolysis rate was achieved. Lu *et al.*¹⁷ studied the hemicellulose hydrolysis in corn stover catalyzed by maleic acid and concluded that increasing maleic acid concentrations from 0.05 to 0.2 mol/L facilitate improvement in xylose yields from 40 to 85 %. Here, it is hypothesized that inorganic salt is used to catalyze the weak organic acid pretreatment for enhancing the hydrolysis efficiency. Sun *et al.*¹⁸ proved that inorganic salt especially ferric nitrate is effective for hemicellulose hydrolysis.

Therefore, in this work, acetic acid was chosen as the suitable weak acid, because it is already present in the lignocellulosic biomass in the form of acetyl groups on the hemicellulose and it can be utilized by methanogens as substrate to produce biogas. Ferric nitrate, as a catalyst, was used to improve the sugar yields of acetic acid pretreatment. The kinetics of acetic acid hydrolysis catalyzed by $\text{Fe}(\text{NO}_3)_3$ of corn stover was investigated compared with that of using acetic acid pretreatment alone.

EXPERIMENTAL

Corn stover was collected from a local farm in Tianjin, China. The composition of the corn stover was (in wt % on

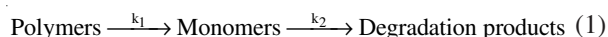
dry basis): glucan of 36.8 %, xylan of 18.4 %, araban of 2.6 %, klason lignin of 17 % and others of 25.2 %.

Experimental setup: Pretreatment was carried on in a 500 mL titanium reactor (PCF02 (05)-10/TA2, Shandong, China). The reactor can withstand at a pressure of 12 MPa and a temperature of 320 °C. The reactor has a 10 °C/min of heating rate and a 16 °C/min of typical cooling rate. The agitation was set at 200 rpm and pretreatment time initiated when the temperature was up to the selected value.

Methods: Pretreatments were carried on in a media containing 1, 3 or 5 g CH₃COOH/100 g distilled water. The concentration of Fe(NO₃)₃ used was 0.05 mol/L and reaction times were 15, 30, 45 and 60 min. The temperature used was 120 °C. All experiments used a ratio of 9 g water/g solid, each dry corn stover sample (15 g) and 135 g solution was loaded into the reactor. After pretreatment, the reactor was removed from the heating jacket and then placed in an ice bath to halt the reaction. The reactor was kept sealed, until the reactor was cooled to about 50 °C. Then the wet material was filtered through vacuum filtration, obtaining a solid phase and a liquid phase for further analysis. The composition of the hydrolysates (glucose, xylose, arabinose and acetic acid) was determined by HPLC.

Monomeric sugars and acetic acid in the liquor were determined by HPLC (LabAlliance) with a refractive index detector by using a column (BioRad Aminex HPX-87H, 300 × 7.8 mm) at 65 °C and 5 mmol/L H₂SO₄ as a mobile phase at a flow rate of 0.6 mL/min. All liquid samples were autoclaved with 8 % sulfuric acid for 1 h at 121 °C to break oligomeric sugars down into monomeric form, which is easily detected by HPLC. Sugar recovery standard (SRS) was used to determine a correction factor through the concentrations of sugars before and after autoclaving.

Kinetic model: It has been accepted that the model is a two-step consecutive pseudo-first-order irreversible reaction. The first model was used successfully by Saeman in 1945, which was designed for the hydrolysis of cellulose using sulphuric acid. Later it was developed for the hydrolysis of hemicelluloses fraction, in which xylan was firstly hydrolyzed to xylose and then the xylose was hydrolyzed to degradation products^{19,20}. In this work, two-fraction (Saeman) model was used to determine the kinetic parameters of hemicelluloses and cellulose hydrolysis reaction using acetic acid pretreatment catalyzed by Fe(NO₃)₃ solution and using acetic acid alone, respectively. The model could be written as follows:



where k_1 is the rate of polymers release, min⁻¹; k_2 is the rate of monomers degradation, min⁻¹. Based on the model and solving differential equation, eqn. 2 could be obtained, which expresses the relationship between monomers concentration x and time t :

$$x = \frac{k_1 x_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + x_0 e^{-k_2 t} \quad (2)$$

where x_0 and x'_0 represented the initial concentrations of polymers and monomers, respectively. The polymers generalized could be glucan, xylan and araban, while degradation

products could be furfural, formic acid and levulinic acid. It has been assumed that x'_0 is close to 0, so

$$x = \frac{k_1 x_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

The kinetic parameters for the hydrolysis of corn stover was estimated by nonlinear regression analyses using the Newton's method (Solver, Microsoft Excel 2007) to minimize the sum of the squares of deviations between experimental and theoretical values. All testes were carried out in triplicate and the related data were expressed as the average values.

By comparing the kinetic parameters for the hydrolysis of corn stover using acetic acid pretreatment catalyzed by Fe(NO₃)₃ and acetic acid alone, it could be verified whether Fe(NO₃)₃ could promote the hydrolysis of corn stover using acetic acid pretreatment.

RESULTS AND DISCUSSION

Kinetic parameters for the hydrolysis of hemicelluloses: The two-fraction model has not included oligomer kinetics and here the kinetic parameters obtained were according to the xylose concentration in the hydrolyzates only. Therefore the model could not distinguish the xylose hydrolyzed directly from hemicelluloses or from xylane oligomer. Fitting the experimental data under different pretreatment conditions to eqn. 3, the kinetic parameters for the hydrolysis of hemicelluloses were shown in Table-1. It can be seen that k_1 increased but k_2 decreased with increasing the concentration of acetic acid and k_1 was higher than k_2 for corn stover using acetic acid pretreatment catalyzed by Fe(NO₃)₃, while k_1 was smaller than k_2 for acetic acid pretreatment alone. The selectivity factor ($S = k_1/k_2$, the ratio of xylan hydrolysis rate to xylose degradation rate) was used to evaluate the efficiency of the catalytic reaction condition. In Table-1 the S values were higher than 1 under the conditions catalyzed by Fe(NO₃)₃, which implied the xylose degradation rate was slower than that of its formation and it revealed that Fe(NO₃)₃ was a more efficient catalyst for the hydrolysis of hemicelluloses in corn stover. For the S values of less than 1 using acetic acid alone, it demonstrated that xylose degraded more easily and the relatively high concentrations of acetic acid has an inhibitor for the formation of xylose.

TABLE-1
KINETIC PARAMETERS FOR THE HYDROLYSIS OF HEMICELLULOSES IN CORN STOVER USING ACETIC ACID PRETREATMENT WITH Fe(NO₃)₃ AND WITHOUT Fe(NO₃)₃

CH ₃ COOH (%)	Fe(NO ₃) ₃ (mol L ⁻¹)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	R ²	S
1	0	0.0168	0.0499	0.9936	0.34
3	0	0.0176	0.0452	0.9931	0.39
5	0	0.0175	0.0371	0.9946	0.47
1	0.05	0.0459	0.0087	0.9939	5.28
3	0.05	0.0558	0.0075	0.9891	7.44
5	0.05	0.0675	0.0041	0.9843	16.46

Fig. 1 shows the comparison between experimental data of xylose concentrations and those calculated with the two-

fraction model. The statistical parameters R^2 corroborated that the two-fraction model fitted very well.

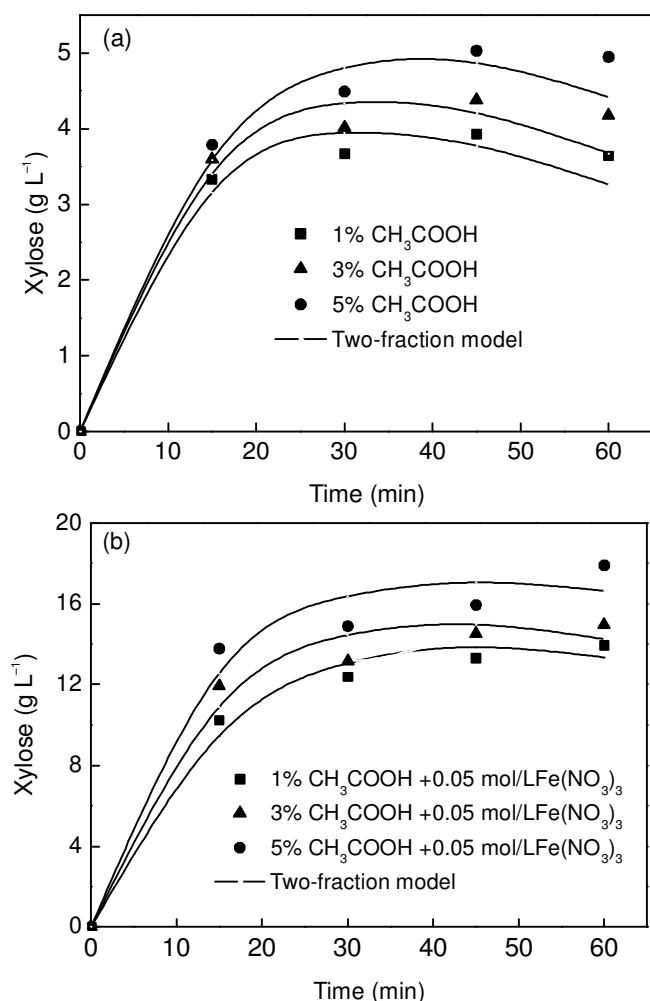


Fig. 1. Experimental and predicted dependence of xylose generated during the hydrolysis at 120 °C on time (a) using acetic acid alone; (b) acetic acid pretreatment catalyzed by 0.05 mol/L $\text{Fe}(\text{NO}_3)_3$.

Kinetic parameters for the hydrolysis of cellulose: The kinetic parameters were obtained based on the glucose concentration in the hydrolyzates. Table-2 shows that the kinetic parameters for the hydrolysis of cellulose. It can be seen that k_1 and k_2 decreased but the S values increased with increasing the concentration of acetic acid using acetic acid pretreatment alone, which implied higher concentration of acetic acid has a inhibitor for the formation of glucose and the glucose degradation rate was slower than that of its formation. When catalyzed by $\text{Fe}(\text{NO}_3)_3$, k_1 increased but k_2 decreased with increasing the concentration of acetic acid and the formation of glucose was faster than that of its degradation. In addition, the efficiency of the hydrolysis of cellulose catalyzed by $\text{Fe}(\text{NO}_3)_3$ was lower than that of the hydrolysis of hemicelluloses.

Fig. 2 shows the comparison between experimental data of glucose concentrations and those calculated with the two-fraction model. The statistical parameters R^2 showed that the two-fraction model of glucose fitted better under acetic acid-pretreatment catalyzed by $\text{Fe}(\text{NO}_3)_3$ than that of acetic acid pretreatment alone.

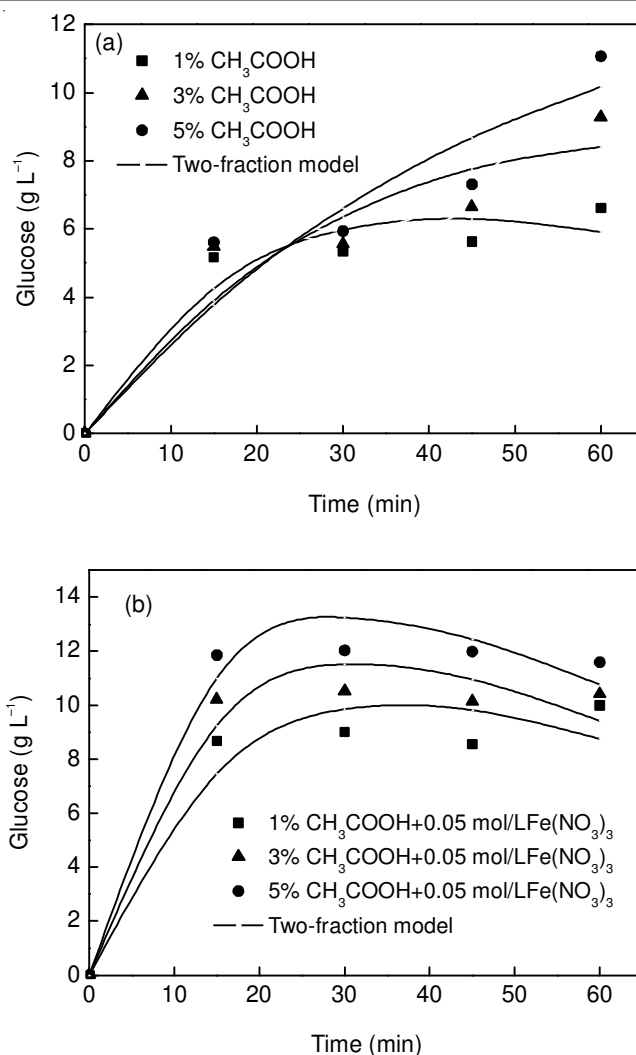


Fig. 2. Experimental and predicted dependence of glucose generated during the hydrolysis at 120 °C on time (a) using acetic acid alone; (b) acetic acid pretreatment catalyzed by 0.05 mol/L $\text{Fe}(\text{NO}_3)_3$.

CH_3COOH (%)	$\text{Fe}(\text{NO}_3)_3$ (mol·L ⁻¹)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	R^2	S
1	0	0.0198	0.0276	0.9607	0.72
3	0	0.0157	0.0119	0.9456	1.32
5	0	0.0141	0.0041	0.9505	3.44
1	0.05	0.0370	0.0194	0.9606	1.91
3	0.05	0.0493	0.0176	0.9797	2.80
5	0.05	0.0621	0.0140	0.9866	4.44

Generalized models: By comparing the kinetic parameters for the hydrolysis of hemicelluloses and cellulose using acetic acid pretreatment with $\text{Fe}(\text{NO}_3)_3$ and without $\text{Fe}(\text{NO}_3)_3$, it suggested that $\text{Fe}(\text{NO}_3)_3$ as a catalyst was effective for improving the hydrolysis efficiency of corn stover, therefore, here a generalized model for predicting the products in the hydrolyzates under the conditions catalyzed by $\text{Fe}(\text{NO}_3)_3$ was mainly developed. Kinetic parameters were correlated with acetic acid concentration (C) by the following empirical eqns:

$$k_i = k_0 C^n \quad (4)$$

where i is an integer in the range of 1-2, k_0 and n are regression parameters and C is the acetic acid concentration expressed in wt %. In the xylose model, k_1 correlated with acetic acid concentration as shown in eqn. 5, k_2 as shown in eqn. 6 of Table-3. Combining eqns. 5 and 6 of Table-3 with the kinetic models, it is possible to predict the xylose concentration for any acid concentration and time over the range under consideration (1-5 % acetic acid and 0-60 min). A similar method was also used to predict the concentration of glucose and others.

TABLE-3
GENERALIZED MODELS FOR THE PREDICTION OF KINETIC
PARAMETERS OF CORN STOVER HYDROLYSIS
USING ACETIC ACID PRETREATMENT
CATALYZED BY $\text{Fe}(\text{NO}_3)_3$ AT 120 °C

Products	Models Eq.	R ²
Xylose	$k_1 = 0.1352C^{0.2397}$ (5)	0.9784
	$k_2 = 0.0019C^{-0.3426}$ (6)	0.8578
Glucose	$k_1 = 0.1615C^{0.3259}$ (7)	0.9882
	$k_2 = 0.0089C^{-0.1726}$ (8)	0.9088

Conclusion

Ferric nitrate as a catalyst of acetic acid pretreatment, was effective for the hydrolysis of corn stover. The kinetic parameters under the conditions catalyzed by $\text{Fe}(\text{NO}_3)_3$ implied that the addition of $\text{Fe}(\text{NO}_3)_3$ could increase the rate of xylose and glucose formed and decelerate the degradation rate of sugars formed in the hydrolyzates. And it made the formation rate of these sugars was greatly faster than that of its degradation. In addition, the efficiency of catalytic reaction for the hydrolysis of hemicelluloses was higher than that of cellulose.

ACKNOWLEDGEMENTS

The authors are grateful to the National Nature Science Foundation of China (No. 21106097) for the financial support of this work.

REFERENCES

- G.W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, **106**, 4044 (2006).
- M. Carrier, A. Loppinet-Serani, D. Denux, J.-M. Lasnier, F. Ham-Pichavant, F. Cansell and C. Aymonier, *Biomass Bioenergy*, **35**, 298 (2011).
- C.X. Wan and Y.B. Li, *Bioresour. Technol.*, **102**, 9788 (2011).
- N. Mosier, R. Hendrickson, N. Ho, M. Sedlak and M.R. Ladisch, *Bioresour. Technol.*, **96**, 1986 (2005).
- A.P. Redding, Z. Wang, D.R. Keshwani and J.J. Cheng, *Bioresour. Technol.*, **102**, 1415 (2011).
- B. Zhang, L. Wang, A. Shahbazi, O. Diallo and A. Whitmore, *Bioresour. Technol.*, **102**, 9308 (2011).
- J.R. Jensen, J.E. Morinelly, K.R. Gossen, M.J. Brodeur-Campbell and D.R. Shonnard, *Bioresour. Technol.*, **101**, 2317 (2010).
- C. Cara, E. Ruiz, J.M. Oliva, F. Sáez and E. Castro, *Bioresour. Technol.*, **99**, 1869 (2008).
- T.A. Lloyd and C.E. Wyman, *Bioresour. Technol.*, **96**, 1967 (2005).
- X. Yang, S. Zhang, Z. Zuo, X. Men and S. Tian, *Bioresour. Technol.*, **102**, 7840 (2011).
- S. Jin and H.Z. Chen, *Process Biochem.*, **42**, 188 (2007).
- S. Zhu, Y. Wu, Z. Yu, X. Zhang, H. Li and M. Gao, *Bioresour. Technol.*, **97**, 1964 (2006).
- A.K. Mathew, K. Chaney, M. Crook and A.C. Humphries, *Bioresour. Technol.*, **102**, 6547 (2011).
- H. Yu, X. Zhang, L. Song, J. Ke, C. Xu, W. Du and J. Zhang, *J. Biosci. Bioeng.*, **110**, 660 (2010).
- A.T.W.M. Hendriks and G. Zeeman, *Bioresour. Technol.*, **100**, 10 (2009).
- R. Zhao, Z. Zhang, R. Zhang, M. Li, Z. Lei, M. Utsumi and N. Sugiura, *Bioresour. Technol.*, **101**, 990 (2010).
- Y.L. Lu and N.S. Mosier, *Biotechnol. Bioeng.*, **101**, 1170 (2008).
- Y. Sun, X. Lu, S. Zhang, R. Zhang and X. Wang, *Bioresour. Technol.*, **102**, 2936 (2011).
- R. Aguilar, J.A. Ramírez, G. Garrote and M. Vázquez, *J. Food. Eng.*, **55**, 309 (2002).
- J.E. Morinelly, J.R. Jensen, M. Browne, T.B. Co and D.R. Shonnard, *Ind. Eng. Chem. Res.*, **48**, 9877 (2009).