

Delignification Kinetics of Corn Stover with Aqueous Ammonia Soaking Pretreatment

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Soaking aqueous ammonia (SAA) pretreatment of corn stover was carried out at three temperatures (30, 50, and 70 °C) and three concentrations of ammonia solution (5, 15, and 25 wt.%). The delignification kinetic model, based on three first-order reactions, was applied to describe the kinetic behavior of lignin removal from corn stover during SAA pretreatment. The first, second, and third terms were based on the initial, bulk, and residual phases of delignification, respectively. The results showed that the model fitted well with the data obtained from the experiments. The activation energies for the delignification reactions were estimated as 61.05 and 59.46 kJ/mol in the bulk and residual phases, respectively. Delignification selectivity increased with increasing reaction temperature.

Keywords: Delignification; Lignin; Corn stover; Kinetics; Soaking aqueous ammonia pretreatment

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INTRODUCTION

Lignin is a large and complex aromatic, hydrophobic, amorphous heteropolymer. It is formed by the random coupling of three phenylpropanoid units: *p*-coumaryl, coniferyl, and sinapyl alcohols, which are linked together by a set of linkages (phenolic- α -O-4-linkages or phenolic- β -O-4-linkages) to make a complicated matrix (Sun *et al.* 2012; Yang *et al.* 2012; Mood *et al.* 2013). It is closely associated with cellulose and hemicelluloses and acts as a binder, which imparts a negative effect on the digestibility of biomass (Behera *et al.* 2014; Singh *et al.* 2014).

One of the best strategies to convert biomass into biofuel is to break down the lignin seal in order to make cellulose and hemicelluloses more accessible to enzymatic hydrolysis (Himmel *et al.* 2007; Mood *et al.* 2013; Zheng *et al.* 2014). Some studies reported that the enzymatic degradation of cellulose and hemicelluloses is negatively related to the lignin content of the biomass. Liew *et al.* (2012) have demonstrated that the higher level of cellulose and hemicelluloses degradation in wheat straw was associated with relatively lower level of lignin content. Some researchers also reported that lignin removal or decrease of cellulose crystallinity could improve the biodegradability of biomass (Zheng *et al.* 2009; Kim *et al.* 2014). Therefore, to improve the digestibility of lignocellulosic biomass, a suitable pretreatment step is required, which would remove lignin and decrease the degree of crystallinity of the cellulosic component during the conversion of lignocellulosic materials into biofuels.

Generally, chemical pretreatment has become one of the most promising methods to improve the biodegradability of biomass by removing lignin and hemicelluloses, and to decrease the degree of crystallinity in cellulose component (Hendriks and Zeeman

2009; Zheng *et al.* 2014). Until now it has been considered that sodium hydroxide is the most popular base used in alkaline pretreatment to improve the biofuel yield from lignocellulosic biomass, including wheat straw, rice straw, corn stover, and so on (Chen *et al.* 2010; Zhu *et al.* 2010; Chandra *et al.* 2012). However, the Na^+ ion remaining in the process of sodium hydroxide pretreatment can inhibit the anaerobic digestion processes, especially methanogenesis. Additionally, the disposal of Na^+ ion containing effluent from anaerobic digestion systems have a negative effect on the environment such as soil salinization and water pollution (Zheng *et al.* 2014). At present, there has been growing interest in using soaking aqueous ammonia (SAA) pretreatment for biomass to increase the biofuel yield during bioconversion by delignification as well as swelling of lignocelluloses, which can retain nearly 100% of cellulose and most of hemicelluloses for subsequent fermentation reaction (Kim and Lee 2005, 2007; Kim *et al.* 2009). Moreover, aqueous ammonia can be recycled from the effluent and reused, which is beneficial to reduce the environmental pollution caused by waste disposal.

Generally, lignin removal is the principal chemical process taking place during pretreatment. The process of delignification, for simplicity can be considered to occur in three stages: initial, bulk, and residual according to several entities of lignin components dissolving at different rates (Gilarranz *et al.* 1999; Oliet *et al.* 1999; Kim and Holtzapple 2006). The consecutive kinetic model assumes that the different lignin entities in biomass react successively during delignification process according to first-order kinetic models, which was applied to calculate the lignin fractions and the specific delignification rate constants (Shatalov and Pereira 2005). At present, the delignification kinetics of lignocellulosic materials has been reported by several authors with the aim of obtaining data that make it possible to achieve more selective delignification. Oliet *et al.* reported that delignification of *Eucalyptus globulus* in ethanol was modeled as a consecutive dissolution (1999). It is also reported that the ethanol-alkali delignification process can be considered as a complex of n-parallel first-order reactions (Shatalov and Pereira 2005). The majority of these studies have been performed with kraft pulping processes. Little information is available about the delignification kinetics of the chemical pretreatment processes. In this study, a kinetic model of delignification with three first-order reactions was used to describe the kinetics of removal of lignin during soaking aqueous ammonia (SAA) pretreatment of corn stover, which will be helpful to develop new and less input process for pretreatment. Furthermore, the kinetic results can afford considerable information for further research on biofuel production from lignocellulosic materials. The effect of reaction temperature and aqueous ammonia concentration on the selectivity of delignification in SAA pretreatment was studied. Based on the delignification kinetics parameters, the activation energy (E_a) was estimated for SAA pretreatment.

EXPERIMENTAL

Materials

Air-dried ground corn stover was obtained from a local farm (Zhengzhou, China). The corn stover was screened to a nominal size of 0.25 to 0.3 mm. The main composition of the corn stover, which was determined following NREL methods, was: 33.7 ± 0.5 wt.% glucan, 18.5 ± 0.7 wt.% xylan, and 14 ± 0.3 wt.% klason lignin (Sluiter *et al.* 2008). Aqueous ammonia (28 wt.%) was purchased from Fengchuan chemical reagent science and technology Ltd. (Tianjin, China). Deionized water was used for all experiments.

Aqueous Ammonia Soaking Pretreatment

Corn stover was treated with 5 to 25 wt.% of aqueous ammonia in glass bottles with screw cap at 30, 50, and 70 °C for 1 to 48 h. Solid-to-liquid ratio of 1: 8 was applied, and no stirring was done during soaking. After soaking, the solid was separated by filtration, and it was then washed with deionized water until pH reached 7.0. Neutralized corn stover was dried at 105 °C for 8 h before compositional analysis.

Analysis

The solid samples, such as treated/untreated corn stover were analyzed for carbohydrate contents and Klason lignin following NREL chemical analysis and testing standard protocol (Sluiter *et al.* 2008; Huang *et al.* 2015). Each sample was analyzed in triplicates. Sugars were determined using an Agilent 1260 Series HPLC (Agilent Technologies Inc., USA) using an Aminex HPX-87H column (300 mm×7.8 mm). A refractive index detector was used for HPLC analysis. Dilute H₂SO₄ solution (0.005 M) was used as the mobile phase at a flow rate of 0.55 mL/min, and the column temperature was maintained at 60 °C. The amounts of the sugar components were calculated based on external standard curves constructed with authentic samples.

Kinetic Model, Delignification Parameters and Delignification Selectivity

In this study, the fraction of residual lignin (R_L) was defined as,

$$R_L = \frac{L}{L_0} \quad (1)$$

where L and L_0 are the lignin contents (g lignin/100 g raw biomass) of treated biomass and untreated biomass at time zero, respectively. The fraction of residual lignin is defined as R_L (g lignin remaining/g lignin in raw biomass).

The general equation for delignification kinetics was applied to fit the fraction curves of residual lignin (R_L) with respect to time, which is described as,

$$R_L = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) \quad (2)$$

where t (h) is the time period when data were collected. This equation defines three stages, a_1 , a_2 , a_3 (g lignin remaining/ g lignin in raw biomass), which are the maximum fractions of lignin fragments removed in the initial, bulk, and residual stages, respectively; k_1 , k_2 , and k_3 (h⁻¹) are the reaction rate constants for different stages (Kim and Holtzapple 2006). Because $R_L = 1$ at $t = 0$, the a_1 , a_2 and a_3 comply with condition:

$$a_1 + a_2 + a_3 = 1 \quad (3)$$

Based on time period (t) when the data were collected, the equation was redefined according to different stages, as below:

$$R_L = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) \quad 0 \leq t \leq r \quad (4)$$

$$R_L = a_1 \exp(-\infty t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) \quad p \leq t \leq r \quad (5)$$

$$R_L = a_1 \exp(-\infty t) + a_2 \exp(-\infty t) + a_3 \exp(-k_3 t) \quad q \leq t \leq r \quad (6)$$

Equation 4 defines the information on initial, bulk, and residual delignification stages ($0 \leq t \leq r$). Equation 5 defines the information on bulk and residual delignification stages ($p \leq t \leq r$). Equation 6 just defines the residual delignification stage ($q \leq t \leq r$). In these equations “ p ” is the time period when the initial delignification stage completed, “ q ” is the time period when the initial and bulk delignification stages completed, and “ r ” is the time period when the last sample was collected.

Delignification model parameters (a_i and k_i , $i = 1, 2$, and 3) in Eq. 1 were estimated by using the ‘Solver’ function in Microsoft Excel 2007 based on the minimization of root mean squares and the following constraints: $0 \leq a_i \leq 1$, $a_i(30\text{ °C}) = a_i(50\text{ °C}) = a_i(70\text{ °C})$, and $k_i \geq 0$, $i = 1, 2$, and 3 .

The delignification selectivity based on the loss of lignin vs the loss of total solids operated by SAA pretreatment was defined as follows,

$$\text{Selectivity} = \frac{\Delta L}{\Delta Y_T} = \frac{L_0 - L}{Y_{T0} - Y_T} \quad (7)$$

where, Y_T and Y_{T0} (g solids remaining/ 100 g raw biomass) are the pretreatment yield of the total solids obtained after SAA pretreatment and untreated biomass at time zero, respectively.

Activation Energy for Delignification

The delignifying portions (a_i , $i = 1, 2$, or 3) depended on the chemical reaction in the initial, bulk, and residual phases. The activation energies for each phase were calculated from the Arrhenius equation:

$$k_i = A_i e^{-\frac{E_{ai}}{RT}} \quad (8)$$

Derivation of Eq. 8 results in Eq. 9,

$$\ln k_i = \ln A_i - E_{ai} / RT \quad \text{For } i = 1, 2, \text{ or } 3 \quad (9)$$

where A_i is the pre-exponential factor (1/h) for i -th phase; E_{ai} is the activation energy (kJ/mol) for i -th phase; R is the gas constant (8.3143×10^{-3} kJ/(mol·K)); and T is the temperature in Kelvin scale.

RESULTS AND DISCUSSION

Effect of Aqueous Ammonia Concentration, Reaction Temperature, and Time on Delignification Selectivity

As shown in Fig. 1(a), the lignin contents of treated corn stover (L , g lignin/100 g raw biomass) and solid recovery yield (Y_T , g solid remained/100 g raw biomass) exhibited a good linear relationship in SAA pretreatment under three different ammonia concentrations (5, 15, and 25 wt.%) at 30 °C for 1 to 48 h. At 50 and 70 °C, the lignin contents of treated corn stover and solid recovery yield also showed a similar linear pattern (Figs. 1(b) and (c)) ($R^2 \geq 0.96$).

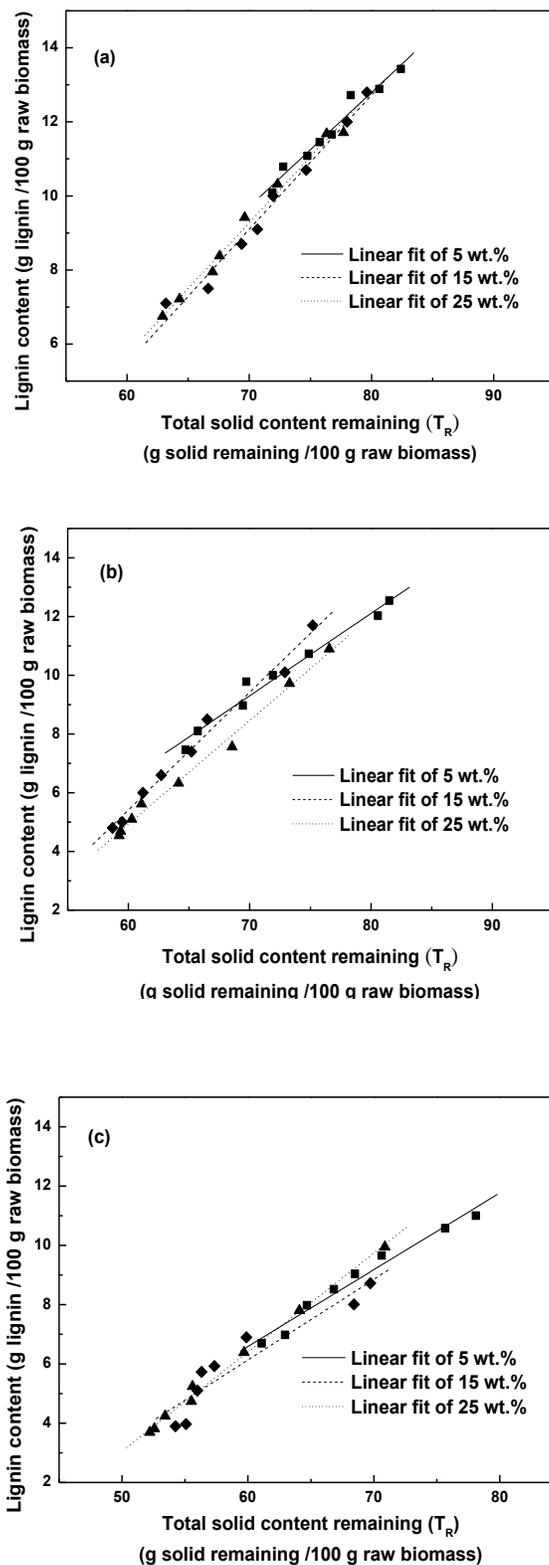


Fig. 1. Lignin contents (L) versus the pretreatment yield of total solid (Y_T) remaining after aqueous ammonia pretreatment in different conditions: at 5 wt.% of ammonia concentration (■), 15 wt.% of ammonia concentration (◆), and 25 wt.% of ammonia concentration (▲) condition at (a) 30, (b) 50, and (c) 70 °C, for 1 to 48 h, respectively

Experiments of SAA pretreatment with the ammonia concentrations of 5, 15, and 25 wt.% at 30, 50, and 70 °C for 1, 6, and 48 h were further investigated, and the resulting delignification selectivities (obtained from Eq. 7) are shown in Table 1. When the processing temperature was lower than 50 °C, the selectivity of lignin removal increased with the increase of the temperature. However, when ammonia concentrations were 5 wt.% and 15 wt.%, respectively, the selectivity of lignin removal was less increased with temperature from 50 to 70 °C. When the treatment temperature increased from 50 to 70 °C at ammonia concentration of 25 wt.%, the delignification selectivity tended to decrease because of the more extensive solubilization of solid and slight growth of lignin removal rate. Therefore, the effect of temperature on the delignification selectivity was significant under low temperature (50 °C), whereas temperature above 50 °C has no effect on the delignification selectivity. It was observed that delignification selectivity increased with the increase of reaction time in SAA pretreatment experiments with 5, 15, and 25 wt.% ammonia loading at 30, 50, and 70 °C.

The effect of ammonia concentration on selectivity of lignin removal at different temperature is given in Table 1.

Table 1. Effect of Aqueous Ammonia Concentration, Temperature, and Reaction Time on the Selectivity of Delignification with SAA Pretreatment

Ammonia concentration (wt.%)	Reaction time (h)	Temperature (°C)	ΔL (g lignin removed/ 100 g raw biomass)	ΔY_T (g solid removed/ 100 g of raw biomass)	Delignification selectivity (g lignin removed/ g solid removed)	
5	1	30	0.57	17.58	0.0324	
		50	1.46	18.49	0.0790	
		70	3	21.88	0.1371	
	6	6	30	1.28	21.7	0.0590
			50	3.27	25.12	0.1302
			70	4.34	29.38	0.1477
		48	30	3.91	28.1	0.1392
			50	6.54	35.29	0.1853
			70	7.31	38.91	0.1879
15	1	30	1.2	20.37	0.0589	
		50	2.3	24.8	0.0927	
		70	5.28	38.45	0.1373	
	6	6	30	3.3	25.35	0.1302
			50	5.5	31.57	0.1742
			70	7.1	40.12	0.1770
		48	30	6.9	36.83	0.1874
			50	9.2	41.3	0.2228
			70	10.1	45.76	0.2207
25	1	30	2.29	22.29	0.1027	
		50	3.1	23.44	0.1322	
		70	4.05	29.13	0.1391	
	6	6	30	3.68	27.67	0.1330
			50	6.44	33.07	0.1947
			70	7.61	40.31	0.1888
		48	30	7.25	37.08	0.1955
			50	9.46	40.75	0.2321
			70	10.31	45.68	0.2257

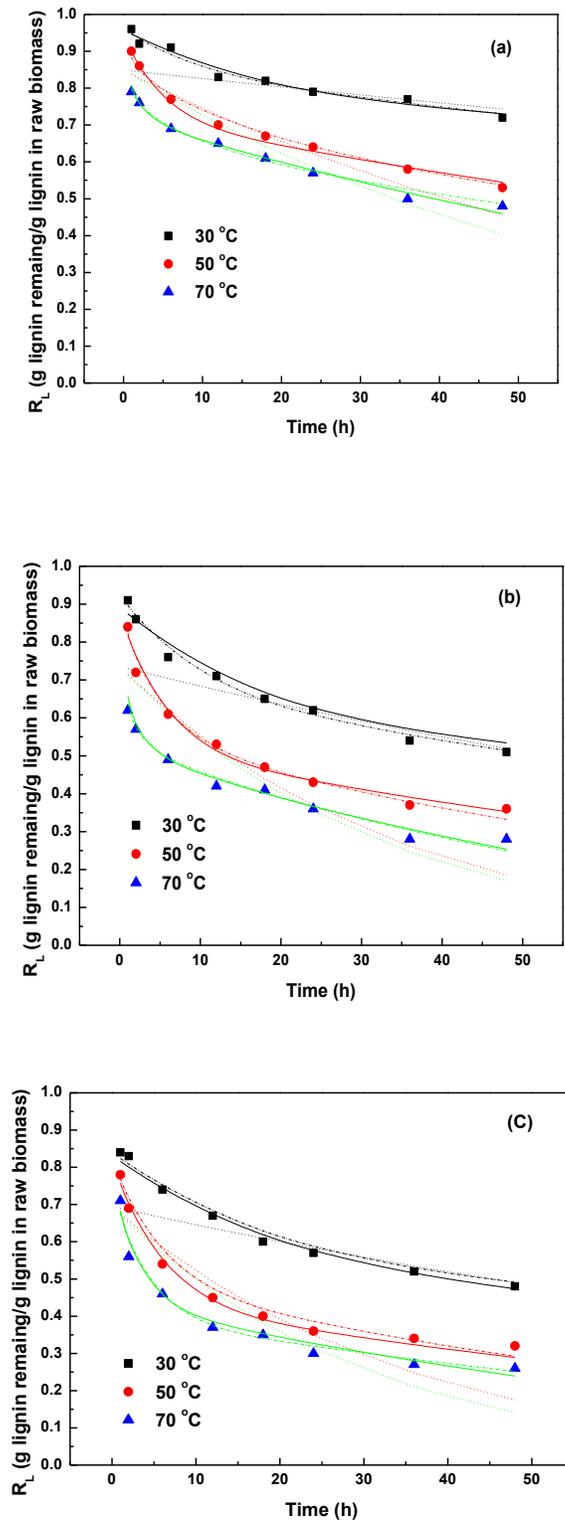


Fig. 2. Experimental and predicted data, (Eq. (4) (...), Eq. (5) (—), Eq. (6) (---)), for R_L at different temperatures and aqueous ammonia concentrations during SAA pretreatment of corn stover. (a) ammonia concentration of 5 wt.%; (b) ammonia concentration of 15 wt.%; (c) ammonia concentration of 25 wt.%

It could be seen that the selectivity of lignin removal showed a similar behavior during SAA pretreatment at 30, 50, and 70 °C. It was obvious that the delignification selectivity was less increased with the increase of ammonia concentration. However, a slight increase was observed in the ammonia concentration of 15 wt.% and 25 wt.% after 6 h. It was probable that the decrease of remained solid above 15 wt.% ammonia loading after 6 h resulted from the loss of other components, rather than the loss of lignin.

Kinetics of Delignification

The delignification of corn stover treated by SAA pretreatment was performed with 5, 15, and 25 wt.% aqueous ammonia at 30, 50, and 70 °C. All experiments were performed with triplicate, and means were given. As shown in Fig. 2, the results for the fraction of residual lignin (R_L) obtained from experiments indicated that the loss of lignin increased with the increase of reaction time. For instance, it was observed from Fig. 2(a) that increase of temperature from 30 to 70 °C had substantial influence on the loss of lignin during SAA pretreatment with 5 wt.% ammonia loading. Moreover, the plots of lignin removal with 5 wt.% ammonia loading showed a similar pattern with 15 and 25 wt.% ammonia loading from Figs. 2(b) and (c).

Table 2. Kinetic and Statistical Parameters of Lignin Removal for the 5, 15, and 25 wt.% Ammonia Concentration Pretreatments

Ammonia concentration (wt.%)	n ^a	Temperature (°C)	k_1 (h ⁻¹)	k_2 (h ⁻¹)	k_3 (h ⁻¹)	Root mean square residual
5	1	30			2.765E-03	0.024657
		50			1.301E-02	0.014177
		70			1.551E-02	0.024657
	2	30		4.687E-02	5.136E-04	0.001288
		50		2.579E-01	5.903E-03	0.001223
		70		9.429E-01	9.435E-03	0.00128
	3	30	1.155E-01	5.638E-03	2.314E-03	0.001077
		50	8.278E-01	4.946E-02	4.609E-03	0.001078
		70	9.637E-02	1.413E+00	5.980E-03	0.001089
15	1	30			7.268E-03	0.085029
		50			2.868E-02	0.08212
		70			3.041E-02	0.085029
	2	30		5.025E-02	1.034E-03	0.023651
		50		2.131E-01	8.362E-03	0.018543
		70		9.760E-01	1.520E-02	0.018463
	3	30	1.879E-02	1.166E-01	3.733E-03	0.014533
		50	1.168E-01	4.244E-01	9.989E-03	0.014526
		70	8.468E-01	1.720E+00	1.597E-02	0.014533
25	1	30			7.268E-03	0.080202
		50			2.868E-02	0.075964
		70			3.322E-02	0.080202
	2	30		4.241E-02	1.077E-03	0.016205
		50		2.029E-01	8.994E-03	0.017345
		70		4.640E-01	1.293E-02	0.020512
	3	30	4.168E-02	1.567E-04	3.450E-05	0.017585
		50	1.696E-02	2.818E-04	2.199E-01	0.019105
		70	9.704E-03	1.013E+00	2.790E-01	0.019108

^a n= the number of finite terms in the delignification kinetic model: n=1 for Eq. (6); n=2 for Eq. (5); n=3 for Eq. (4)

The delignification kinetic models with three first-order reactions (Eqs. 4 through 6) were used to fit the curves of R_L obtained from the experiments in Fig. 2, respectively. For example, in Fig. 2(a), the change of R_L with reaction time extension obtained from SAA pretreatment with 5 wt.% ammonia loading at 30 °C was fitted by three formulas, Eqs. 4, 5, and 6, respectively. The data obtained from experiments with 5 wt.% ammonia loading at 50 and 70 °C had the same regression analysis. The kinetic and statistical parameters of delignification for 5 wt.% ammonia concentration SAA pretreatment at 30, 50, and 70 °C are shown in Table 2. The results of parameter estimation for constants, a_1 , a_2 , and a_3 , obtained from regression analyses of delignification data in 5 wt.% ammonia concentration pretreatment are shown in Table 3. The results obtained from SAA pretreatment with 15 and 25 wt.% ammonia loadings were used the same calculation procedures as that with 5 wt.% ammonia loading.

Table 3. Results of Parameter Estimation for Constants, A_1 , A_2 , and A_3 , Obtained from Regression Analyses of Delignification Data in 5, 15, and 25 wt.% Ammonia Concentration Pretreatments

Ammonia concentration (wt.%)	n^a	a_1 (g lignin remaining/ g lignin in raw biomass)	a_2 (g lignin remaining/ g lignin in raw biomass)	a_3 (g lignin remaining/ g lignin in raw biomass)	Total
5	1			0.85	0.85
	2		0.24	0.72	0.96
	3	0.12	0.20	0.65	0.97
15	1			0.74	0.74
	2		0.37	0.53	0.90
	3	0.16	0.23	0.54	0.93
25	1			0.69	0.69
	2		0.39	0.44	0.83
	3	0.32	0.12	0.40	0.84

^a n = the number of finite terms in the delignification kinetic model: $n = 1$ for Eq. (6); $n = 2$ for Eq. (5); and $n = 3$ for Eq. (4)

Because of the large values of the root mean square residuals, the model Eq. 6, which represented one finite-term (for $n = 1$) did not fit the experimental data. For $n = 3$ (three finite-term model, Eq. 4), the model made clearly the best fit because of the smallest values of root mean square residuals (Table 2). However, it did not meet the initial condition, $a_1 + a_2 + a_3 = 1$ (Table 3). Also, it showed the poorest linear relationship between $\ln k_i$ and $1/T$ used to calculate the activation energies and the pre-exponential factors in Eq. 9. Given both the residual and the linearity of $\ln k_i$ vs $1/T$, the most suitable model for the kinetics of lignin removal was Eq. 5 ($n = 2$) for the ammonia pretreatment with 5, 15, and 25 wt.% of ammonia loading as follows:

$$R_L = 0.04 \exp(-\infty t) + 0.24 \exp(-k_2 t) + 0.72 \exp(-k_3 t) \quad (5 \text{ wt.\% of ammonia loading}) \quad (10)$$

$$R_L = 0.1 \exp(-\infty t) + 0.37 \exp(-k_2 t) + 0.53 \exp(-k_3 t) \quad (15 \text{ wt.\% of ammonia loading}) \quad (11)$$

$$R_L = 0.17 \exp(-\infty t) + 0.39 \exp(-k_2 t) + 0.44 \exp(-k_3 t) \quad (25 \text{ wt.\% of ammonia loading}) \quad (12)$$

In Eqs. 10, 11, and 12, $k_1 \rightarrow \infty$ which means that the initial delignification was too fast to be tested at the first time of sampling ($p \leq t$) (Kim and Holtzaple 2006).

Compared with the fraction of delignification in the initial phase (a_1), bulk phase (a_2), and residual phase (a_3) from Eqs. 10, 11, and 12, it was observed that the fraction of lignin removal in the initial phase increased with the increase of ammonia concentration. About 0.04% of the total lignin was removed in the initial phase in ammonia pretreatment with 5 wt.% of ammonia loading, whereas the major fraction of lignin removal in the initial phase increased to 0.17% for ammonia pretreatment with 25 wt.% of ammonia loading.

Clearly, delignification in the initial phase was promoted with increase of ammonia concentration. Moreover, the behavior of the bulk phase delignification for 15 wt.% ammonia loading was similar to that for 25 wt.% ammonia loading. In the present study the maximum fraction of lignin removal in the residual phase (a_3) between temperatures 30 to 70 °C decreased when the ammonia concentration was increased from 5 to 25 wt.%.

Approximately 72% and 45% of the total lignin was removed in the residual phase for ammonia pretreatment with 5 wt.% and 25 wt.% of ammonia loading, respectively. In summary, with the increase of ammonia concentration from 5 to 25 wt.%, a_1 and a_2 for initial-phase and bulk-phase delignification increased from 0.04% to 0.17% and from 0.24% to 0.39%, respectively, whereas a_3 for residual-phase delignification decreased from 0.72% to 0.44%. In other words, the major fraction of lignin removal tended to move from the residual to the initial and bulk phase with increase of ammonia loading from 5 to 25 wt.%. It was believed that the initial delignification occurred very quickly in the beginning of pretreatment, *e.g.*, during the heating up periods, in most cases (Kim and Holtzapfle 2006).

Activation Energy

From the Arrhenius plot $\ln k_i$ (h^{-1} , $i = 1, 2$, or 3) versus $1/T$ (K^{-1}), activation energies for both (bulk, $i = 2$, and residual, $i = 3$) phases in Eq. 5 were calculated, as shown in Table 4. The parameter R^2 showed a good agreement between experimental and predicted data for all regressions ($R^2 \geq 0.93$). The average values obtained ($E_{a2} = 61.05$ kJ/mol and $E_{a3} = 59.46$ kJ/mol) were similar to those reported for other pretreatment studies (shown in Table 5). Using three phase model, E_a values of the bulk and residual phases (E_{a2} and E_{a3}) were tested as 50.15 and 54.21 kJ/mol in the oxidative lime pretreatment reactions, respectively.

The value of E_a obtained in the present work also compared well with other lignocellulosic materials using the same model. For instances, E_a in the bulk phases was 42 kJ/mol using bagasse (Table 5). However, these values were much smaller than the E_a for wood and Hemp woody core as shown in Table 5. The values of activation energies for delignification of corn stover were similar to E_a for bagasse, but much smaller than that of wood and Hemp woody core, because corn stover and bagasse may have a more favorable structure than wood and Hemp woody core for lignin removal in alkaline conditions (Kim and Holtzapfle 2006). The values of pre-exponential factor vary greatly among raw materials due to the difference of the structure and composition of the material (Ranganathan *et al.* 1985). Therefore, it is not possible compare our result with others of the literature.

Table 4. Parameters Obtained in the Fitting using the Arrhenius Equation for Delignification of Corn Stover by SAA Pretreatment

Ammonia concentration (wt.%)	Temperature (°C)	Bulk phase			Residual phase		
		E_{a2} , (kJ/mol) ^a	P.F. (1/h)	R ²	E_{a3} , (kJ/mol) ^a	P.F. (1/h) ^b	R ²
5	30	65.74	18.264	0.99	64.36	18.264	0.94
	50						
	70						
15	30	64.89	22.726	0.99	59.16	16.825	0.97
	50						
	70						
25	30	52.53	17.789	0.99	54.88	15.212	0.94
	50						
	70						
Average		61.05	19.593		59.46	16.767	

^a E_{a2} and E_{a3} are the activation energies of bulk and residual delignification, respectively

^bP.F. stands for pre-exponential factor

Table 5. Activation Energies for Delignification Modeled in Eq. 5

Materials	Pretreatment	Activation energy, E_{a2} (kJ/mol) ^a	Activation energy, E_{a3} (kJ/mol) ^a	Investigator
Corn stover	Lime	50.15	54.21	Kim <i>et al.</i> (Kim and Holtzaple 2006)
Wood	Lime	120-130	110-117	Chiang <i>et al.</i> (1990)
Hemp Woody core	Soda	127.3	108.9	Dolk <i>et al.</i> (1989)
Bagasse	Na ₂ O	42.0	—	Sabatier <i>et al.</i> (1993)
Corn stover	Aqueous ammonia	61.05	59.46	In this study

^a E_{a2} and E_{a3} are the activation energies of bulk and residual delignification, respectively

CONCLUSIONS

1. Delignification selectivity increased with the increase of reaction temperature and ammonia concentration, respectively.
2. The delignification kinetic model of corn stover was developed as two finite terms of the first order reaction corresponding to the bulk and residual phases of delignification in SAA pretreatment. Moreover, at low ammonia concentration, residual phase delignification dominated, whereas the delignification rate in the residual phase decreased with increase of ammonia concentration.
3. The activation energies calculated were 61.05 and 59.46 kJ/mol in the bulk and residual phases, respectively.

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