

Delignification Kinetics Study on the Tetrahydrofurfuryl Alcohol/HCl Pulping of Rice Straw

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ABSTRACT: In this study, the delignification kinetics of tetrahydrofurfuryl alcohol (THFA)/HCl pulping of rice straw was investigated. In the atmospheric pressure pulping, two phases of different delignification rates were observed which were closely related to the amount of HCl and temperature. Equations for the transition time of these two phases at various temperatures and catalyst dosages were derived. For optimal cooking control, the transition time of these two phases can be calculated. The cooking showed very low activation energies, which, in phase I and phase II, were only 26.5 kJ and 32.2 kJ mol⁻¹, respectively. At phase I pulping, delignification was the main reaction with minimal dissolution of carbohydrate fractions. Consequently, the yield loss was low. In phase II, however, when the residual lignin content was less than about 5%, the dissolution of the carbohydrate was greater than the lignin removal, causing a marked reduction in pulp yield. Comparisons of K_I/K_C (ratio of delignification rate and rate of carbohydrate dissolution) and $\Delta L/\Delta C$ (ratio of lignin removed and carbohydrate dissolved during pulping) values in phases I and II were made. Results showed that both values were greater in phase I, and both values reached their maxima at 120 °C and catalyst dosage of 0.020 mol L⁻¹.

1. INTRODUCTION

The organosolv pulping studies include the use of phenols,^{1–4} methanol,⁵ ethanol,^{6–9} butanol,¹⁰ ketones,^{11–13} and organic acids, etc.^{14–17} These methods were applied mainly to the pulping of softwoods and hardwoods. There were many papers using organosolv methods to pulp rice straw as well; these included Ghose et al.¹⁸ using butanol; Navaee-Ardeh et al.^{19,20} using ethanol, soda–ethanol–water, and dimethylformamide; Pourjoozi et al.²¹ using ethanol–water; Mohammadi-Rovshandeh et al.²² using diethylene glycol, a mixture of diethylene glycol and ethylene glycol, and a mixture of diethylene glycol, ethylene glycol, and 2% NaOH; Ghozatloo et al.^{23,24} using dimethylformamide; Gonzalez et al.²⁵ using ethylene glycol, diethylene glycol, ethanolamine, and soda; Tavallali et al.²⁶ and Ziaie-Shirkolaei²⁷ using soda–(ethanol, diethylene glycol, dimethyl formamide); Nada and El Saied²⁸ using phenol, ethylene glycol, and diethylene glycol; and Rodriguez et al. using ethanolamine and diethanolamine.^{29,30} To have bases for optimal control of the pulping process, certain studies on delignification kinetics of rice or wheat straw by organosolv processes were undertaken. These included the following: Huang and Shi³¹ studied rice straw pulping kinetics and mechanisms and suggested that delignification during soda-based cooking in the presence of anthraquinone could be divided into three phases; Abdul-Karim et al.³² studied the kinetics of kraft pulping of wheat straw and found that delignification was controlled by a chemical reaction, which was first-order; Gonzalo et al.³³ found that about 90% of the lignin was dissolved in the rapid initial phase; Singh et al.³⁴ studied the delignification process of wheat straw by sulfite ions buffered with sodium hydroxide and found the kinetics of delignification to be second-order with respect to lignin; and Park et al.³⁵ systematically studied the mechanisms and kinetics of delignification and silica removal of rice straw, both delignification and silica removal reactions were suggested to be pseudo-first-order reaction.

Among the organosolv pulping processes, those involving tetrahydrofurfuryl alcohol (THFA) were capable of pulping at atmospheric pressure; therefore, it possesses the benefits of low energy use and low capital investment. Bogomolov et al.,^{36–38} Johansson et al.,³⁹ and Aaltonen et al.⁴⁰ all published papers on using THFA to delignify birch and pine and to pulp birch, spruce, and eucalyptus. These prior studies involved softwoods and hardwoods. As per its application to agricultural waste materials, only our previous paper⁴¹ studied the THFA pulping of rice straw catalyzed by adding HCl. This method showed a high delignification efficiency resulting in a relatively high pulp yield.

The purpose of investigating the pulping kinetics was to discover the parameters of pulping engineering, effectively control the pulping process, and determine the optimal operational conditions. This information could determine how to run such a process with lower chemical charge, shorter digestion time, higher pulp quality, and higher pulp yields.⁴² The type and quality of the material, cooking temperature, chemical charge, liquor to material ratio, wood species, and chip size and thickness all affect the process.⁴³ In general, for wood chips cooked with the kraft pulping process, delignification can be divided into the initial phase, the bulk phase, and the final phase.^{44–47} The reaction taking place in the initial phase is mainly the diffusion of the cooking liquor; the bulk phase entails the maximal delignification efficiency, and the final phase is where pulp quality control occurs.⁴⁸ If the three phases can be understood and controlled, the optimal cooking conditions for the best quality pulp with the maximum economic benefits can be attained.⁴⁹

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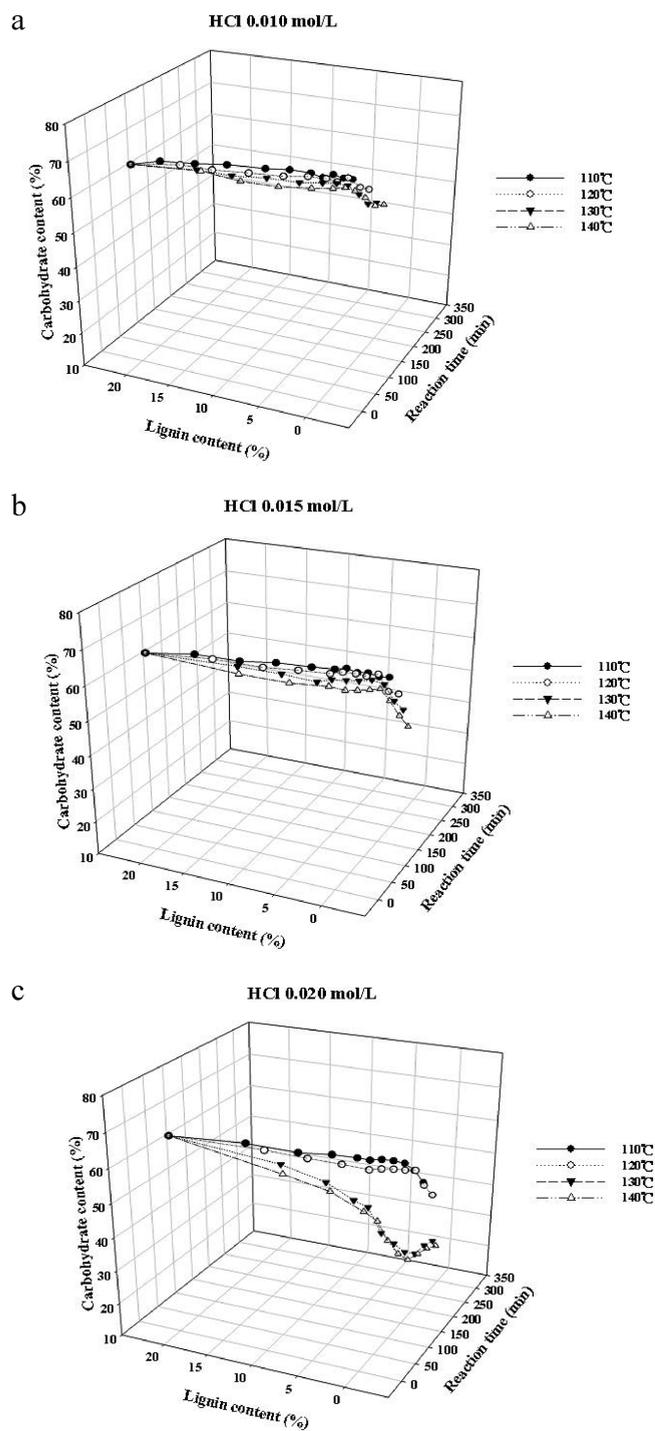


Figure 1. Graphs of chemical composition for rice straw pulped with THFA/HCl methods. The pulping conditions entailed the following: THFA, 9.7 mol/L; HCl, 0.010, 0.015, and 0.020 mol/L. Temperature, 110–140 °C; pulping time, 0–300 min.

The goal of this work was to establish the delignification kinetics of the main phenomena involved in treatment of tetrahydrofurfuryl alcohol pulping of rice straw at atmospheric pressure catalyzed by adding HCl. Temperature, reaction time, and catalyst concentration were considered as operational variables. From the experimental data, phenomenological, kinetic models giving a quantitative interpretation of the experimental

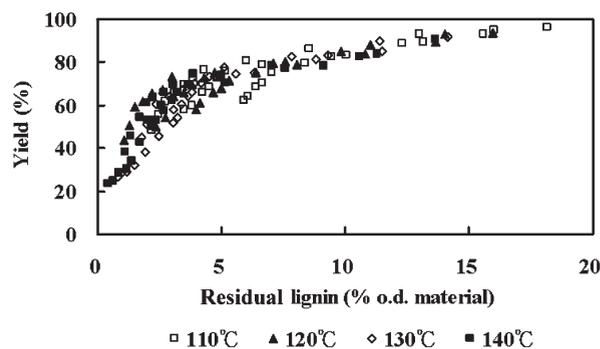


Figure 2. Variation of pulp yield with residual lignin content (L_r), showing the selectivity of HCl-catalyzed delignification of rice straw by THFA. Note: The pulping conditions entailed the following: THFA, 9.7 mol L⁻¹; HCl, 0.010–0.020 mol L⁻¹; liquor to solids ratio, 10; pulping time, 0–300 min; pulping temperature, 110 °C–140 °C.

results were developed. The understanding provides a basis for optimal control of the pulping process.

2. EXPERIMENTAL SECTION

2.1. Materials. Rice (*Oryza sativa*) straw was obtained from commercial rice straw ropes, which were cut into segments of ca. 3 cm. The material was air-dried before use. Chemical analysis of the material indicated a holocellulose content of $68.2 \pm 1.8\%$ (with $50.2 \pm 1.1\%$ α -cellulose and $18.0 \pm 0.8\%$ β - + γ -cellulose); $20.1 \pm 0.8\%$ lignin, $12.6 \pm 0.5\%$ ash, and $2.6 \pm 0.2\%$ extractives.

2.2. THFA/HCl Pulping of Rice Straw at Atmospheric Pressure. A 100 g amount of the 3 cm segments of rice straw was placed in a round-bottom flask with a 9.7 mol L⁻¹ aqueous solution of THFA and various amounts of HCl catalyst (0.010, 0.015, and 0.020 mol L⁻¹). The liquor to material ratio was adjusted to 10:1. Then the digestion of the rice straw at atmospheric pressure was carried out respectively at 110, 120, 130, and 140 °C, and digestions were conducted each in a time series, and one sample was taken every 30 min interval for a total digestion time of 300 min. The samples were washed with sufficient amounts of water and 2% NaOH solution at 70 °C to produce pulp.^{36,37,39} The air-dried pulp was then analyzed.

2.3. Evaluation of the Chemical Properties of the Pulp. The starting material and the products obtain from them were characterized according to the following standard methods: κ number (TAPPI T236 om-85), ash (TAPPI T211 om-93), alcohol–benzene extractives (TAPPI T204 os-76), holocellulose (the Wise method, as stipulated by the Japan Wood Association, 1985), cellulose and hemicellulose content (JIS P9001), and lignin (TAPPI T222 om-88). All test data shown (Figure 1) are the average of triplicate analyses.

3. RESULTS AND DISCUSSION

3.1. Lignin and Carbohydrate Selectivity of the THFA Pulping of Rice Straw. To ascertain the correlation of the delignification reaction and carbohydrate dissolution during the THFA/HCl digestion of rice straw, the pulp yields were plotted against the residual lignin contents (Figure 2). Figure 2 shows that when the residual lignin content decreased from 19 to 5%, the decrease in pulp yield was proportional to the lignin removed. Dissolution of substances other than lignin was minimal at this

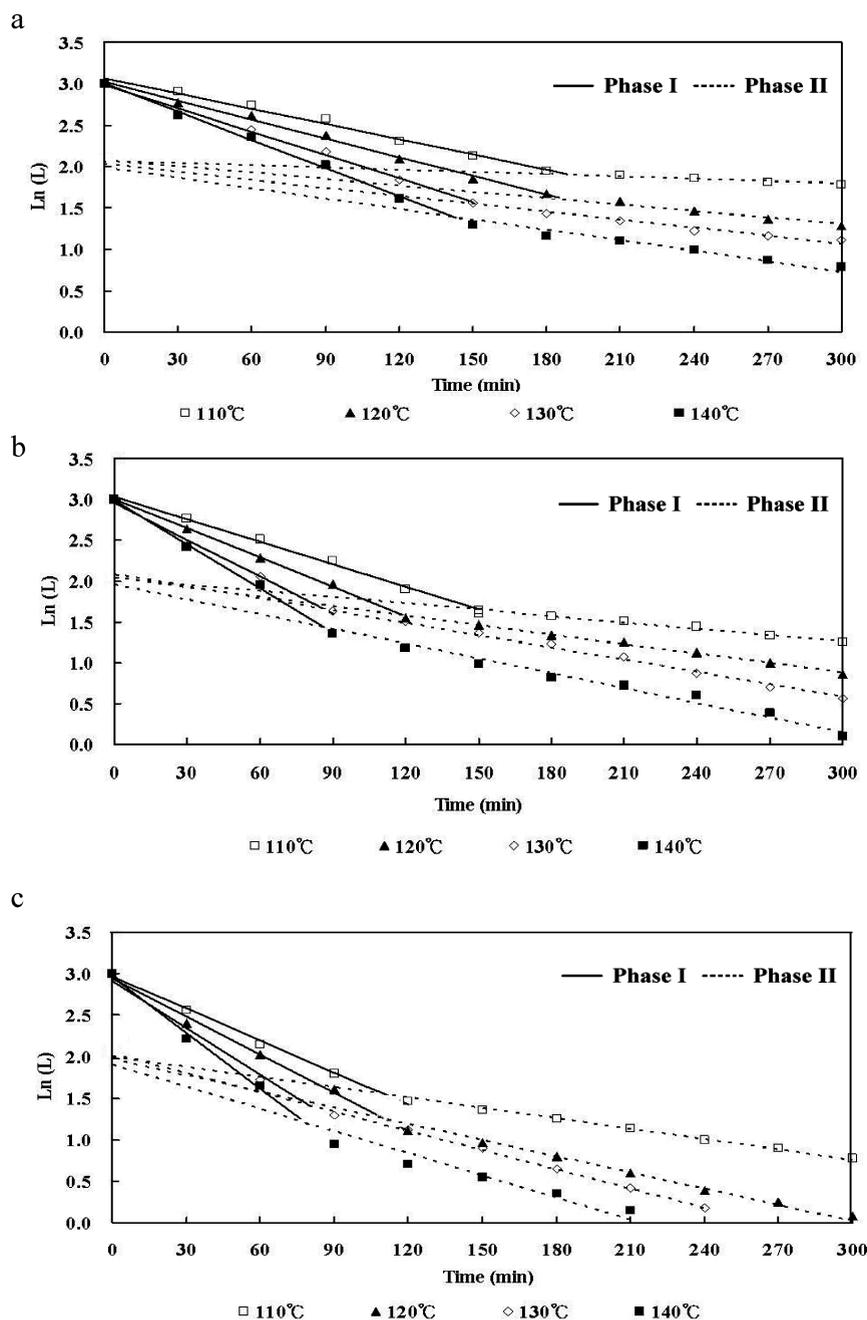


Figure 3. Kinetics of tetrahydrofurfuryl alcohol delignification of rice straw. Note: The pulping conditions entailed the following: THFA, 9.7 mol L^{-1} ; liquor to solids ratio, 10; pulping time, 0–300 min; pulping temperature, 110, 120, 130, and $140 \text{ }^\circ\text{C}$; HCl, (a) 0.010, (b) 0.015, and (c) 0.020 mol L^{-1} .

stage. However, when the residual lignin content was $<5\%$, the rate of pulp yield loss rapidly increased. As a result, when the residual lignin content was between 19 and 5%, the main reaction of pulping was the delignification reaction with a low yield loss. At a residual lignin content of $<5\%$, however, the carbohydrate dissolution predominated over delignification, leading to rapid yield losses. Figure 3 shows the division of the pulping into two phases. In the initial stage (phase I), delignification predominated with a minor carbohydrate loss and slow rate of yield decrease. At phase II, when the residual lignin content was $<5\%$, the reaction shifted to carbohydrate dissolution with a rapid yield loss, which predominated over the delignification reaction.

3.2. Kinetic Study of the Delignification Reaction. Figure 3 shows the residual lignin content of the pulp after the THFA/HCl pulping of rice straw at different pulping temperatures (110, 120, 130, and $140 \text{ }^\circ\text{C}$) and catalyst dosages (HCl, 0.010, 0.015, and 0.020 mol L^{-1}). The graph shows that at different catalyst dosages and temperatures, each series of delignification reactions could be broken into two phases. The different reactions can be seen as two lines of different slopes. Phase I is represented by the steeper slope, while phase II is shown by the flatter slope which displays the latter stages of pulping. The beginning of phase II depends on the pulping temperature and catalyst dosage. These results were similar to those of El-Sakhawy et al.⁵⁰ They pulped

Table 1. Rate Constants of Delignification and Carbohydrate Removal for THFA/HCl Pulping of Rice Straw

phase	HCl (mol/L)	temp (°C)	time ^a (min)			K_L ^b (min ⁻¹)	K_C ^c (min ⁻¹)	K_L/K_C	$\Delta L/\Delta C$	
			t_0	t_1	t_2				d	e
phase I	0.010	110	0	180		0.0061	0.0008	7.63	1.47	
		120	0	180		0.0076	0.0009	8.44	1.51	
		130	0	150		0.0094	0.0010	9.40	1.74	
		140	0	150		0.0113	0.0012	9.42	1.66	
	0.015	110	0	150		0.0092	0.0009	10.22	1.78	
		120	0	120		0.0120	0.0010	12.00	2.03	
		130	0	90		0.0150	0.0014	10.71	1.91	
		140	0	90		0.0180	0.0017	10.59	1.70	
	0.020	110	0	120		0.0128	0.0010	12.80	2.07	
		120	0	120		0.0153	0.0010	15.30	2.25	
		130	0	90		0.0188	0.0031	6.06	0.96	
		140	0	90		0.0224	0.0038	5.89	0.87	
phase II	0.010	110		180	300	0.0018	0.0009	2.00	0.12	
		120		180	300	0.0026	0.0012	2.17	0.19	
		130		150	300	0.0032	0.0014	2.29	0.22	0.22
		140		150	300	0.0042	0.0015	2.80	0.25	0.32
	0.015	110		150	300	0.0026	0.0011	2.36	0.22	
		120		120	300	0.0039	0.0014	2.79	0.24	0.26
		130		90	300	0.0050	0.0017	2.94	0.22	0.41
		140		90	300	0.0059	0.0022	2.68	0.21	0.45
	0.020	110		120	300	0.0042	0.0014	3.00	0.23	0.13
		120		120	300	0.0065	0.0017	3.82	0.27	0.55
		130		90	240	0.0077	0.0039	1.97	0.17	0.22
		140		90	210	0.0089	0.0056	1.59	0.17	0.26

^a t_0 , starting time (min) of the phase I pulping; t_1 , elapsed time (min) of the ending of phase I pulping and the starting of the phase II pulping; t_2 , elapsed time (min) to the termination of phase II pulping. ^b K_L , rate constants of delignification. ^c K_C , rate constants of carbohydrate removal. ^d $\Delta L/\Delta C$, selectivity of delignification = % lignin delignification/% carbohydrate removal. ^e $\Delta L/\Delta C$, pulp at target $\kappa = 20$.

wheat straw with an alkaline ethanol solution and differentiated the pulping reaction into a bulk and residual phase on the basis of different slopes. The presence of two phases is different from what is often observed in the kraft pulping of wood chips where initial, bulk, and residual phases can be differentiated.^{51,52}

In phase I, the delignification reaction of the THFA/HCl pulping of rice straw was rapid and tended to increase with increasing cooking temperatures and catalyst dosage. The rapid reaction was probably because rice straw is a porous structure with pores much larger than those of the woody plants, thus, ensuring the penetration of the cooking liquor and a rapid delignification reaction.⁵³ The partitioning of delignification into two phases was in agreement with Aaltonen et al.⁴⁰ in their study of the use of THFA/HCl to pulp Japanese cedar wood chips, El-Sakhawy et al.⁵⁰ in the use of alkaline ethanol to pulp wheat straw, and Huang et al.⁵³ in the use of NH_4OH – KOH to pulp rice straw. In the following section, the effects of employing cooking temperatures of 110–140 °C, and a HCl catalyst dosage of 0.010, 0.015, and 0.020 mol L⁻¹ on the delignification kinetics will be reported.

In studies on pulping kinetics, the assumption is that, at a constant temperature, the delignification rate is proportional to the amount of residual lignin in the pulp and the concentration of chemicals in the liquor. In this case, the reaction rate of the THFA/HCl pulping of rice straw can be represented with the following equation:

$$-dL/dt = K_0[\text{HCl}]^n L \quad (1)$$

where $-dL/dt$ is the rate of delignification, L is the residual lignin content (% on oven-dried rice straw), t is the reaction time (min), K_0 is the rate constant of delignification, $[\text{HCl}]$ is the catalytic concentration of the cooking liquor, and $n = 1$ as the reaction order. According to the studies of Meshgini and Sarkanen,⁵⁴ Johansson and Miksche,⁵⁵ Sarkanen and Hoo,⁵⁶ Hoo et al.,⁵⁷ Shimanda et al.,⁵⁸ and Nimz and Robert,⁵⁹ when catalyzed by HCl, the pulping reaction is assumed to be first-order.

At a particular $[\text{HCl}]$ and under constant liquor composition and constant temperature pulping conditions, eq 1 takes the form

$$-dL/dt = KL \quad (2)$$

Integrating eq 2 gives

$$\ln L = -Kt + \ln L_0 \quad (3)$$

where L_0 is the initial lignin content.

On the basis of eq 3, when the logarithms of residual lignin contents are plotted against the cooking time, a straight line results, the slope of which is an indication of the delignification rate for the particular cooking condition employed. Figure 3 shows three typical reaction rate plots for three levels of HCl concentration. At each cooking temperature, the data points are represented as two straight lines of different slopes, indicating the presence of two first-order reactions of different rate constants. The line corresponding to the initial cooking stage and exhibiting a steeper slope represents phase I (solid line), while the line for the later cooking stage represents phase II (dotted line). Table 1

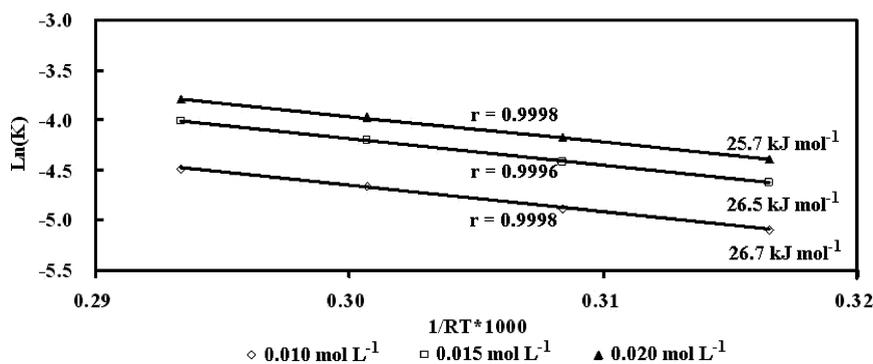


Figure 4. Arrhenius plots for bulk delignification of rice straw at different HCl concentrations.

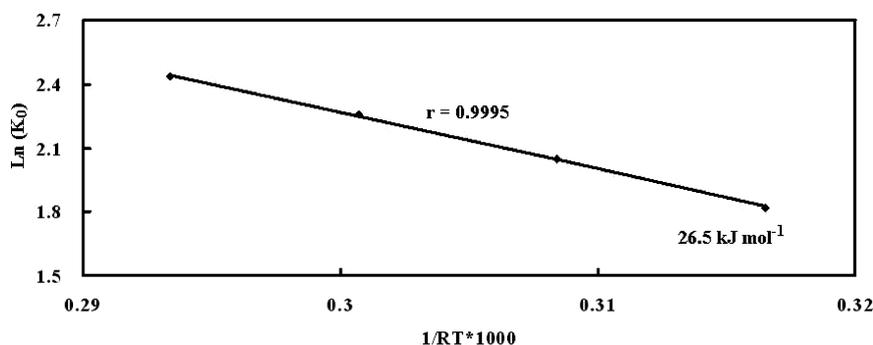


Figure 5. Arrhenius plots for bulk delignification of rice straw: HCl-dependent curve.

shows the calculated phase I and phase II delignification rate constants of the THFA/HCl pulping of rice straw.

Table 1 shows that the phase I delignification rate constants correlate with the HCl catalyst concentration and cooking temperature. Increasing the HCl concentration increased the rate of delignification and the amount of lignin removed as well. This phenomenon was similar to those observed by Parajo et al.,⁶⁰ Vazquez et al.,⁶¹ and El-Sakhawy et al.⁵⁰ Furthermore, when the HCl concentration doubled, the reaction rate constant would also double. When the cooking temperature increased from 110 to 140 °C, the rate constants also doubled.

The delignification rate constant (K_0) correlates to cooking temperature in correlation with the Arrhenius equation:

$$K_0 = Ae^{(-E_a/RT)} \quad (4)$$

where A is a preexponential factor, E_a is the activation energy for the delignification, R is the gas constant, $8.314 \text{ J (mol K)}^{-1}$, and T is the absolute temperature (K).

The logarithmic form of the Arrhenius equation appears as

$$\ln K_0 = \ln A - (E_a/R)(1/T) \quad (5)$$

On the basis of eq 5, the phase I activation energies at different catalyst concentrations were determined for reaction rate constants of K_{110} , K_{120} , K_{130} , and K_{140} . Figure 4 shows the plots of $\ln(K)$ versus $1/RT$. The linear regressions of the plots provided the slopes of the regression lines. Thus, for liquor HCl concentration of 0.010, 0.015, and 0.020 mol L^{-1} , the delignification reaction activation energies were respectively 26.7, 26.5, and 25.7 kJ mol^{-1} , with the highest HCl concentration (0.020 mol L^{-1}) examined producing the lowest activation energy.

In comparison with the K_0 values of the three HCl concentrations used, the delignification rate in eq 1 was expected to change

with variations in $[\text{HCl}]$. In this case, the slopes (S) of the straight lines in Figure 3 and Table 1 could be used to calculate the independent reaction rates K_0 , through the application of the following equation:

$$S = K_0[\text{HCl}] \quad (6)$$

The S values are plotted against $[\text{HCl}]$. The slopes of these straight lines should depend on temperature and reflect K_0 .

Figure 5 shows $\ln(K_0)$ values plotted against $1/RT$ for linear regression. The slope of the regression line represents the overall activation energy at a value of 26.5 kJ mol^{-1} . The intercept of the regression line is the natural logarithmic frequency factor, which was 2.72×10^3 . Thus, the phase I kinetic equation was derived as follow:

$$-dL_1/dt = 2.72 \times 10^3 e^{-26.5/RT} [\text{HCl}]L_{01} \quad (7)$$

L_{01} is the initial lignin content in phase I.

The results for the rate constants of the phase II delignification reaction were estimated from Figure 2 and listed in Table 1. The reaction rate constants exhibited trends similar to those in the phase I. The activation energy for the phase II delignification reaction was derived using the same methodology as for phase I. The overall activation energy for phase II was 32.2 kJ mol^{-1} . The intercept of the regression line was the natural logarithm of the frequency factor, which was 5.75×10^3 . Thus, the kinetic equation for the phase II delignification was derived as follow:

$$-dL_2/dt = 5.75 \times 10^3 e^{-32.2/RT} [\text{HCl}]L_{02} \quad (8)$$

L_{02} is the pseudo-initial lignin content (7.7%) of phase II.

3.3. Transition Point between Phase I and Phase II. The above result shows the phase I and II kinetic equations of the THFA/HCl pulping of rice straw. To have optimal control over

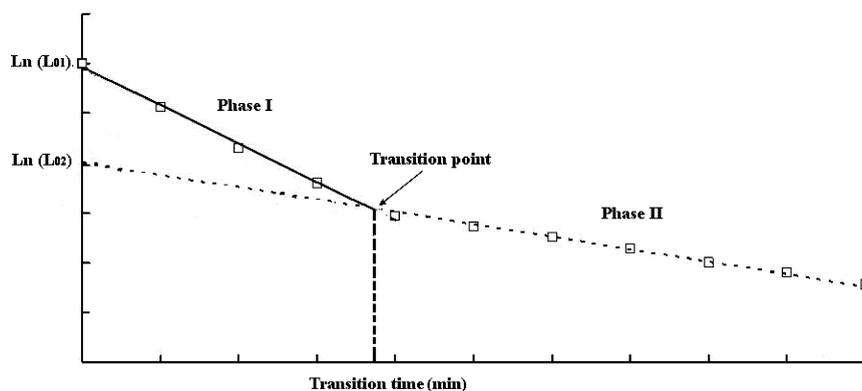


Figure 6. Establishing the transition point between phase I and phase II. Note: L_{01} is the initial lignin content of phase I; L_{02} is the pseudoinitial lignin content of phase II.

Table 2. Transition and Target Time for THFA/HCl Pulping of Rice Straw

HCl (mol/L)	temp (°C)	transition time (min)	target time ^a (min)
0.010	110	194	>300
	120	190	>300
	130	153	297
	140	134	227
0.015	110	144	>300
	120	117	244
	130	95	190
0.020	140	79	161
	110	111	227
	120	108	146
	130	86	124
	140	70	107

^a Time required to reach resulting pulp with a target $\kappa = 20$.

the pulping method, the transition point between phase I and phase II must be established (see Figure 6). The kinetic equations for phases I and II can also be described by the following equations:

$$\text{phase I: } \ln L = -K_1 t + \ln L_{01}$$

$$\text{phase II: } \ln L = -K_2 t + \ln L_{02}$$

where K_1 is the delignification rate constant of phase I, K_2 is the delignification rate constant of phase II, L_{01} is the initial lignin content of phase I, L_{02} is the pseudoinitial lignin content of phase II, and t is the reaction time (min).

At the transition point between phase I and phase II, the two kinetic lines intersected; hence eq 9 must be equal to eq 10:

$$-K_1 t + \ln L_{01} = -K_2 t + \ln L_{02} \quad (11)$$

$$\ln L_{01} - \ln L_{02} = K_1 t - K_2 t \quad (12)$$

$$\ln(L_{01}/L_{02}) = (K_1 - K_2)t \quad (13)$$

then the transition time is obtained

$$t = \ln(L_{01}/L_{02}) / (K_1 - K_2) \quad (14)$$

Table 2 shows the transition time at various cooking temperatures and catalyst dosages as derived from eq 14. The table shows that, along with increased cooking temperature and catalyst

dosage, the transition time shifted to an earlier time. The lowest transition time occurred at a cooking temperature of 140 °C and a catalyst dosage of 0.020 mol L⁻¹. It occurred at 70.5 min from the beginning of the cooking.

In addition, Table 2 shows the results of setting a pulp κ target of 20 and applying eq 10 to calculate the time required to reach phase II delignification. As the table shows, increasing the cooking temperature and catalyst dosage shortens the time for the pulp to reach $\kappa = 20$. For a cooking temperature of 140 °C and catalyst dosage of 0.020 mol L⁻¹, the time required to reach $\kappa = 20$ was 106.9 min. As for the K_L/K_C (ratio of delignification rate and rate of carbohydrate dissolution) and $\Delta L/\Delta C$ (ratio of lignin removed and carbohydrate dissolved during pulping) values to reach $\kappa = 20$, we shall discuss them in the next section.

3.4. Activation Energy and Reaction Rate. Summarizing the above, when the THFA/HCl organosolv process was applied to pulp rice straw, it gave a phase I delignification activation energy of 26.5 kJ mol⁻¹. This value was between the values (16–131 kJ mol⁻¹) reported for the pulping of rice or wheat straws using different methods. Huang and Shi³¹ applied soda–AQ pulping to rice straw and found the activation energy to be 49.7 kJ mol⁻¹. Gonzalo et al.³³ applied soda and kraft pulping to wheat straw and found the activation energy to be 93 kJ mol⁻¹, while Abdual-Karim et al.³² used the kraft process to cook wheat straw and obtained an activation energy of 131 kJ mol⁻¹. From these, we noted that the THFA/HCl pulping of rice straw generated an activation energy that was much lower than those of chemical pulping. However, the different organosolv pulping processes used by these researchers must also be compared to arrive at the true value of the THFA/HCl pulping of rice straw. El-Sakhawy et al.⁵⁰ performed alkaline ethanol pulping of wheat straw and found an activation energy of 16 kJ mol⁻¹. Huang et al.⁵³ used NH₄OH–KOH to cook rice straw and found an activation energy of 35.6 kJ mol⁻¹, while Dang and Nguyen⁶² applied ethanol–H₂SO₄ to cook wheat straw and established an activation energy of 128 kJ mol⁻¹. Thus, the THFA/HCl pulping of rice straw produced a kinetic reaction with an activation energy that was not much different from those of alkaline ethanol or NH₄OH–KOH and much lower than ethanol–H₂SO₄. Furthermore, when the pulping kinetics were compared with those of softwoods and hardwoods, such as those for spruce, birch,^{63,64} and *Eucalyptus globulus*,^{65–67} with different pulping methods, their activation energies were all much higher than that found in the present study. Consequently, the THFA/HCl pulping of rice straw was found to be a method that pulps easily and has low activation energy.

In the phase I reaction, the cooking liquor possessed high lignin selectivity which was different from that of the kraft pulping of wood chips. Zhai and Lee⁶⁸ noted that the lignin of grasses is mainly distributed at the middle lamella and cell corners of the fiber, which have a higher lignin content than those in woody plants. Huang et al.⁵³ noted that rice straw was a more porous structure than wood; thus, a faster delignification reaction occurred at the initial stage of cooking. Aaltonen et al.⁴⁰ pulped Japanese cedar using THFA/HCl and observed that the chemicals attacked mainly the lignin in the middle lamella. If this is true, then, in the THFA/HCl pulping of rice straw, the liquor accesses the middle lamella layers through the rice straw's more porous structure and selectively attacks the lignin there, causing the phase I reaction to proceed faster. As for the dissolution of carbohydrates, Zhai and Lee⁶⁸ suggested that the carbohydrates of grasses exhibited massive dissolution only when delignification reaction reached ca. 90%. However, in the present study, when phase I delignification reached about 80% at the higher cooking temperatures of 130 and 140 °C and catalyst dosages of 0.015 and 0.020 mol L⁻¹, the dissolution of carbohydrate began to increase markedly. Hence, the K_C value (dissolution rate of carbohydrate) of phase I tended to increase rapidly after this point (Table 1). Table 1 shows that the K_L/K_C values of phase I were always much greater than those of phase II. At a catalyst concentration of 0.020 mol L⁻¹ and a cooking temperature ≤ 120 °C, the K_L/K_C ratios were greater than those obtained at higher cooking temperatures (130 and 140 °C). At a cooking temperature of 120 °C and catalyst concentrations of 0.020 mol L⁻¹, the K_L/K_C ratio of phase I reached a maximum. Moreover, at a catalyst dosage of 0.020 mol L⁻¹ and cooking temperatures of 110–120 °C, the $\Delta L/\Delta C$ value increased from 2.07 to 2.25, indicating that the selectivity improved. However, at the higher cooking temperatures of 130 and 140 °C, the $\Delta L/\Delta C$ value decreased from 0.96 to 0.87, showing a lower selectivity, with the dissolution of carbohydrate outstripping that of lignin.

The phase II reaction during pulping, under all the conditions examined, found that the ratio was between 0.12 and 0.27. This indicated that the loss of the carbohydrate fraction was far greater than that of the lignin dissolution. In other words, the quantity of lignin removed was roughly one-fifth of the carbohydrate, causing a marked decrease in pulp yield, which is indicative of overcooking. Therefore, when the $\Delta L/\Delta C$ at pulp $\kappa = 20$ was examined, the highest value (0.55) was found when pulping at 120 °C using 0.020 mol L⁻¹ of catalyst. This result indicates that similar conditions used for the phase II reaction would obtain minimum carbohydrate dissolution. As for the other conditions noted above, the $\Delta L/\Delta C$ values were between 0.20 and 0.45 (Table 1). The drastic dissolution of carbohydrate fraction over that of delignification entailed serious losses of pulp yields, and this phenomenon will be discussed in a further study.

The above results indicated that the THFA/HCl pulping of rice straw showed a low activation energy and that the HCl catalyst in the cooking liquor facilitated the delignification reaction. In other word, the delignification reaction was highly dependent on the HCl dosage. For carbohydrate dissolution, the loss rate was mitigated at the lower cooking temperature (≤ 120 °C). At a cooking temperature of 120 °C, the pulping process produced a low activation energy with easy delignification while retaining the carbohydrate fractions.

4. CONCLUSIONS

The THFA/HCl pulping of rice straw was composed of two phases, phases I and II, in its delignification reaction. Phase I delignification was highly dependent upon the HCl catalyst concentration in the cooking liquor. Phase I delignification had an activation energy of 26.5 kJ mol⁻¹ and frequency factor of 2.72×10^3 . The phase II delignification reaction had an activation energy of 32.2 kJ mol⁻¹ and a frequency factor of 5.75×10^3 , indicating that the THFA/HCl pulping of rice straw had a low activation energy. Compared to other chemical pulping processes, this process had a superior performance.

As for pulping selectivity, phase I delignification had K_L/K_C values greater than those of phase II. During phase I, at a cooking temperature of 120 °C and a catalyst dosage of 0.020 mol L⁻¹, the maximum K_L/K_C ratio value was attained. Similarly, under the same conditions, the maximum $\Delta L/\Delta C$ was reached. These results indicated that, at 120 °C, the cooking liquor (with its catalyst) mostly attacked the lignin fraction rather than the carbohydrates, and the rate of delignification was faster than that of carbohydrate dissolution. During the phase II reaction, however, at all conditions, the $\Delta L/\Delta C$ values were between 0.12 and 0.27. This indicates that attempting to remove residual lignin caused a substantial carbohydrate loss and led to a rapid decrease in pulp yields. To have more control over the optimal process, we derived equations for calculating the transition times from phase I to phase II. Increasing the cooking temperature and catalyst dosage shortens the time to the transition between the phases. Moreover, when making bleach grade pulp, the κ of the resulting pulp was set at 20 as the target end point; the time required in phase II to reach the end point was also shortened when the cooking temperature and catalyst dosage increased. Thus, when the target pulp κ was 20, at a cooking temperature of 120 °C and HCl catalyst dosage of 0.020 mol L⁻¹, the highest $\Delta L/\Delta C$ value of 0.55 was attained. At that point, the pulp yield, at ca. 66.5% had yet to decrease precipitously. In addition, to reach a pulp of $\kappa = 20$, the $\Delta L/\Delta C$ had to be between 0.20 and 0.45. Thus, despite pulping time, temperature, or an increase in catalyst dosage, the ensuing greater dissolution of the carbohydrate fractions over that of lignin might result in markedly decreased pulp yield.

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