

KINETIC STUDY OF CARBOHYDRATE DISSOLUTION DURING TETRAHYDROFURFURYL ALCOHOL/HCL PULPING OF RICE STRAW

Chen-Lung Ho,^a Keng-Tung Wu,^b Eugene I-Chen Wang,^a and Yu-Chang Su^{b,*}

This study investigated carbohydrate dissolution during tetrahydrofurfuryl alcohol/hydrochloric acid (THFA/HCl) pulping of rice straw, and reaction kinetics equations were derived. For both cellulose and hemicellulose fractions, dissolution during pulping could be separated into two phases. In the initial stage, or phase I, of cellulose dissolution, small amounts were solubilized. In phase II, when delignification reached a level of approximately 85%, along with increases in HCl concentration and cooking temperature, cellulose dissolution accelerated. The dissolution rate of hemicellulose also accelerated. However, the phase I dissolution rate was faster than the phase II rate. From the dissolution rates of carbohydrates (*i.e.*, cellulose and hemicellulose), the activation energies and frequency factors were then calculated, and the reaction kinetic equations were derived. Comparing the experimental data with the predicted data, the pulp compositions, regardless of the contents of lignin, hemicellulose, or cellulose, all showed a high degree of correlation ($R^2 > 0.99$), thus proving that the derived kinetic equations were applicable to the process rationalization of THFA/HCl pulping of rice straw and in the control of pulp chemical compositions.

Keywords: Rice straw; Organosolv pulping; Tetrahydrofurfuryl alcohol pulping; Carbohydrate dissolution; Pulping kinetics

Contact information: a: Division of Wood Cellulose, Taiwan Forestry Research Institute, 53, Nanhai Rd., Taipei, Taiwan 100; b: Department of Forestry, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung, Taiwan 402; *Corresponding author: ycsu@nchu.edu.tw

INTRODUCTION

Cellulose is a renewable resource in nature and is a vital part of the proper utilization of renewable resources. Natural plant cellulose is used as a raw material for making paper. For decades, people have tried using organic solvents to digest plant materials and produce pulps, *i.e.*, organosolv processes (Johansson *et al.* 1987). Organosolv pulping could potentially overcome the pollution problems caused by kraft pulping and provide the means for isolating the main products of pulping (*i.e.*, cellulose, hemicellulose, and lignin), thus producing bioenergy (such as ethanol) or other higher value-added chemicals. In an era of elevating energy costs, organosolv pulping processes could be a promising path for the further progress of biomass energy and materials (Hergert 1998; Hammett *et al.* 2001; Yaser *et al.* 2007; Tu *et al.* 2008).

Among organosolv pulping processes of lignocellulosic material, tetrahydrofurfuryl alcohol (THFA) pulping can be conducted under atmospheric pressure, having the advantages of low energy consumption, low equipment requirements, and a low investment cost. Bogomolov *et al.* (1979a-c), Johansson *et al.* (1987), and Aaltonen *et al.* (1990) have reported on the delignification reactions of THFA pulping of birch and pine,

as well as the pulping of birch, spruce, and *Eucalyptus*. These studies have focused on both softwood and hardwood species. Only two studies of THFA pulping of agricultural waste, such as rice straw, have been reported. In a first report, THFA pulping of rice straw with an HCl catalyst was investigated (Ho *et al.* 2009). Digestion was conducted at 120 °C under atmospheric pressure for 4 h at 30 min time increments. The pulping characteristics, chemical properties of the resulting pulp, and the handsheets' physical properties were evaluated. Pulp yields were generally 15 to 20% higher than those from soda-AQ (Bhardwaj *et al.* 2005), kraft (Rodriguez *et al.* 2008), and soda (Rodriguez *et al.* 2008) pulping processes. In the initial pulping stage, delignification was found to proceed at an extremely high rate, while the dissolution of carbohydrate fractions was relatively low. In addition, a greater proportion of hemicellulose dissolved compared to cellulose. As a consequence of hemicellulose losses, the resulting pulps tended to have poorer physical properties than those obtained using the kraft process.

In a second report (Ho *et al.* 2011), the delignification kinetics of atmospheric pressure pulping of rice straw using the THFA/HCl organosolv pulping process was investigated. The effects of independent variables on the rate constants, delignification activation energy, and various frequency factors were discussed, and delignification reaction kinetic equations for phase I and phase II were derived. In phase I, 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 approximately 5%, dissolution of carbohydrates was greater than lignin removal, causing a marked reduction in pulp yield. Both phases exhibited fairly low activation energies of 26.5 and 32.2 kJ mol⁻¹, respectively. Huang and Shi (1986) applied soda-AQ pulping to rice straw and found the activation energy to be 49.7 kJ mol⁻¹. Abdul-Karim *et al.* (1995) used the kraft process to cook wheat straw and obtained an activation energy of 131 kJ mol⁻¹, while Gonzalo *et al.* (1998) applied soda and kraft pulping to wheat straw and found the activation energy to be 93 kJ mol⁻¹. From these results, it can be noted that the THFA/HCl pulping of rice straw generated an activation energy that was much lower than those of chemical pulping, revealing the superiority of the pulping method.

A lack of understanding persists about the behaviors of carbohydrate dissolution during THFA/HCl pulping, particularly with regard to the possible dissolution of cellulose and hemicellulose under different pulping conditions. Therefore, in this study, the carbohydrate dissolution kinetics of rice straw during THFA/HCl pulping process were studied. Various influential factors, such as catalyst dosage, cooking temperature, and pulping time were investigated. Their effects on carbohydrate dissolution rates and activation energies were obtained to derive a set of carbohydrate dissolution kinetic equations. The aim was to understand the effects of individual factors to:

- 1) Provide a basis for control of the pulping process as a way to predict the pulp composition, and
- 2) Allow manipulation of the cellulosic or hemicellulosic contents of pulp for optimal bioenergy feedstock pretreatment or raw material for manufacturing certain specialty papers.

EXPERIMENTAL

Materials

Rice (*Oryza sativa*) straw was obtained from commercial rice straw ropes, which were cut into segments of approximately 3 cm. The material was air dried before use. Chemical analysis of the material indicated contents of $50.2 \pm 1.1\%$ cellulose, $18.0 \pm 0.8\%$ hemicellulose, $20.1 \pm 0.8\%$ lignin, $12.6 \pm 0.5\%$ ash, and $2.6 \pm 0.2\%$ extractives.

THFA/HCl Pulping of Rice Straw at Atmospheric Pressure

The pulping method was conducted according to Ho *et al.* (2009, 2011). One hundred grams of the 3 cm segments of rice straw were 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 (L kg^{-1}). The digestion of the rice straw at atmospheric pressure was carried out, respectively, at 110, 120, 130, and 140 °C, and one sample was taken every 30 min interval for a total digestion time of 300 min. The samples obtained were washed with sufficient amounts of water and 2% NaOH solution at 70 °C (Johansson *et al.* 1987; Bogomolov *et al.* 1979a, b), and the air-dried pulp was then analyzed for further study.

Evaluation of the Chemical Properties of the Pulps

The starting material and the obtained products were characterized according to the following standard methods: TAPPI T236 (kappa number), TAPPI T211 (ash), TAPPI T204 (ethanol/benzene-soluble extractives), TAPPI T222 (lignin), and for holocellulose a modified Wise method was used, based on the Japanese Wood Association (1983). Upon obtaining the holocellulose fraction, it was extracted with 17.5% NaOH to isolate hemicellulose at 15 °C for 2 h. The residue, after ash content correction, was also taken to be cellulose.

RESULTS AND DISCUSSION

Investigation of the Phase Distinctions During Cooking

A 9.7 mol L^{-1} THFA water solution was added to 0.010, 0.015, and 0.020 mol L^{-1} HCl catalyst, and digested at temperatures 110, 120, 130, and 140 °C for 300 min. After 30 min, the digestion unit was stopped and the resulting pulp composition was analyzed. The results are shown in Fig. 1a and 1b.

In Fig. 1a, the delignification and dissolution of carbohydrates obtained at a time series of different cooking temperatures and catalyst dosages indicated that when the delignification increased from 0% to 85%, the main thrust of the pulping reaction was delignification, with minimal amounts of dissolved carbohydrates. Whereas when the delignification was > 85%, the carbohydrate dissolution accelerated and the rate tended to increase with increasing catalyst dosage and digestion temperature. The sooner the pulp reached delignification greater than 85%, the faster the inflection point in carbohydrate dissolution occurred.

However, at the highest catalyst charge of 0.020 mol L^{-1} and at a temperature > 130 °C, carbohydrate dissolution was extremely rapid, leading to drastically reduced

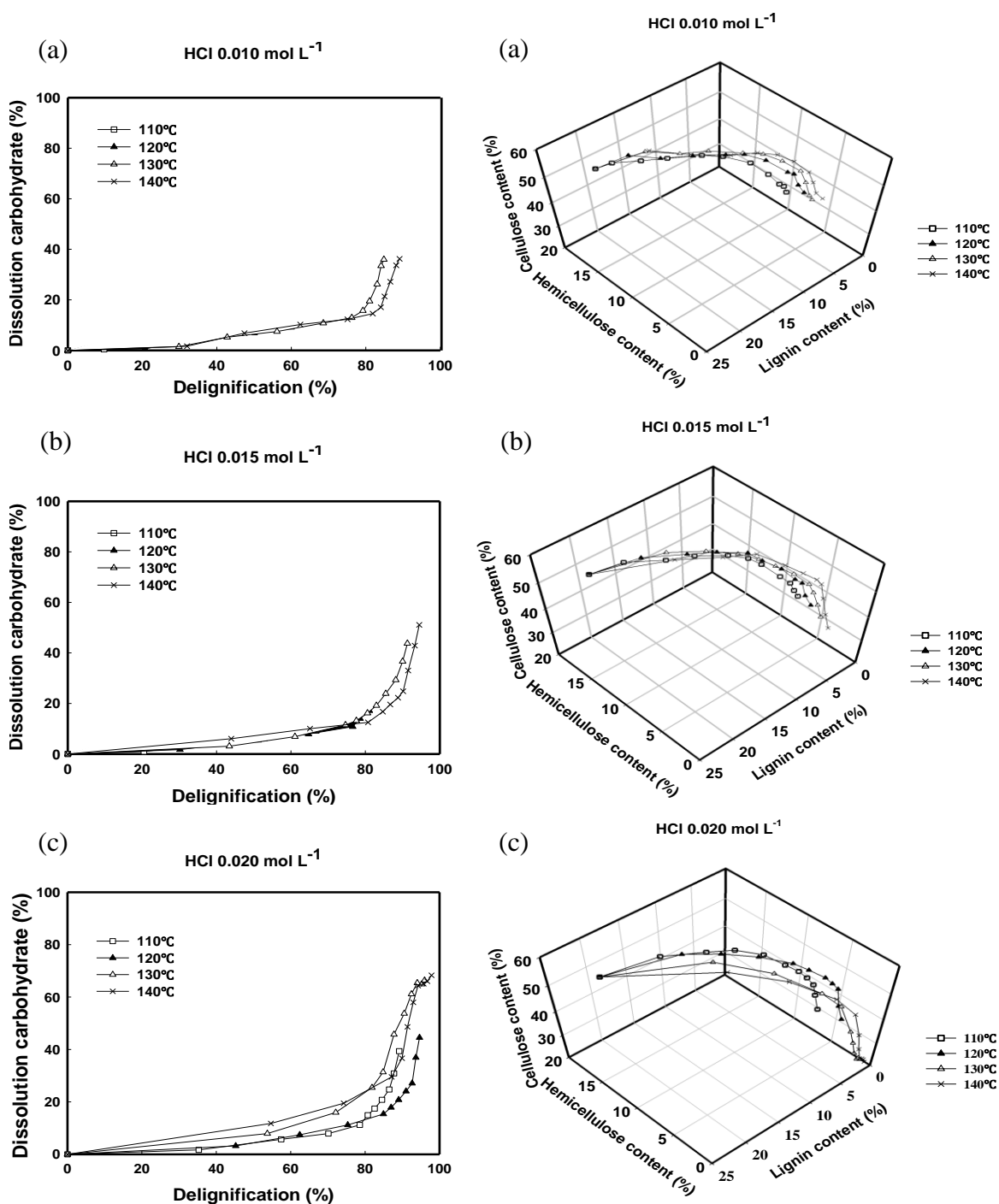


Fig. 1. a. Variation of carbohydrate dissolution with the degree of delignification; b. Graphs of chemical composition for rice straw pulped with THFA/HCl methods
 Note: The pulping conditions were THFA: 9.7 mol L⁻¹, liquor-to-solids ratio: 10 (L kg⁻¹), pulping time: 0 to 300 min, pulping temperature 110 °C, 120 °C, 130 °C, 140 °C, HCl: (a) 0.010 mol L⁻¹, (b) 0.015 mol L⁻¹, (c) 0.020 mol L⁻¹

pulp yields (Fig. 2c). Thus, the more severe the cooking conditions were (e.g., higher temperatures), the lower the pulp yield. This study inferred that at delignification less than 85%, the chemicals mainly acted on lignin, leading to mild yield decreases. Whereas

at delignification greater than 85%, the chemicals acted on carbohydrates and led to a far greater carbohydrate loss rate than lignin, causing drastic reductions in pulp yields. The probable reason for this phenomenon is that grasses of Poaceae have lignin contents as a percentage of total lignin in the middle lamella, and cell corner regions are much higher than wood fibers (Zhai and Lee 1989). In addition, Huang *et al.* (2007) noted that rice straw is an intrinsically more porous structure than woody plants. Thus, in the initial stage of pulping, delignification proceeded briskly. Aaltonen *et al.* (1990) cooked Japanese cedar using the THFA/HCl process and noted that the chemicals tended to act on lignin in the middle lamella layers. Hence, when rice straw was cooked with THFA/HCl, the liquor penetrated the porous structure rapidly and acted on the lignin in the middle lamella immediately, causing a rapid delignification in the bulk phase. As for the carbohydrate fractions, Zhai and Lee (1989) proffered that the carbohydrates of Poaceae grasses begin to dissolve more quickly after delignification has removed 90% of the lignin. Thus, in congruency with their observation, when THFA/HCl pulping of rice straw was conducted at a temperature greater than 130 °C, the transition points for rapid carbohydrate dissolution occurred sooner.

To understand the changes occurring to the cellulosic and hemicellulosic fractions of the residual carbohydrate in the pulp, Fig. 1b was plotted. The plot shows that at different temperatures and catalyst dosages, there was a relatively smaller quantity of cellulose dissolution than hemicellulose in the initial stage of cooking. At this time, delignification proceeded rapidly. However, in the later stages of digestion, when residual lignin content reached about 5%, the amount of dissolved cellulose exceeded that in the initial stage.

To further illustrate the changes in residual hemicellulose and cellulose contents in the THFA/HCl pulping time series at different temperatures and catalyst dosages, natural logarithms of the hemicellulose and cellulose values were taken and plotted in Fig. 2 and 3, respectively. Concerning the hemicellulose shown in Fig. 2, even for different catalyst dosages and cooking temperatures, the dissolution of hemicellulose in each time series can be clearly defined in two phases. Those having high cooking temperatures and high catalyst dosages are more distinctively discerned. Thus, two slope values were designated, such that the initial cooking stage with a steeper slope is attributed to phase I (solid line), and the line with a milder slope at the mid to later stage of cooking is phase II (dotted line). During the phase I reaction, THFA/HCl caused a rapid dissolution of hemicellulose, and the rate increased with increasing temperatures and catalyst dosages.

The dissolution behavior of cellulose during pulping is shown in Fig. 3. Under different catalyst dosages and digestion temperatures, the results showed that although there were two distinguishable phases in the dissolution of cellulose during digestion, in phase I there was a minimal dissolution of cellulose. Therefore, there was a rather flat slope of only 1.8×10^{-4} to 1.6×10^{-3} . In phase II, however, the dissolution rates accelerated rapidly, which differed depending on the cooking temperature and catalyst dosage. The slopes were steeper with values ranging from 1.7×10^{-3} to 6.3×10^{-3} .

The dissolution of carbohydrate fractions during THFA/HCl pulping showed the dissolution of hemicellulose starting early, while cellulose had an accelerated dissolution rate in only phase II. The phenomena are most likely caused by their respective DP, chemical structures, and morphological distributions. The DP of hemicellulose is lower compared to that of cellulose. In addition, cellulose is a long chain homopolymer of

glucose units with interspersed crystalline regions, while hemicelluloses are amorphous polysaccharides.

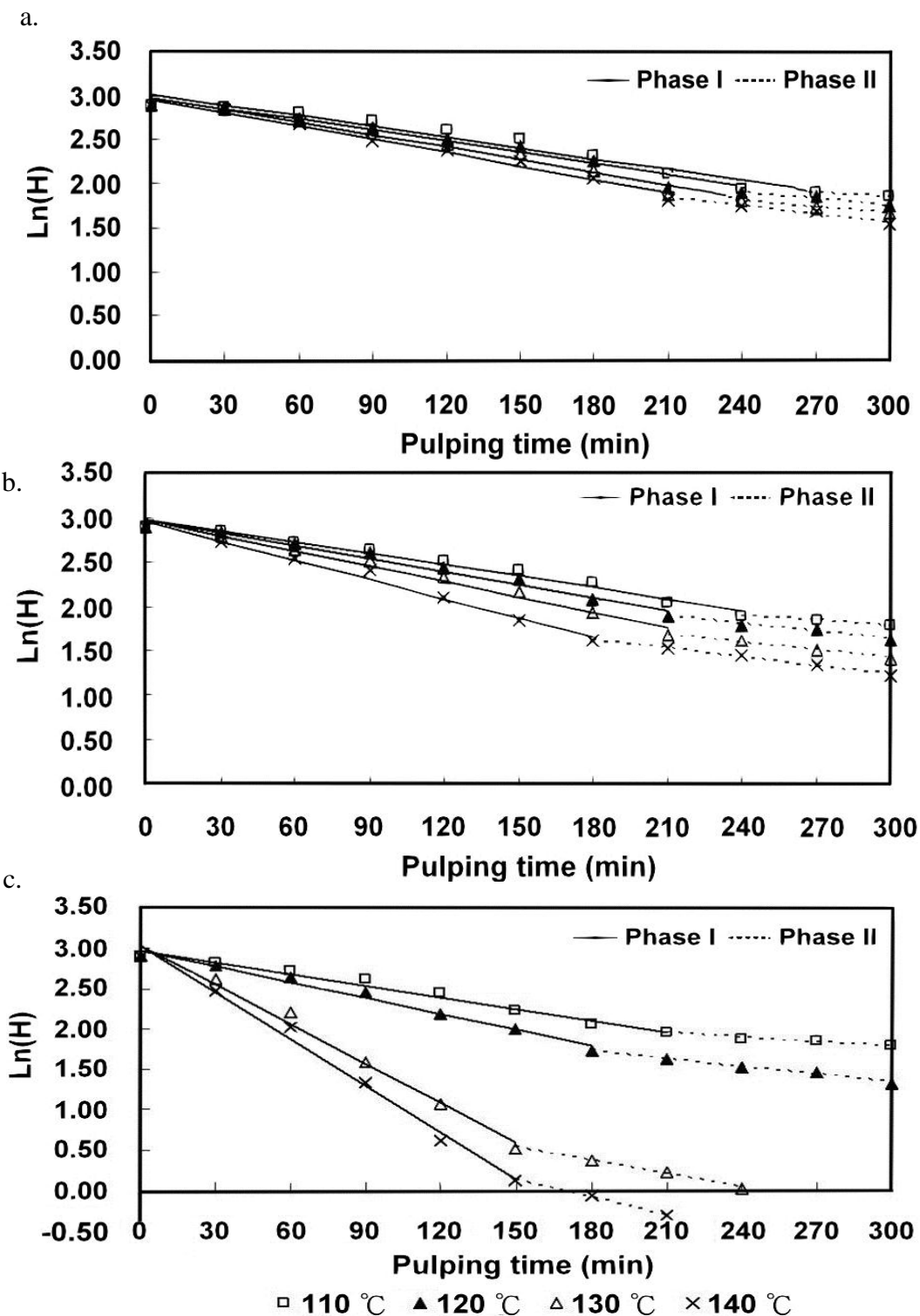


Fig. 2. Kinetics of tetrahydrofurfuryl alcohol hemicellulose dissolution of rice straw
 Note: The pulping conditions were THFA: 9.7 mol L⁻¹, liquor-to-solids ratio: 10 (L kg⁻¹), pulping time: 0 ~ 300 min, pulping temperature: 110 °C, 120 °C, 130 °C, 140 °C, HCl: a. 0.010 mol L⁻¹, b. 0.015 mol L⁻¹, c. 0.020 mol L⁻¹

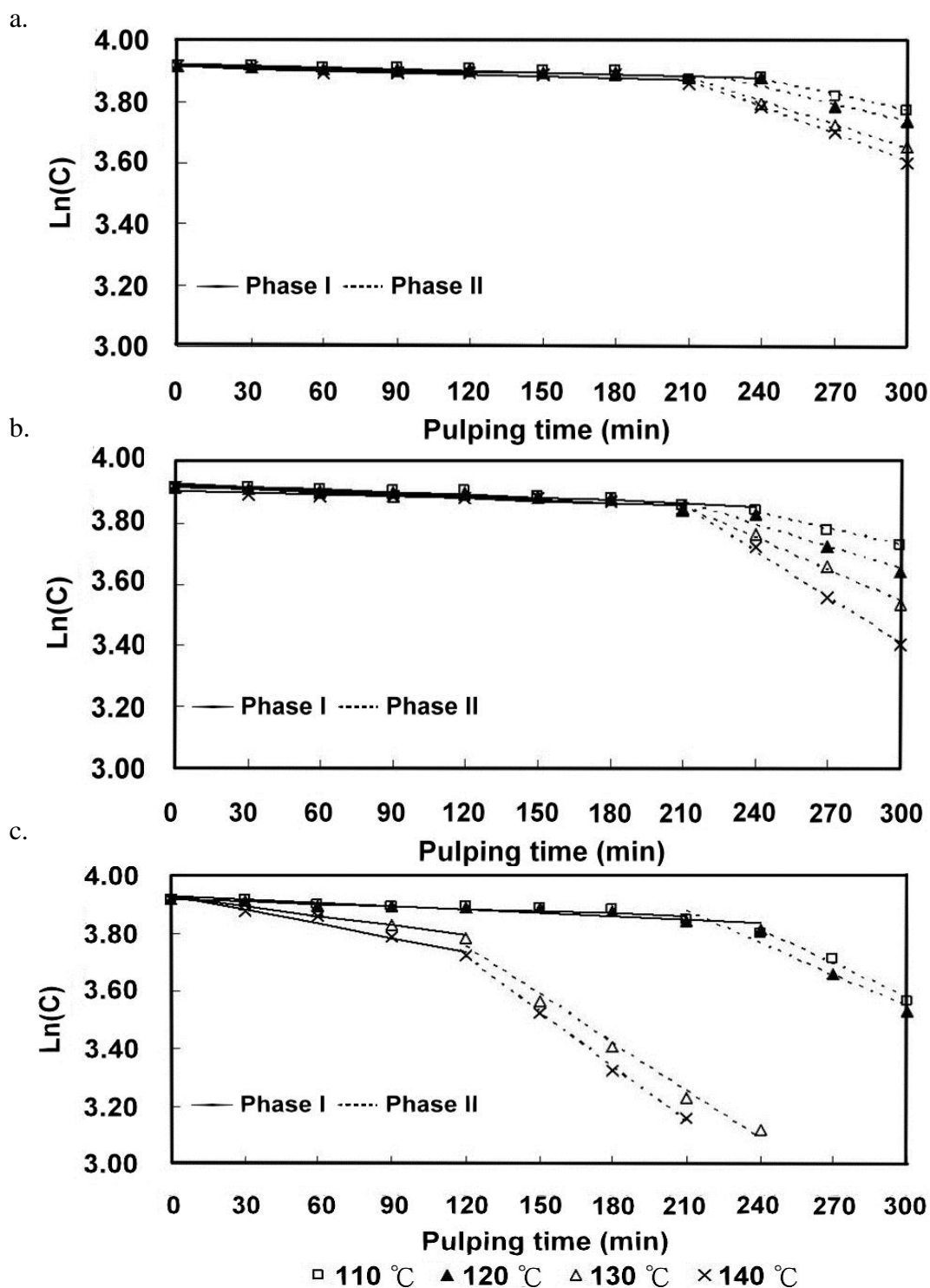


Fig. 3. Kinetics of tetrahydrofurfuryl alcohol cellulose dissolution of rice straw

Note: The pulping conditions were THFA: 9.7 mol L⁻¹, liquor-to-solids ratio: 10 (L kg⁻¹), pulping time: 0 ~ 300 min, pulping temperature: 110 °C, 120 °C, 130 °C, 140 °C, HCl: a. 0.010 mol L⁻¹, b. 0.015 mol L⁻¹, c. 0.020 mol L⁻¹

Cellulose is a structural member of plants and is often surrounded by matrices of other structural polymers, such as lignin and hemicelluloses. Thus, during a pulping reaction, the amorphous hemicellulose can be easily degraded and become soluble. In THFA/HCl pulping, hemicellulose is acid hydrolyzed and dissolved. Therefore, hemicellulose has a clear tendency to dissolve when digestion temperature and catalyst dosage are increased in phase I. By contrast, cellulose, being quasi-crystalline and more inaccessible, was dissolved only to a minor extent in phase I. After most of the encrusting lignin and hemicellulose matrices were removed, or at a later stage when delignification reached a level of approximately 85%, it started to dissolve *en masse*. This is in agreement with Zhai and Lee (1989), who noted that rapid cellulose loss occurred only after delignification reached 90%.

Kinetic Study of Cellulose and Hemicellulose Dissolutions Reaction

It is assumed that the rates of cellulose and hemicellulose dissolutions are proportional to the amounts of remaining cellulose and hemicellulose in the resulting pulp and the concentration of chemicals in liquor, provided the temperature is kept constant. Their rates of reaction during THFA/HCl pulping can be represented by the following equations,

$$-dC/dt = K_C[HCl]^n C \quad (1)$$

$$-dH/dt = K_H[HCl]^n H \quad (2)$$

where $-dC/dt$ is the dissolution rate of cellulose, $-dH/dt$ is the dissolution rate of hemicellulose, C is the cellulose content (% of oven-dried rice straw), H is the hemicellulose content (% of oven-dried rice straw), t is the reaction time, K_C is the dissolution rate constant of cellulose, K_H is the dissolution rate constant of hemicellulose, n is the reaction order, and $[HCl]$ is the catalyst concentration of the cooking liquor.

According to studies of several researchers, when catalyzed by an acidic solution, the pulping reaction is assumed to be first-order (Saeman 1945; Basedow *et al.* 1978; McParland and Grethlein 1982; Maloney *et al.* 1985; Abatzoglou *et al.* 1992; Malester *et al.* 1992; Mok *et al.* 1992; Parajo *et al.* 1995; Camacho *et al.* 1996; Lavarack *et al.* 2002; Bustos *et al.* 2003; Xu *et al.* 2008).

Reaction kinetics of cellulose dissolution

As noted above, the THFA/HCl digestion of cellulose was separated into two phases. Thus, the discussion of the cellulose reaction kinetics is also divided into two phases. First, at a particular HCl concentration and under pulping conditions of constant liquor composition and temperature, Equation 1 takes the form:

$$-dC/dt = K_0 C \quad (3)$$

Equation 4 is the integrated form of Equation 3,

$$\ln C = -K_0 C + \ln C_0 \quad (4)$$

where C_0 is the initial cellulose content.

According to Eq. 3, a plot of the logarithm of cellulose yield versus cooking time should appear as a straight line, the slope of which can serve as a measure of the cellulose dissolution rate valid for the particular cooking conditions applied. Typical plots of such data are shown in Fig. 3 for the three respective HCl concentrations. For each cooking temperature investigated, the experimental points were fitted by two straight lines with different slopes, suggesting the existence of two first-order reactions with different rate constants. The initial line with the flat slope is related to phase I and the latter to phase II. The rate constants calculated for phase I and phase II of rice straw are presented in Table 1. The results show that during phase I digestion, of the cellulose dissolution rate constants, only those corresponding to an HCl concentration of 0.020 mol L⁻¹ and cooking temperatures of 130 and 140 °C exhibited a rapidly increasing rate. This shows that the THFA/HCl pulping entailed a weak dissolution of cellulose in the initial stage of pulping, which differed from the typical cellulose dissolution patterns during kraft pulping.

In phase II, along with increases in the catalyst HCl concentration and cooking temperature, cellulose dissolution accelerated. The shift in rates coincided with a delignification level of *ca.* 85 to 90%. During the phase II cellulose dissolution reaction, at a constant cooking temperature but with a doubled catalyst HCl concentration, the reaction rate constant also doubled. According to the Arrhenius equation,

$$K = A \cdot e^{(-E_a/RT)} \quad (5)$$

where A is an experimental constant, E_a is the activation energy for cellulose dissolution, R is the gas constant, or 8.314 kJ mol⁻¹, and T is the absolute temperature (K).

The logarithmic form of the Arrhenius equation appears as:

$$\ln K = \ln A - (E/R)(1/T) \quad (6)$$

According to Equation 6, the phase II cellulose dissolution activation energies at different catalyst concentrations are presented as reaction rate constants K_{110} , K_{120} , K_{130} , and K_{140} for different digestion temperatures. In other words, these are plots of natural logarithms of the slopes $\ln[K]$ against $1/T$, obtaining the slope of the linear regression. Thus, with catalyst HCl dosages of 0.010, 0.015, and 0.020 mol L⁻¹, the THFA-digested rice straw pulp exhibited cellulose dissolution reaction activation energies of 21.4, 38.5, and 20.7 kJ mol⁻¹, respectively. The catalyst dosage of 0.020 mol L⁻¹ exhibited the lowest phase II activation energy.

In comparison with the K_c values corresponding to the three HCl concentrations used, the cellulose dissolution rates in Equation 1 were expected to change with variations in [HCl]. In this case, the slopes (S) of the straight lines in Fig. 3 and Table 1 could be used to calculate the independent reaction rates K_c , through the application of the following equation:

$$S = K_c[\text{HCl}] \quad (7)$$

The S values are plotted against [HCl]. The slopes of these straight lines should depend on temperature and reflect K_c .

Table 1. Rate Constants of Cellulose (K_C) and Hemicellulose (K_H) Dissolution for THFA/HCl Pulping of Rice Straw

Phase	HCl (mol L ⁻¹)	Temp. (°C)	Cellulose (C)			Hemicellulose (H)				
			Time ¹⁾			K_C ²⁾ (min ⁻¹)	Time			K_H ³⁾ (min ⁻¹)
			t_0	t_1	t_2		t_0	t_1	t_2	
Phase I	0.01	110	0	240	1.8×10^{-4}	0	270	3.8×10^{-3}		
		120	0	240	1.9×10^{-4}	0	240	4.2×10^{-3}		
		130	0	210	2.0×10^{-4}	0	240	4.7×10^{-3}		
		140	0	210	2.1×10^{-4}	0	210	5.1×10^{-3}		
	0.015	110	0	240	2.9×10^{-4}	0	240	4.3×10^{-3}		
		120	0	210	3.0×10^{-4}	0	210	4.8×10^{-3}		
		130	0	210	3.1×10^{-4}	0	210	5.8×10^{-3}		
		140	0	210	3.2×10^{-4}	0	180	7.2×10^{-3}		
	0.02	110	0	240	3.8×10^{-4}	0	210	5.5×10^{-3}		
		120	0	210	4.0×10^{-4}	0	180	6.5×10^{-3}		
		130	0	120	1.1×10^{-3}	0	150	1.6×10^{-2}		
		140	0	120	1.6×10^{-3}	0	150	1.8×10^{-2}		
Phase II	0.01	110	240	300	1.7×10^{-3}	270	300	1.4×10^{-3}		
		120	240	300	2.4×10^{-3}	240	300	2.4×10^{-3}		
		130	210	300	2.5×10^{-3}	240	300	2.5×10^{-3}		
		140	210	300	2.9×10^{-3}	210	300	3.0×10^{-3}		
	0.015	110	240	300	1.9×10^{-3}	240	300	1.6×10^{-3}		
		120	210	300	3.2×10^{-3}	210	300	2.8×10^{-3}		
		130	210	300	3.4×10^{-3}	210	300	3.0×10^{-3}		
		140	210	300	5.0×10^{-3}	180	300	3.2×10^{-3}		
	0.02	110	240	300	3.9×10^{-3}	210	300	1.8×10^{-3}		
		120	210	300	4.7×10^{-3}	180	300	3.3×10^{-3}		
		130	120	240	5.5×10^{-3}	150	240	5.5×10^{-3}		
		140	120	210	6.3×10^{-3}	150	210	7.1×10^{-3}		

¹⁾ 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 phase II pulping

t_2 , Elapsed time (min) to the termination of phase II pulping

²⁾ K_C , Rate constants of cellulose dissolution

³⁾ K_H , Rate constants of hemicellulose dissolution

When the natural logarithm of the calculated K_c was plotted against $1/RT$ and the slope of the resulting linear regression taken, a reaction activation energy of 61.2 kJ mol^{-1} for this phase was found. Its intercept was the frequency factor in the logarithm, which equals 4.24×10^6 . Thus, the phase I kinetic equation was,

$$-dC_1/dt = 4.24 \times 10^6 \times e^{61.2/RT} \times [\text{HCl}] \times C_{01} \quad (8)$$

where C_{01} is the cellulose content at initial of phase I.

As for the activation energy of phase II cellulose dissolution reaction, in accordance with Eqs. 1 and 3 to 7, a 24.6 kJ mol^{-1} value was obtained; its frequency factor was found to be 4.38×10^2 . The overall phase I cellulose dissolution kinetic equation became,

$$-dC_2/dt = 4.38 \times 10^2 \times e^{24.6/RT} \times [\text{HCl}] \times C_{02} \quad (9)$$

where C_{02} is the initial cellulose content in phase II.

Reaction kinetics of hemicellulose dissolution

As noted above, the dissolution of hemicellulose in a THFA/HCl digestion process can also be distinguished as two separate phases. Dissolution of hemicellulose during THFA/HCl pulping tended to increase with increasing HCl concentration and cooking temperature. The phase I dissolution was always faster than during phase II. This indicated that in the initial stage, acid hydrolysis tended to increase hemicellulose dissolution, while in the phase II reaction, the trend of reaction rate constant was the same as phase I. In other words, it was related to catalyst concentration and cooking temperature.

As for the activation energies of hemicellulose dissolution during phases I and II, the values were 52.5 and 54.8 kJ mol^{-1} , respectively. The logarithmic intercepts as the frequency factors were 4.12×10^6 and 3.33×10^6 , respectively. The phase I and II reaction kinetic equations were as follows:

$$\text{phase I : } -dH_1/dt = 4.12 \times 10^6 \times e^{52.5/RT} \times [\text{HCl}] \times H_{01} \quad (10)$$

$$\text{phase II : } -dH_2/dt = 3.33 \times 10^6 \times e^{54.8/RT} \times [\text{HCl}] \times H_{02} \quad (11)$$

where H_{01} is the initial hemicellulose content in phase I, and H_{02} is the initial hemicellulose content of phase II.

Analysis of Carbohydrate and Lignin Degradation During Pulping

Delignification of a typical THFA/HCl pulping system is shown in Fig. 4. When 9.7 mol L^{-1} of THFA with 0.020 mol L^{-1} HCl catalyst was used to digest rice straw, delignification mainly occurred during the first 120 min when cooking was conducted at 110 and 120 °C. At the higher cooking temperatures of 130 and 140 °C, delignification mostly occurred within the first 90 min. Therefore, delignification efficiency increased along with an extension of digestion time. For digestion at 140 °C for 90 min, the maximum delignification rate reached 87.1%.

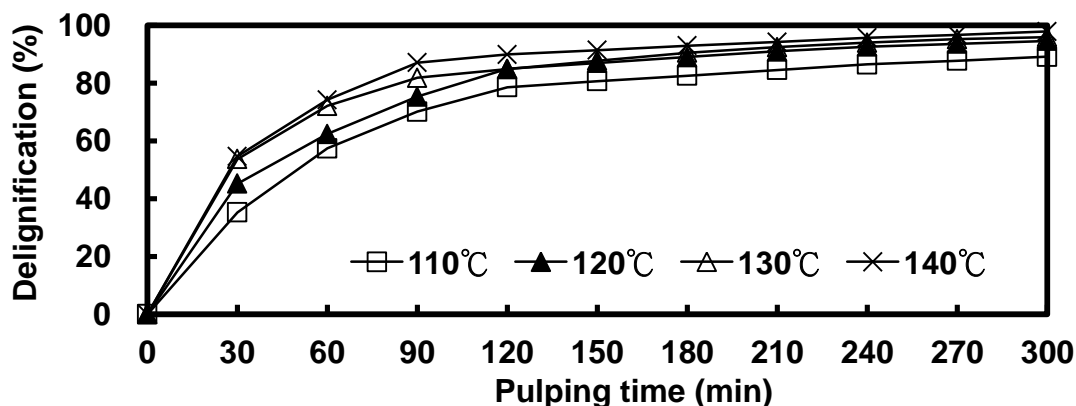


Fig. 4. Kinetics of tetrahydrofurfuryl alcohol delignification of rice straw

Note: The pulping conditions were THFA: 9.7 mol L^{-1} , liquor-to-solids ratio: $10 \text{ (L kg}^{-1}\text{)}$, pulping time: 0 ~ 300 min, pulping temperature: $110 \text{ }^\circ\text{C}$, $120 \text{ }^\circ\text{C}$, $130 \text{ }^\circ\text{C}$, $140 \text{ }^\circ\text{C}$, HCl: 0.020 mol L^{-1}

To illustrate more fully the relationship of delignification reactions on the dissolution of carbohydrate fractions in the THFA/HCl pulping system for rice straw, both the hemicellulose-to-lignin ratio, H_L , which equals $H/L \times 10$ for the dissolved hemicellulose and lignin in liquor, and the corresponding C_L ratio were calculated. Figures 5 and 6 show the changes in the ratios over time. In Fig. 5, at cooking temperatures of 110 and $120 \text{ }^\circ\text{C}$, and 130 and $140 \text{ }^\circ\text{C}$, the value of H_L tended to increase within the intervals of 0 to 150 and 0 to 180 min, respectively. However, in the 180 to 300 min interval, the ratio flattened. The figure indicates that in the initial stage, hemicellulose dissolution increased with increasing time. In the latter stage, however, the H_L ratio only fluctuated due to the fact that most of the hemicellulose already had been dissolved. Also, the delignification of the THFA/HCl pulping gradually reached a maximum. Nevertheless, significant differences in H_L were apparent at different cooking temperatures.

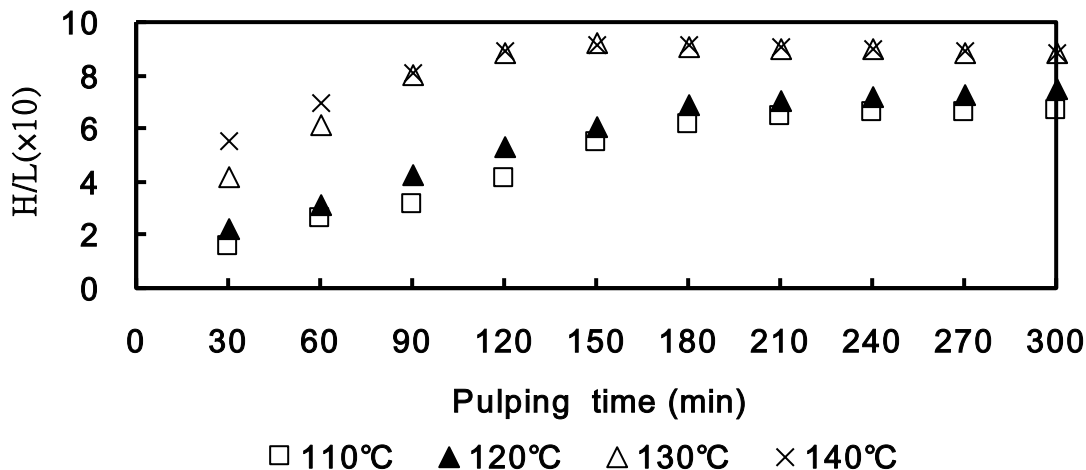


Fig. 5. Ratios of dissolved hemicellulose and lignin content during cooking

Note: 1. $H_L = H/L \times 10$; H : dissolved hemicellulose content (%); L : dissolved lignin content (%)

2. The pulping conditions were THFA: 9.7 mol L^{-1} , liquor-to-solids ratio: $10 \text{ (L kg}^{-1}\text{)}$, pulping time: 0 to 300 min, pulping temperature: $110 \text{ }^\circ\text{C}$, $120 \text{ }^\circ\text{C}$, $130 \text{ }^\circ\text{C}$, $140 \text{ }^\circ\text{C}$, HCl: 0.020 mol L^{-1}

In the initial stage, the H_L of cooking temperatures 130 and 140 °C were much greater than those obtained at 110 and 120 °C. The results indicated that at a higher temperature (≥ 130 °C), dissolution of hemicellulose was much faster than at a lower temperature (≤ 120 °C) in the initial stage. Thus, to prevent excessive dissolution of hemicellulose (which causes poor paper strength), low temperature digestion is recommended.

Figure 6 shows the relationship between rice straw cellulose dissolution, delignification rates, and cooking time in a THFA/HCl pulping system. Figure 6 shows that at cooking temperatures of 110 and 120 °C, the C_L ratios changed little in the initial stage (0 to 180 min), indicating a scarce amount of cellulose dissolution, with a comparably fair amount of residual lignin. In the latter stage (180 to 300 min), however, the C_L ratios gradually increased because after 180 min, the THFA/HCl pulping system's ability to remove lignin had peaked. Thus, the increase in C_L ratios indicated accelerating cellulose dissolution.

These conditions led to decreased pulp yield and compromised the mechanical strength of cellulosic polymer, causing poor paper strength. Furthermore, the C_L ratios of the liquor from cooking at 130 and 140 °C were much higher than those at lower cooking temperatures.

Deducing from the above results, in a THFA/HCl pulping system of rice straw, when using the liquor conditions of 9.7 mol L⁻¹ THFA and 0.020 mol L⁻¹ HCl catalyst, cooking temperatures higher than 130 °C can be expected to cause excessive dissolution of cellulose and hemicellulose, leading to low pulp yield and poor paper strength. However, when using a lower cooking temperature, though excessive dissolution of carbohydrate fractions could be prevented, the amount of residual lignin in pulp became a concern. In the following section, optimizing the digestion conditions for pulping with desirable properties is discussed.

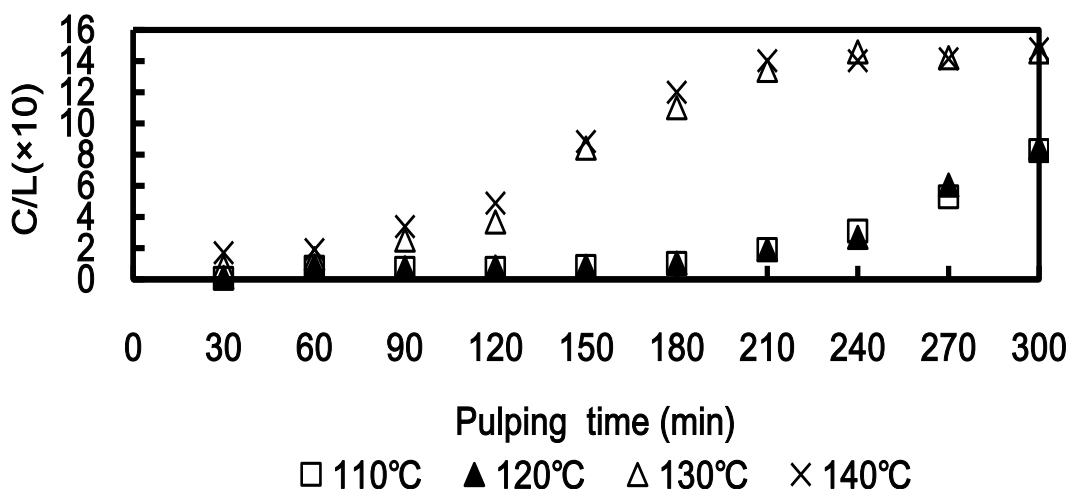


Fig. 6. Ratios of dissolved cellulose and lignin content during cooking

Note: 1. $C_L = C/L \times 10$; C: dissolved cellulose content (%); L: dissolved lignin content (%)

2. The pulping conditions were THFA: 9.7 mol L⁻¹, liquor-to-solids ratio: 10 (L kg⁻¹), pulping time: 0 ~ 300 min, pulping temperature: 110 °C, 120 °C, 130 °C, 140 °C, HCl: 0.020 mol L⁻¹

Optimizing the THFA/HCl Pulping Conditions

The main purpose for studying pulping kinetics is to enable the review of pulping engineering, to rationalize pulping process control, and to comprehend the optimal operational conditions. Thus, pulping can be conducted to achieve the objectives at low chemical charge, short digestion time, high pulp quality, and high yield, as demanded by economic and operational convenience (Wilson and Kerr 1976). Using the THFA/HCl pulping process, the optimal conditions required to produce bleachable grades (kappa numbers 20) for manufacturing liner boards (kappa numbers 40) and corrugated media (kappa numbers 60) are as follows:

Firstly, referring to Eq. 12, which was reported in previous research (Ho *et al.* 2011), to make pulps with kappa numbers 20, 40, and 60 (lignin content of 3.0%, 6.0%, and 9.0%), the required reaction times were calculated according to:

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

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 pseudo-initial lignin content of phase II, and t is the reaction time (min).

The time was then put into Eq. 8 to 11 to calculate the hemicellulose and cellulose contents at kappa numbers 20, 40, and 60. The results are shown in Fig. 7.

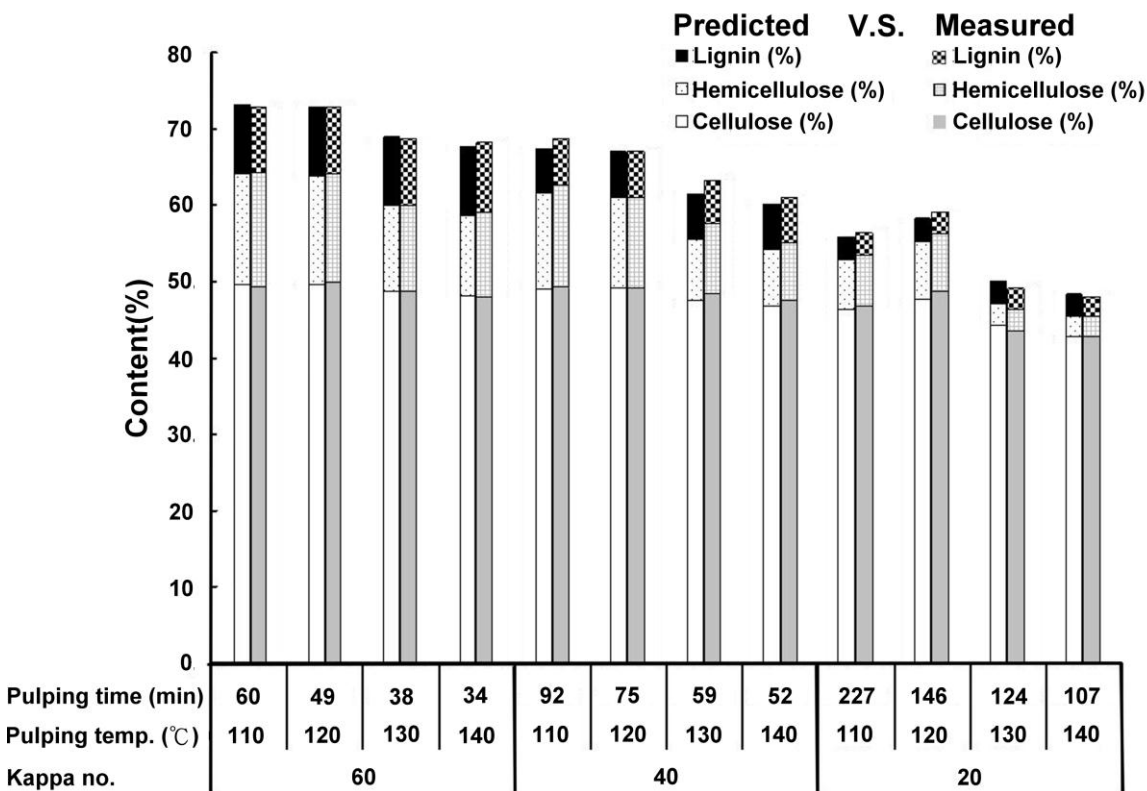


Fig. 7. Comparisons of the predicted and measured yields and composition of resulting pulps of THFA rice straw pulping

Note: Pulping conditions: THFA: 9.7 mol L⁻¹, HCl: 0.020 mol L⁻¹
Ash and extractive contents are not included.

The figure indicates that the time to reach target kappa numbers of 20, 40, and 60 became shorter as the cooking temperature increased. However, at higher temperatures (≥ 130 °C), the extent of cellulose, and particularly hemicellulose, dissolutions were also higher. When digestions were performed at lower temperatures (≤ 120 °C), at the corresponding kappa number, the dissolutions of hemicellulose and cellulose were much milder. Thus, to produce rice straw pulps of kappa numbers 40 and 60, using a THFA charge of 9.7 mol L^{-1} , an HCl catalyst dosage of 0.020 mol L^{-1} , and cooking temperature of 120 °C, the necessary cooking times were 75 and 49 min, respectively. If, however, a pulp with a kappa number of 20 is desired, then the necessary cooking time needed is 146 min, under the same conditions.

In addition, to compare the measurement results with the calculated time requirements, digestions were conducted for the above times. The measured lignin, cellulose, and hemicellulose contents of the resulting pulps were compared with the predicted values. The results are shown in Fig. 8. In particular, the two sets of values match closely ($R^2 > 0.99$). Therefore, this work claims that the derived equations reflect the actual results and can be used to control THFA/HCl pulping processes.

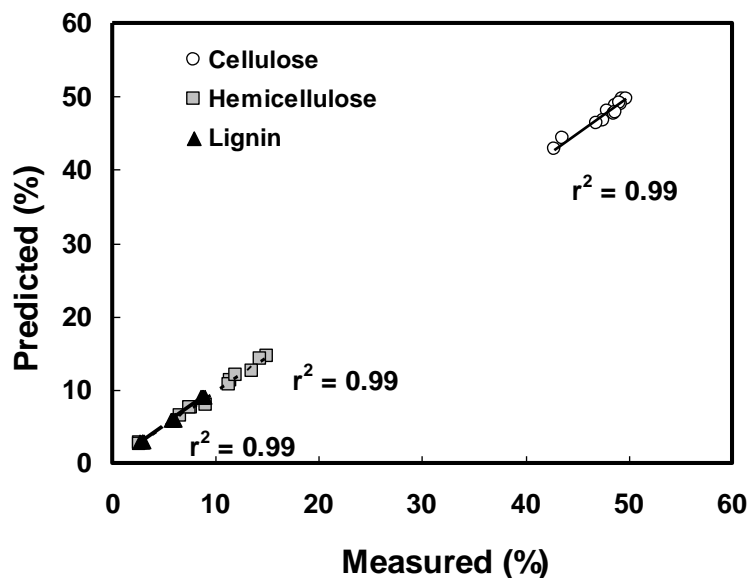


Fig. 8. A comparison of measured and predicted data on chemical composition of resulting pulps at kappa numbers 20, 40, 60 from THFA pulping
 Note: Pulping conditions: THFA: 9.7 mol L^{-1} , HCl: 0.020 mol L^{-1}
 Pulping temp. and pulping time are as shown in Fig. 7.

CONCLUSIONS

1. The dissolutions of rice straw cellulose and hemicellulose during THFA/HCl pulping were separated into two phases. Hemicellulose dissolved rapidly at the initial stage of pulping, while cellulose dissolution was initially slow but increased at a later stage.
2. In the phase I dissolution reaction of cellulose, a scarce amount of cellulose was removed. In phase II, when delignification reached a level of 85 to 90%, cellulose dissolution tended to increase. The activation energy for phase II was 24.6 kJ mol^{-1} ; and the frequency factor was 4.38×10^2 .

3. The dissolution of hemicellulose also increased with increasing temperature and catalyst concentration. The dissolution rate in phase I was faster than in phase II. The activation energies for phase I and II were 52.5 and 54.8 kJ mol⁻¹, respectively; frequency factors were 4.12 x 10⁶ and 3.33 x 10⁶, respectively.
4. In addition, from analysis of the relationship between delignification and carbohydrate dissolution in a THFA/HCl pulp system, it was found that at cooking temperatures exceeding 130 °C, excessive dissolution of cellulose and hemicellulose tended to occur, causing reductions in pulp yield and paper strength.
5. To produce bleachable, liner, and corrugated media grade pulps, kinetic equations at a particular temperature could provide the time requirement for reaching kappa numbers 20, 40, and 60. Hence, a THFA charge of 9.7 mol L⁻¹, HCl of 0.020 mol L⁻¹, cooking temperature of 120 °C, and optimal cooking times of 146, 75, and 49 min, respectively, are required to reach the target kappa numbers. Actual cooking was conducted, verifying the above conditions. Hence, the derived equations are deemed suitable for use as a basis for process control.
6. The derived equations are deemed suitable for use as a basis for process control.

REFERENCES CITED

- Aaltonen, O., Johansson, A., and Ylinen, P. (1990). "Organosolv pulping: Softwood delignification kinetics and selectivity in THFA HCl-pulping," *Wood Processing and Utilization*, J. F. Kennedy, G. O. Phillips, and P. A. Williams (eds.), Ellis-Horwood, Chichester, U.K., 62-68.
- Abatzoglou, N., Chornet, E., and Belkacemi, K. (1992). "Phenomenological kinetics of complex systems: The development of a generalized severity parameter and its application to ligno cellulose fractionation," *Chem. Eng. Sci.* 47, 1109- 1122.
- Abdul-Karim, L., Rab, A., and Polyanszky, E. (1995). "Kinetics of delignification in kraft pulping of wheat straw and hemp," *Tappi J.* 78 (8), 161-164.
- Basedow, A. M., Ebert, K. H., and Ederer, H. J. (1978). "Kinetic studies on the acid hydrolysis of dextran," *Macromolecules* 11, 774-781.
- Bhardwaj, N. K., Goyal, S. K., Gupta, A., Upadhyaya, J. S., and Ray, A. K. (2005). "Soda and soda- anthraquin -one pulping of rice straw," *Appita J.* 58(3), 180-185.
- Bogomolov, B. D., Groshev, A. S., Popova, G. I., and Vishnyakova, A. (1979a). "Wood delignification with tetrahydrofurfuryl alcohol. Comparison of delignification capacity of tetrahydrofurfuryl alcohol and other organic solvents," *Khim. Drev.* 4, 21-24.
- Bogomolov, B. D., Groshev, A. S., Popova, G. I., and Vishnyakova, A. P. (1979b). "Wood delignification with tetrahydrofurfuryl alcohol. Delignification of birchwood," *Khim. Drev. (Riga)* 6, 43-46.
- Bogomolov, B. D., Groshev, A. S., Popova, G. I., and Vishnyakova, A. P. (1979c). "Method of delignifying lignocellulosic materials," USSR Patent 672.260.
- Bustos, G., Ramrez, J. A., and Garrote, G. (2003). "Modeling of the hydrolysis of sugarcane vavase with hydrochloric acid," *Appl. Biochem. Biot.* 104, 51- 68.
- Camacho, F., Gonzalez-Tello, P., and Jurado, E. (1996). "Microcrystalline-cellulose hydrolysis with concentrated sulphuric acid," *J. Chem. Technol. Biot.* 67, 350- 356.
- Gonzalo, E., Lindgren, C., and Lindstrom, M. (1998) "Kinetics of wheat straw

- delignification in soda and kraft pulping,” *J. Wood Chem. Technol.* 18, 69-82.
- Hammett, A. L., Youngs, R. L., Sun, X. F., and Chandra, M. (2001) “Nonwood fiber as an alternative to wood fiber in China pulp and paper industry,” *Holzforschung* 55, 219-224.
- Hergert, H. L. (1998). “Developments in Organosolv Pulping,” *Environmentally Friendly Technologies for the Pulp and Paper Industry*, R. A. Young, and M. Akhtar (eds.), John Wiley & Sons, New York, U.S.A., 5-68.
- Ho, C. L., Wang, E. I. C., and Su, Y. C. (2009). “Tetrahydrofurfuryl alcohol (THFA) pulping of rice straw,” *J. Wood Chem. Technol.* 29, 101-118.
- Ho, C. L., Wu, K. T., Wang, E. I. C., and Su, Y. C. (2011). “Delignification kinetics study on the tetrahydrofurfuryl alcohol (THFA)/HCl pulping of rice straw,” *Ind. Eng. Chem. Res.* 50, 3849-3857.
- Huang, G. X., Shi, J., and Langrish, T. (2007). “NH₄OH-KOH pulping mechanisms and kinetics of rice straw,” *Bioresour. Technol.* 98, 1218-1223.
- Huang, G., and Shi, Y. (1986). “Studies on the mechanism and the kinetics of rice straw pulping,” *China Pulp Pap.* 5(3), 35-40.
- Johansson, A., Ebeling, K., Aaltonen, O., Aaltonen, P., and Ylinen, P. (1987). “Wood pulping with aqueous tetrahydrofurfuryl alcohol,” *Paperi ja Puu* 69, 500-504.
- Lavarack, B. P., Griffin, G. J., and Rodman, D. (2002). “The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products,” *Biomass Bioenerg.* 23, 367- 380.
- Malester, I. A., Green, M., and Shelef, G. (1992). “Kinetics of dilute acid hydrolysis of cellulose originating from municipal solid wastes,” *Ind. Eng. Chem. Res.* 31, 1998-2003.
- Maloney, M. T., Chapman, T. W., and Baker, A. J. (1985). “Dilute acid hydrolysis of paper birch: Kinetic study of xylan and acetyl- group hydrolysis,” *Biotechnol. Bioeng.* 27, 355-361.
- McParland, J. J., and Grethlein, H. E. (1982). “Converse kinetics of acid hydrolysis of corn stover,” *Sol. Energy* 28, 55-63.
- Mok, W. S. L., Antal, M. J., and Varhegyi, G. (1992). “Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose,” *Ind. Eng. Chem. Res.* 31, 94-100.
- Parajo, J. C., Alonso, J. L., and Santos, V. (1995). “Kinetics of catalyzed organosolv processing of pine wood,” *Ind. Eng. Chem. Res.* 34, 4333-4342.
- Rodriguez, A., Moral, A., Serrano, L., Labidi, J., and Jimenez, L. (2008) “Rice straw pulp obtained by using various methods,” *Bioresour. Technol.* 99, 2881-2886.
- Saeman, J. F. (1945). “Kinetics of wood saccharification. Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature,” *Ind. Eng. Chem. Res.* 37, 43-52.
- Tu, Q., Fu, S., Zhan, H., Chai, X., and Lucia, L. A. (2008). “Kinetic modeling of formic acid pulping of bagasse,” *J. Agric. Food Chem.* 56, 3097-3101.
- Wilson, C. A., and Kerr, A. J. (1976). “The kinetics of kraft pulping - Industrial evaluation of a proposed batch digester control method,” *Appita J.* 30, 55-58.
- Xu, C., Pranovich, A., Vähäsalo, L., Hemming, J., Holmbom, B., Schols, H. A., and Willför, S. (2008). “Kinetics of acid hydrolysis of water-soluble spruce o-acetyl galactoglucomannans,” *J. Agric. Food Chem.* 56, 2429-2435.

- Yaser, Z. S., Jamshid, M. R., Pejman, R. C., and Bagher Khajeheian, M. (2007). "Study on cellulose degradation during organosolv delignification of wheat straw and evaluation of pulp properties," *Iranian Polymer J.* 16(2), 83-96.
- Zhai, H. M., and Lee, Z. Z. (1989). "Ultrastructure and topochemistry of delignification in alkaline pulping of wheat straw," *J. Wood Chem. Technol.* 9, 387-406.

Article submitted: Aug. 6, 2012; Peer review completed: Sept. 4, 2012; Revised version received: Sept. 24, 2012; Accepted: Oct. 11, 2012; Published: October 16, 2012.