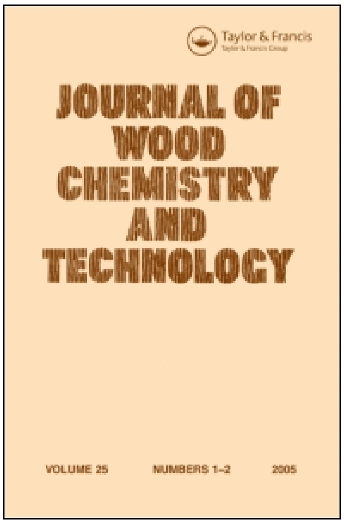

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ISOTHERMAL REACTION KINETICS OF KRAFT DELIGNIFICATION OF DOUGLAS-FIR

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ABSTRACT

Kraft delignification of Douglas-fir (*Pseudotsuga menziesii*) wood meal was carried out under an instantaneous isothermal condition with a liquor-to-wood ratio of 50 to investigate the effects of reaction temperature and chemical concentration on the rate of delignification. The temperatures studied were in the range of 120 to 175°C. Three levels of [HO^-] and three levels of [HS^-] concentrations were investigated. In each case an efficient mechanical agitation of the pulping liquor was maintained and the delignification was extended to reach its completion. Using a nonlinear regression analysis on the delignification results, a single kinetics equation was resolved to describe the effect of temperature and chemical concentration on the rates of delignification for the initial, bulk, and final phases. This equation also revealed that the amounts of lignin removed due to the chemical reactions in the initial, bulk, and final phases were 18.8, 71.4, and 3.8%, respectively. About 6% of the total lignin was dissolved into the pulping solution before any significant chemical reaction occurred to the lignin core. The activation energies of delignification reactions in the initial, bulk, and final phases were 85.8, 123.8, and 110.0 kJ/mole, respectively. The Ln(pre-exponential factors) were 22.5, 30.5, and 23.4 m^{-1} for the initial, bulk, and final phases, respectively. The rate of delignification was strongly affected by the presence of [HO^-] in the bulk and final phases. Whereas, [HS^-] had a significant effect on the rate of delignification only in the bulk phase. These chemical effects were also quantified.

INTRODUCTION

Voluminous studies on the kinetics of kraft delignification have provided us a composite concept which proposes that the kraft delignification proceeds with initial, bulk, and final (or residual) phases. Traditionally, kinetic studies of the delignification reaction have been carried out separately for these three phases. The current investigation takes a different approach in which the delignification is carried out from its onset till the completion to cover the entire process within a wide range of temperatures (120 to 175°C). Unlike most pulping kinetic studies, the current delignification kinetics experiments are done under an instantaneous isothermal condition. Other reaction conditions are also selected to simulate as closely as possible a homogeneous reaction. Based on this study, an overall delignification kinetics equation is resolved to quantitatively illustrate the effects of temperature and chemical concentrations on the rate of delignification for the initial, bulk, and final phases.

MATERIALS AND METHODS

Air-dried Douglas-fir (*Pseudotsuga menziesii*) wood chips, provided by the Weyerhaeuser Paper Company, were ground to wood meal (pass 60 mesh) which was then extracted with benzene-ethanol (2:1 by volume) for 48 hours to remove extractives. To study the temperature effect, the pulping liquor with an effective alkali of 45 g NaOH/L and a sulfidity of 30% was used. The kinetic runs were done at 120, 140, 150, 160, and 175°C with a liquor-to-wood ratio of 50. To investigate the effect of chemical concentration, the kinetic runs were carried out at 120 and 170°C with three levels of $[HO^-]$ concentrations at 1.61, 1.13, and 0.81 M while maintaining the $[HS^-]$ concentration constant at 0.23 M and three levels of $[HS^-]$ concentrations at 0.15, 0.32, and 0.51 M while maintaining the $[HO^-]$ concentration constant at 1.45 M. A liquor-to-wood ratio of 50 was used.

The delignification reaction was carried out in a specially designed stainless steel autoclave (350 mL in volume). A set of two autoclaves (B1 and B2) were coupled as shown in Figure 1. B1 contained a proper amount of pulping liquor and B2 contained the wood meal (K) in a thick-walled Teflon beaker (J) in which a few stainless steel balls (L) were added. B1 was then sealed and heated in a aluminium block (A) pre-heated to the selected temperature. When the temperature of the pulping liquor in B1 reached the selected temperature, measured by a thermocouple (F), and B2 was vacuumed and sealed, B1 and B2 were connected with a flexible stainless steel tube (I) through the quick-connects (D) attached to the autoclaves. After B2 was also put into the heating block for about 5 minutes, the hot pulping liquor in B1 was pumped by N_2 gas into B2 through the on-off ball valves (E) which were shut off after the liquor had been transferred. In this way, the hot liquor can be completely transferred and an isothermal environment in B2 can be reached within 5 seconds. After this, the delignification reaction was then carried out at the selected temperature in autoclave B2 which was constantly rocked at a 110° rocking angle. The stainless steel balls were used to aid the agitation to the pulping solution and wood meal. The Teflon beaker in B2 was used to protect the wood meal from being burned during the 5-minute heat-up period.

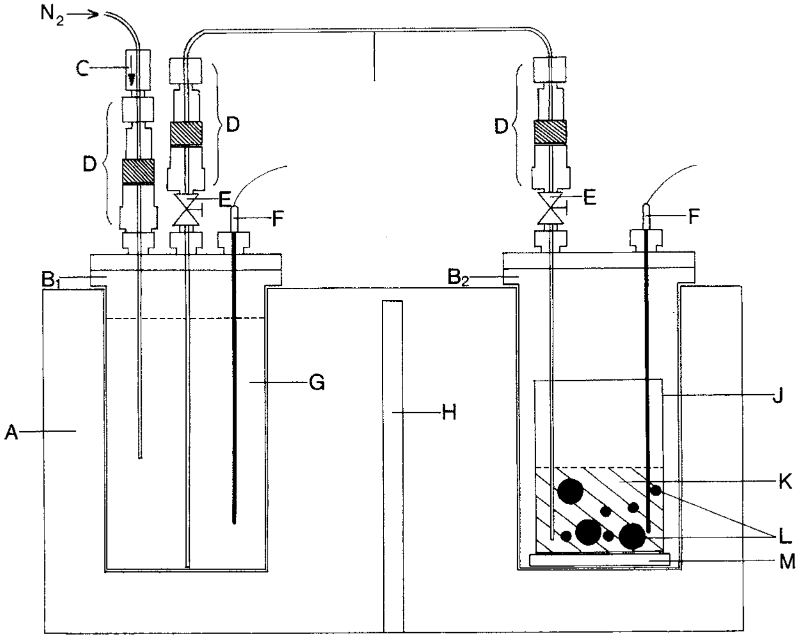

FIGURE 1. Apparatus for isothermal delignification kinetics study. (A): heating aluminium block, (B1 and B2): stainless steel autoclaves, (C): back pressure valve, (D): quick-connects, (E): on-off valves, (F): thermocouples, (G): pre-heated pulping liquor, (H): cartridge heater, (I): flexible stainless steel tube, (J): thick-walled Teflon beaker, (K): wood meal, (L): stainless steel balls, and (M): Teflon sheet.

At the selected time, the delignification was terminated by quenching the autoclave in ice water. The wood meal was washed with water repeatedly under vacuum until the washing became neutral and then air dried. The Klason plus acid soluble and acetyl bromide lignin contents of the delignified wood meal were determined according to Chiang and Funaoka.[1]

RESULTS AND DISCUSSION

It is known that the wood pulping process is a heterogeneous reaction. Consequently, a true reaction kinetics of a pulping process is almost impossible to obtain. For this reason and due to the inconsistent pulping conditions, the published kinetics data do not exactly agree with each other even for an identical wood species. In order to approach as closely as possible the true reaction kinetics, kinetic runs in this study were carried out using wood meal as the raw material under an instantaneous isothermal condition with a high liquor-to-wood ratio (50) and an efficient mechanical agitation of the reaction mixtures.

In addition to the well known effect of the particle size of wood on the liquor penetration,[2,3] the mechanical agitation of the reaction mixtures was found to be another important factor affecting the extent of delignification. Several means of mechanical agitation have been tried using the pulping apparatus described in the MATERIALS AND METHODS section. These included rocking at a 60° angle, rocking at a 60° angle with stainless steel balls inside of the autoclave, and rocking at a 110° angle with stainless steel balls. The results were compared with the results of using a commercially available Parr reactor which had an internal propeller driven at a speed of 700 rpm to provide a vigorous mechanical agitation to the pulping contents. As shown in Table 1 and by comparing pulping experiments 1, 2, 3, and 4, it was obvious that a nearly identical extent of delignification could be obtained with a mechanical agitation provided by either a combination of rocking (60 °) plus stainless steel balls (experiment #3) or by the stirring action of the Parr reactor (#4) (+ signs: with; - signs: without). Delignification in these two systems was better than in the cases of rocking without stainless steel balls (# 2) and no agitation (# 1). Of course, using wood meal (pass a 60 mesh screen) was more suitable than using pin chips (#5 and 6) for the kinetics study.

Based on the pulping results (#1, 2, 3, and 4), it seemed that the mechanical agitation provided in our pulping apparatus was as efficient as that in the Parr reactor. However, these experiments were done at a low temperature (80°C). When pulping was done at a higher temperature (150 °C), the combination of rocking at a 60 angle plus stainless steel balls became less efficient for the delignification reaction as compared to the stirring action provided by the Parr reactor. This can be clearly seen by comparing experiments 7 and 8 or 9 in Table 1 (8 and 9 are duplicate). Apparently, rocking at a 60° angle only provided a mild agitation which caused a localized movement of stainless steel balls and wood meal, generating a gradient of the alkalinity in the pulping liquor. This chemical concentration gradient might also be caused by the high liquor to wood ratio. To eliminate this concentration gradient, the rocking of the autoclave should pass the horizontal level to ensure a free movement of the stainless steel balls and wood meal. To meet such a requirement, the rocking angle was changed to 110° and the pulping results obtained using this new system (#10 and 11, duplicate) were again almost identical to that obtained by using a Parr reactor (#8 and 9). Based on these screening experiments, it can be stated that a vigorous agitation of the reactor contents must be maintained during the reaction to obtain reliable kinetic data. This is specially true when pulping runs are carried out at elevated temperatures.

TABLE 1

The Effect of Mechanical Agitation on the Extent of Kraft Delignification of Douglas-Fir.

Experiment #	1	2	3	4	5	6	7	8	9	10	11
Sample type	meal	meal	meal	meal	pin chips	pin chips	meal	meal	meal	meal	meal
Time (hr)	2	2	2	2	2	2	1.5	1.5	1.5	1.5	1.5
Temperature (°C)	80	80	80	80	80	80	150	150	150	150	150
Rocking (60°)	-	+	+	-	-	+	+	-	-	-	-
Rocking (110°)	-	-	-	-	-	-	-	-	-	+	+
S.S. balls	-	-	+	-	-	-	+	-	-	+	+
Parr reactor	-	-	-	+	-	-	-	+	+	-	-
Pulp yield (% of OD wood)	89.98	89.69	88.73	88.24	92.24	91.25	69.25	57.18	58.68	57.45	56.70
Lignin dissolved (% of total lignin)	7.63	8.76	10.09	10.54	4.83	6.55	64.15	69.25	69.48	70.42	70.30

The use of a high liquor-to-wood ratio for the delignification reaction in this study was chosen to maintain a constant concentration of the reaction chemicals. This was confirmed by checking the concentration of effective alkali before and after the delignification reaction. Consequently, the system used in this study (a) minimizes the concentration change of the pulping chemicals, (b) eliminates the problem of concentration gradient of the pulping liquor, (c) ensures an isothermal environment for the delignification instantaneously, and (d) minimizes the liquor penetration problem.

Based on a previous study on the delignification of western hemlock, it was shown that 7% of the total lignin could be extracted by 1 N NaOH at room temperature.[4] Similarly, a maximum of about 6% of the lignin could be extracted by the kraft pulping liquor at room temperature after 48 hours using the conditions described in the MATERIALS AND METHODS , as shown in Fig. 2. The removal of 6% lignin at room temperature was probably caused by chemical reactions such as phenolic α-ether hydrolysis. In this study, this 6% lignin was not considered as a part of the lignin core that responded to the chemical reactions at elevated temperatures.

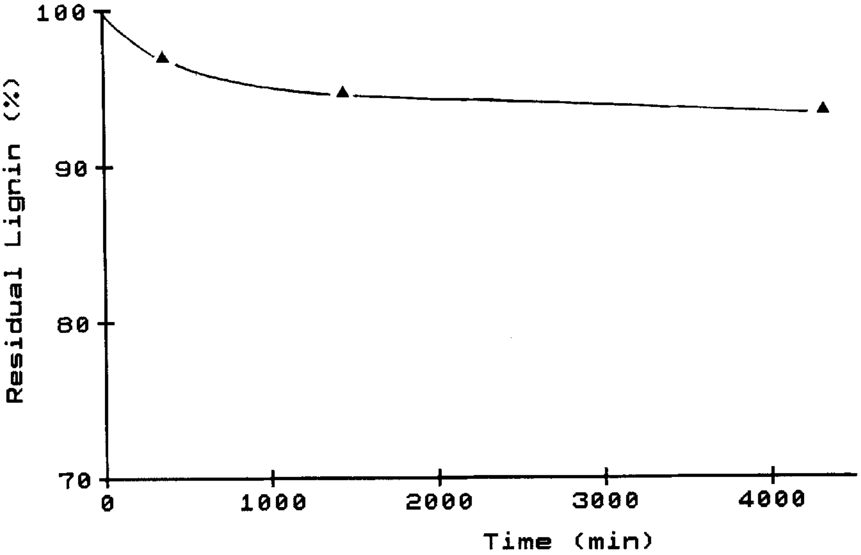

FIGURE 2. Delignification of Douglas-fir wood meal at room temperature.

Effect of Temperature on the Rate of Kraft Delignification Reaction

When kinetic runs were done at the selected temperatures, it became clear that the delignification at each temperature was a continuous reaction, as indicated by the smooth curves shown in Figure 3. Generally, kraft delignification has been considered to proceed in three separate stages--initial, bulk, and final phases. In each phase, the delignification is of apparent first order with respect to the lignin content of the wood.[5,6,7] The first-order rate equations for these three reaction phases can be expressed as:

$$L_{ri} = L_i \exp(-k_i\, t) \qquad (1)$$

$$L_{rb} = L_b \exp(-k_b\, t) \qquad (2)$$

$$L_{rf} = L_f \exp(-k_f\, t) \qquad (3)$$

In these equations, L_{ri}, L_{rb}, and L_{rf} represent the amounts of residual lignins left in the delignified wood at time t in the initial (i), bulk (b), and final (f) phases, respectively. L_i, L_b, L_f are the original amounts of the lignins to be dissolved in the initial, bulk, and final phases, providing that these values are independent of temperature and hydroxyl ion concentration. The reaction rate constants for these three phases are k_i, k_b, and k_f.

Consequently, based on these equations, the three reaction phases would resolve to three intercepting straight lines in a semi-logarithmic rate plot of log(residual lignin content) vs. reaction time. The slopes of these three straight lines thus represent the delignification rate constants for the corresponding phases. Traditionally, such a plot is also used as a norm in estimating the amounts of lignins that can be removed in each phase by "extrapolating" the straight lines (usually made out of 3 or 4 data points)[8,9] to time zero. With a sufficient amount of data points at each temperature studied, such a semi-logarithmic plot, as shown in Figure 4, indicates that the kraft delignification reaction cannot be resolved unambiguously to three intercepting straight lines. Nevertheless, for each temperature, three intercepting straight lines could be forced to form. Then the formation of three intercepting straight lines becomes arbitrary, depending upon the choice of the transition point from one phase (straight line) to the next. This would also affect the extrapolated values at time zero and most likely constitutes one of the important factors that contribute to the inconsistency of the published results on delignification kinetics.

Instead of using the semi-logarithmic rate plot to pinpoint the transition points from initial phase to bulk phase and from bulk phase to final phase, and to illustrate the

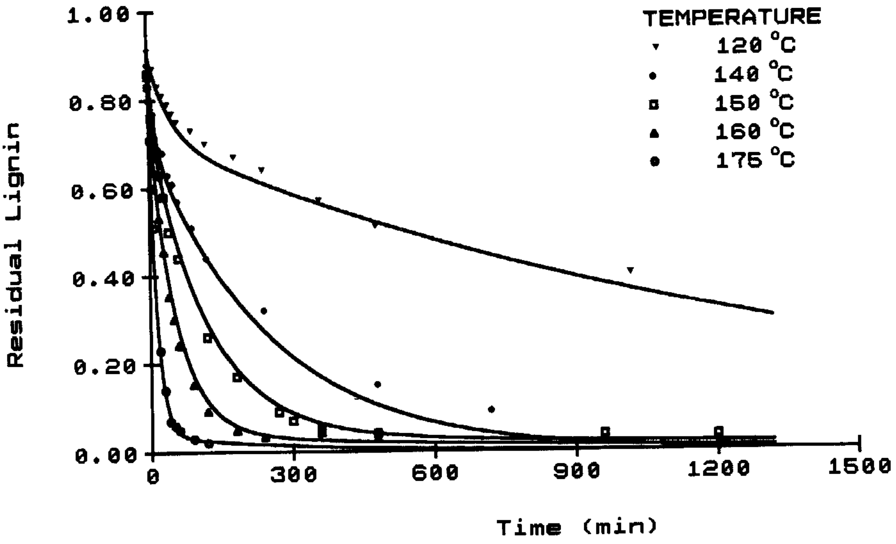

FIGURE 3. Lignin removal as a function of time.

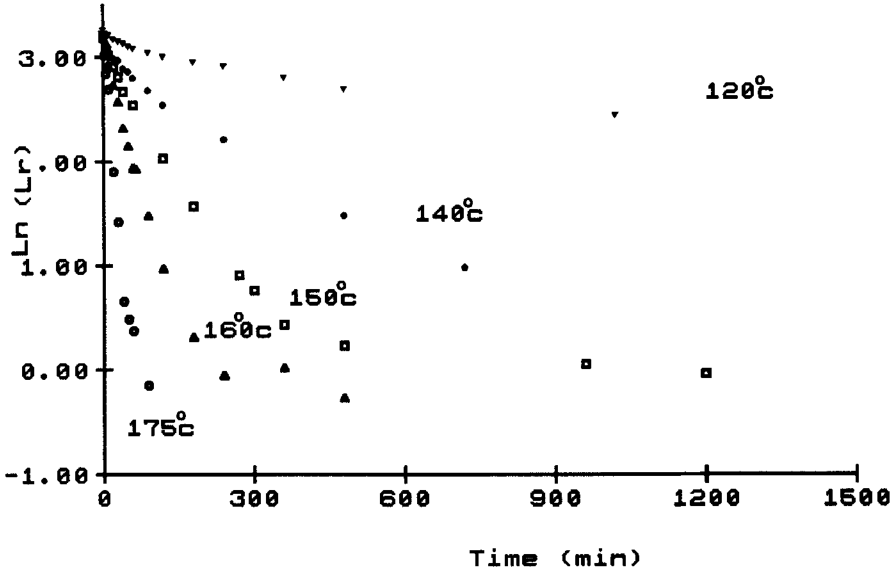

FIGURE 4. Semi-logarithmic rate plot.

delignification kinetics for these three phases separately, Equations 1, 2, and 3 can actually be combined into one equation, Equation 4, to describe the entire delignification process.

$$L_{ri} + L_{rb} + L_{rf}$$

$$= L_r = L_i \exp(-k_i\, t) + L_b \exp(-k_b\, t) + L_f \exp(-k_f\, t) \qquad (4)$$

L_r is the total residual lignin left at time t. The parameters, L_i, L_b, L_f, k_i, k_b, and k_f, in this equation can be obtained by fitting the data points in Figure 3 into this mathematical model using a nonlinear regression routine of the SAS program (SAS Institute Inc., Cary NC, USA). In Figure 3, the points are the actual experimental data and the curves are generated according to Equation 4 using the SAS program. Using this statistical approach, rate constants for the initial, bulk, and final delignification reactions carried out at different temperatures were obtained, as shown in Table 2.

Based on Equation 4, the amount of lignin that can be removed in each phase can also be obtained statistically instead of using the "extrapolating" technique. These values are shown in Table 3. According to the rate constants (Table 2) and to the Arrhenius plot (Figure 5), the pre-exponential factors, A_i, A_b, and A_f, and the activation energies Ea_i, Ea_b, and Ea_f for the three phases of delignification reactions were calculated and are shown in Table 3.

Table 2.

Delignification Rate Constants.

T	k_i	k_b	k_f
(°C)	(	m^{-1}	)
120	0.022	0.00066	
140	0.092	0.0040	
150	0.160	0.0085	0.00061
160	0.240	0.018	0.0012
175		0.067	0.0034

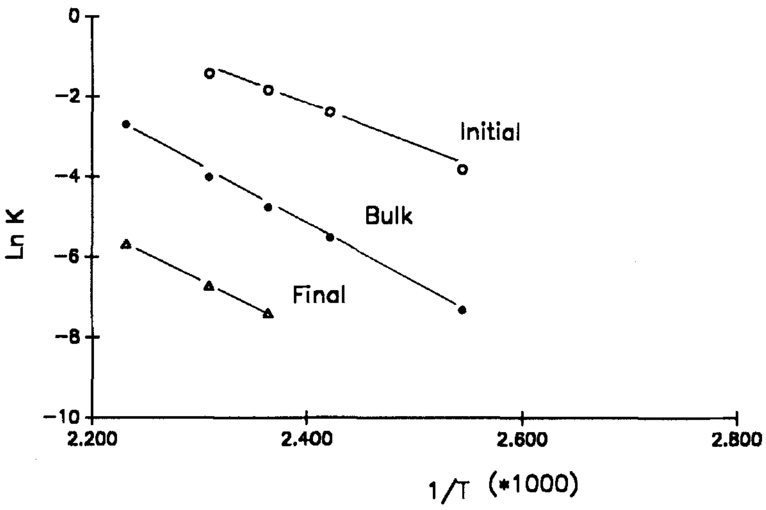

FIGURE 5. Arrhenius plot.

Table 3.

The Values of the Parameters in Equation 4.

	L (%of total lignin)	Ea (kJ/mole)	A (m^{-1})
i	18.8	85.8	5.91×10^{9}
b	71.4	123.8	1.76×10^{13}
f	3.8	110.0	1.45×10^{10}

Since the amount of lignin that was immediately dissolved in the kraft pulping liquor was 6% for Douglas-fir (Figure 2), the total amount of lignin which could be removed during the initial phase was actually 24.8%. This value is in excellent agreement with the value of 24% obtained by Kondo and Sarkanen[7] and of 23% obtained by Wilder and Daleski.[3] Over 70% of the lignin was removed during the bulk phase delignification. About 4% of the lignin left after the bulk delignification phase. It was observed that, under a constant hydroxyl and hydrosulfide ion concentration, L_i and L_b were independent of temperature. However, the L_f value of 4% was essentially independent of the temperature only when the temperatures were higher than 150 °C. This can be clearly seen in Figure 3. Consequently, only the data obtained for reaction temperatures higher than 150 °C were used to investigate the reaction kinetics of the final phase delignification (see Table 2). Under such a consideration, the term of $[L_f \exp(-k_f t)]$ in the general equation 4 is valid and the values of k_f (Table 2) and the value of Ea_f (Table 3) are reliable. This 4% lignin was highly condensed.[1,10] The removal of this type of condensed lignin in the final phase proceeded rather slowly at rates that were between 15 to 20 times slower than the bulk delignification in the temperature range of 150 to 175 °C.

According to Gierer[11] and Ljunggren[12] the cleavage of phenolic α-aryl ether linkages in lignin dominates the initial phase of delignification and has an activation energy of 78 kJ/mole based on model compound studies.[12] Based on the current study, the activation energy of the initial phase delignification, 85.8 kJ/mole, was slightly higher than the value of 78 kJ/mole. The value of 78 kJ/mole was obtained based on the model compounds which had only one type of α-aryl ether linkage. Whereas, in the initial phase of wood pulping, the cleavage of this type of ether linkage was the main reaction and with probably some minor reactions in cleaving phenolic β-aryl ether linkages in the later stage of the initial phase. The activation energy of cleaving β-aryl ether linkages is significantly higher than the value of 78 kJ/mole.[12] Consequently, a slightly higher value of activation energy in delignification of wood than in the cleavage of model compounds should be expected.

In the bulk phase delignification, the cleavage of phenolic β- aryl and non-phenolic β-aryl ether linkages is the major reaction.[11] Using veratrylglycerol- β-guaiacyl ether types of model compounds, Gierer and Ljunggren[13] and Ljunggren[12] found that the cleavage of phenolic β-guaiacyl ether linkages had an activation energy of 121 kJ/mole under kraft pulping conditions. Under the same conditions, the cleavage of non-phenolic β-guaiacyl ether linkages had an activation energy of 123 kJ/mole.[12,14] Both values are nearly identical to the value of 123.8 kJ/mole found in the current study, suggesting that the delignification system applied in this study was very close to a homogeneous reaction system. This value is reasonably close to that utilized by Vroom[15] for the derivation of the H-factor (134 kJ/mole).

However, the reaction conditions used in the current study were selected to simulate as closely as possible a homogeneous reaction.

The final phase of delignification is by far the least investigated one. An activation energy of 120 kJ/mole was reported for kraft delignification[9] and a value of 115.4 kJ/mole was found for soda delignification.[17] Both values are in good agreement with the value of 110.0 kJ/mole found in this study. One difficulty to investigate the reaction kinetics of the final delignification was the acquisition of reliable data on the residual lignin contents. In this study, both Klason plus acid soluble lignin and acetyl bromide lignin contents[1] were determined for the pulp samples with a low lignin content to provide reproducible data. Treatment of thses data with a nonlinear regression routine of the SAS program, a value of L_f was generated and utilized to investigate the kinetics of the final delignification reaction.

Effects of $[HO^-]$ and $[HS^-]$ Concentrations on the Rate of Kraft Delignification Reaction

If the concentrations of $[HO^-]$ and $[HS^-]$ are considered as variables for the rate equation, the constants k's in Equation 4, for instance k_i, should be expressed as Equation 5.

$$k_i = k_i' [HO^-]^{ai} [HS^-]^{bi} \qquad (5)$$

In this equation, k_i' is the true first-order rate constant for the initial phase delignification, ai and bi are the reaction orders with respect to $[HO^-]$ and $[HS^-]$ concentrations for the initial phase delignification, respectively. In order to investigate the effect of $[HO^-]$ concentration on the rate of delignification, the kinetic experiments were carried out by holding $[HS^-]$ concentration at a constant level, while using three levels of $[HO^-]$ concentrations. Under this condition, Equation 5 can be rewritten as Equation 6.

$$k_i = k_i'' [HO^-]^{ai} \qquad (6)$$

$$\text{where } k_i'' = k_i' [HS^-]^{bi} \qquad (7)$$

Based on Equation 6, the value of ai can be obtained as the slope of a plot of $\ln(k_i)$ vs. $\ln([HO^-])$, where the value of k_i can be obtained using the same statistical approach as in the previous section. Similarly, the reaction orders of a and b can be obtained for the bulk (ab and bb) and final (af and bf) delignification phases.

For chemical concentration effects, the delignification experiments were carried out at 120 and 170°C. The lignin removal as a function of time is shown in Figure 6 for the reactions carried out at 120 and 170 C with three different concentrations of [HO⁻] and a constant concentration of [HS⁻]. It can be seen from this figure that the extents of lignin removal in the early stages of delignification were nearly identical regardless of the difference in the [HO⁻] concentration. Figure 7 shows the lignin removal as a function of time at 120 and 170 °C with three levels of [HS⁻] concentrations and a constant concentration of [HO⁻].

Based on Figure 6, the values of k_i's were obtained for the initial, bulk, and final delignification phases according to the approach described previously using a SAS program. The k_i's and [HO⁻] were then used to calculate the values of a's according to Equation 6, as shown in Figure 8 which illustrates the effect of [HO⁻] on the rate of delignification for the initial, bulk and final phases. Data obtained at the reaction temperature of 120°C were analyzed to illustrate the chemical concentration effect on the rate of delignification for the initial and bulk phases, whereas the data obtained at the reaction temperature of 170°C were analyzed to illustrate the effect on the rate of delignification for the bulk and final phases. In a similar way, the effect of [HS⁻] on the rate of delignification was obtained, as shown in Figure 9. Table 4 summaries the values of reaction orders with respect to [HO⁻] (a's) and [HS⁻] (b's) concentrations for the three phases of delignification carried out at 120 and 170°C.

As shown in Table 4 and the slopes of the lines in Figure 8, the exponent a for the initial phase is nearly zero under the temperatures (120 and 170°C) and [HO⁻] concentrations (0.8 to 1.6 M) studied. This indicates that as long as the [HO⁻] is kept in the range of 0.8 to 1.6 M, the removal of lignin in the initial phase of kraft pulping should proceed with a similar rate in the temperature range of 120 to 170°C with a [HS⁻] concentration of about 0.2 M. Under the conditions selected in this study, the delignification reaction in the initial phase also proceeded with zero-order with respect to [HS⁻] concentration. It is understandable that any set of conditions selected in this study is sufficient enough to provide an extensive reaction of cleaving phenolic α-aryl ether linkages in the initial phase in which this type of reaction is the predominant one.[11] These findings are in agreement with previous studies on softwood kraft delignification kinetics[16] and on model compounds kinetics.[12,13,14]

In the bulk phase, the rate of delignification was greatly influenced by both [HO⁻] and [HS⁻] concentrations (Table 4). However the influence of [HS⁻] was weaker than that of [HO⁻]. Slightly higher reaction order with respect to [HO⁻] was observed for the reaction carried out at a high temperature (170°C), whereas the reaction orders with respect to [HS⁻] did not vary profoundly with temperatures.

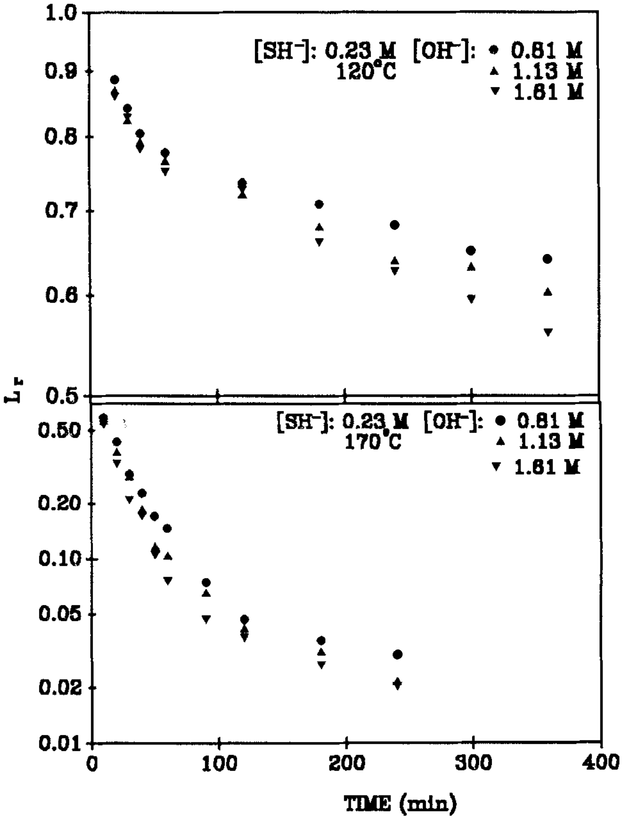

FIGURE 6. Lignin removal as a function of time at different levels of [HO⁻] concentrations.

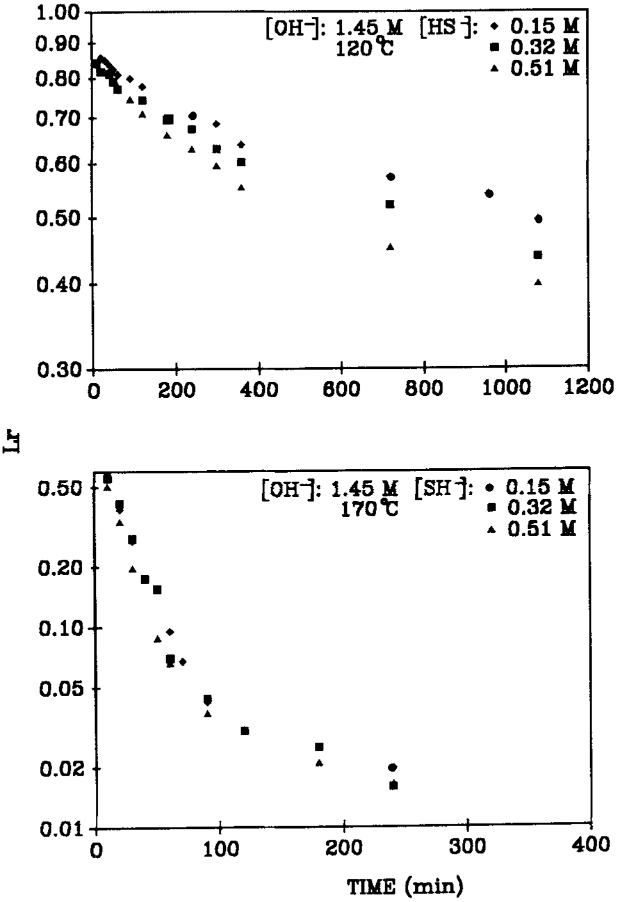

FIGURE 7. Lignin removal as a function of time at different levels of [HS⁻] concentrations.

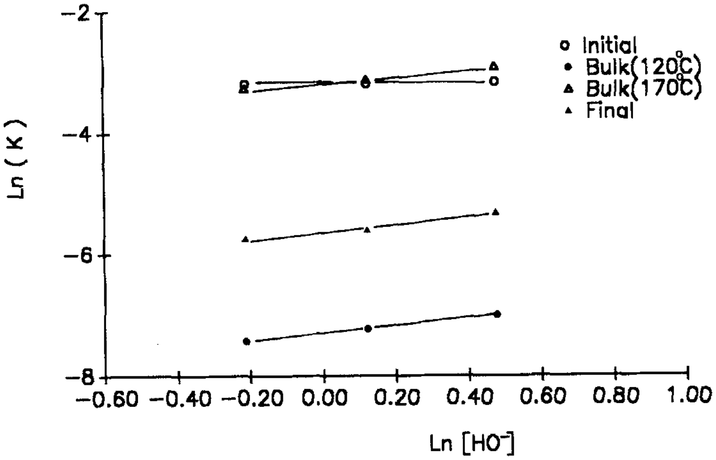

FIGURE 8. Effect of [HO⁻] on the rate of delignification.

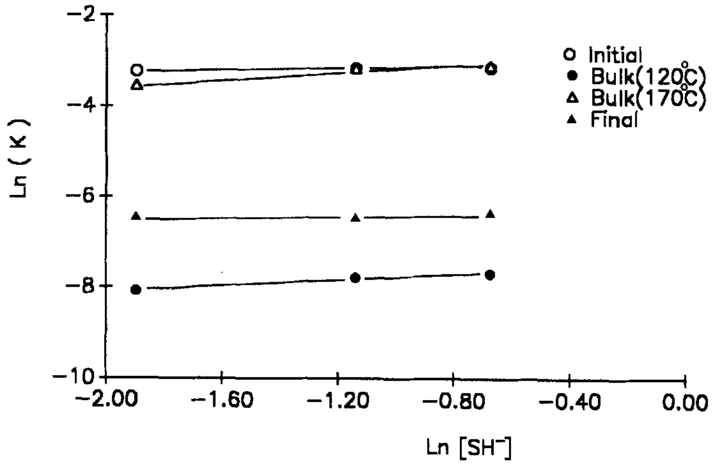

FIGURE 9. Effect of [HS⁻] on the rate of delignification.

Table 4

Reaction Orders with Respect to Reactant Concentrations for Delignification of Douglas-Fir

	Reaction order (a) with respect to $[HO^-]$	Reaction order (b) with respect to $[HS^-]$
i	~0	~0
b	0.512 at 120°C 0.615 at 170°C	0.33 at 120°C 0.39 at 170°C
f	0.622 at 170°C	~0

The reaction orders of 0.512 to 0.615 with respect to $[HO^-]$ and of 0.33 to 0.39 with respect to $[HS^-]$ are different from the values of 0.7 to 0.8 and of 0.1 to 0.4, respectively, reported by Norden and Teder.[9] However, in their study: (a) the reaction was carried out under an non-isothermal condition for a period of 100 minutes prior to a constant temperature were used. These conditions are clearly not optimal for determining true kinetic parameters of delignification. Of special difficulty are the changing chemical concentrations which occur at such low liquor-to-wood ratios. For instance, under conditions similar to those employed by Norden and Teder, over 50% of the effective alkali can be consumed when the pulping temperature reaches 170°C in a softwood kraft cook.[18] The consumption of effective alkali still continues at the peak temperature of 170°C.[18] Consequently, comparison of results presented in the literature must be made with an understanding of the reaction conditions applied.

The final delignification phase was also greatly influenced by $[HO^-]$ concentration but not by $[HS^-]$. It has been speculated that the main delignification reaction in this phase is the alkali promoted cleavage of carbon-carbon linkages originally present or generated by condensation reactions.[1,11,12] Consequently, the role of $[HS^-]$ in delignification is insignificant in the final delignification phase.

ACKNOWLEDGEMENT

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