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Theoretical Model of the Kraft Pulping Process

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A mathematical model consisting of a series of differential equations describing the combined diffusion and kinetics within a wood chip during kraft pulping has been derived and solved. Literature data were used to derive the lignin, carbohydrate, and alkali kinetic equations and the alkali diffusivity equation. Model predictions are compared with experimental data from a variety of studies with good results. The model also provides insight to reject formation by revealing the conditions at the chip center throughout the cook.

Introduction

The kraft pulping process, introduced in 1879, is the dominant pulping process today and is likely to remain so in the near future. This is primarily because of the process's relative insensitivity to the wood condition, its favorable energy and chemical recovery capabilities, and the excellent properties of the pulp which it produces. In the past 25 years many studies of the kinetics and transport behavior of the kraft pulping process have been made. With the data from these studies, kraft pulping models of varying complexity have been developed for control and design purposes.

The simplest of these models are those which assume that the pulping reaction rates are kinetically controlled. One of the earliest kinetic model was developed by Vroom (1957), who used an Arrhenius type expression for the reaction rate temperature dependence to derive the "*H* factor". The *H* factor, which combines the cooking temperature and cooking time into one variable, is at the heart of many control schemes used for kraft pulping today.

Many empirical kinetic models have been derived. Typical of these is Hatton's (1973) model which predicts the kappa number and yield for a variety of wood species with an equation of the form

$$Y \text{ or } K = \alpha - \beta[(\log H)(\mathrm{EA})^n]$$

where Y is the yield, K is the kappa number, α and β are adjustable parameters, H is the H factor, and (EA) is the effective alkali. These empirical models may be quite complex. For example, the model of Bailey et al. (1969) uses five variables in a twenty-term polynomial to predict pulp kappa numbers.

Semitheoretical kinetic models have been derived by Kerr (1970) and Smith (1975). In Kerr's model the form of the delignification rate equation is

$$\mathrm{d}L/\mathrm{d}t = -k[\mathrm{OH}]L$$

where L is the lignin content, t is the time, k is the rate constant, and [OH] is the effective alkali concentration. The alkali consumption rate in Kerr's model is assumed to be a linear function of the delignification rate for each delignification period. The H factor is used to account for the time–temperature behavior. Pulp kappa numbers are predicted with Kerr's model given the time–temperature behavior and the initial effective alkali concentration. In a later paper by Kerr and Uprichard (1976), Kerr's model is refined to incorporate, empirically, the pulping variables sulfidity, chip size, chip moisture content, and liquor to wood ratio.

The most complex kinetic model is Smith's (1975), in which wood is divided into five species: high-reactivity lignin, low-reactivity lignin, cellulose, galactoglucomannan, and arabinoxylan. The form of the kinetic equation Smith uses for each species is

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = (k_1[\mathrm{OH}] + k_2[\mathrm{OH}][\mathrm{S}])C$$

Where C is the wood species concentration, [OH] is the alkali concentration, [S] is the sulfide concentration, and k_1 and k_2 are rate constants. Smith adjusted the values for the activation energies and frequency factors in the rate equations until his model fit the data of Daleski (1965). Smith calculated the stoichiometric coefficients relating the alkali and sulfide consumption to the lignin and carbohydrate degradation by using chemical data from an industrial kraft cook. Smith also used the industrial data to check the accuracy of his model.

Even the best kinetic models cannot predict the overall pulping rate in commercial chips. Commercial pulp chips are large enough to cause the reaction rates to be limited by diffusion as well as chemical kinetics. Hartler and Ostberg (1959) and Hartler and Onisko (1962) found that increasing the chip thickness above three millimeters results in increased screenings accompanied by less delignification. Screenings at a given lignin content were also found to increase with cooking temperature for a given chip thickness. Work done by Lightfoot and Premont (1962), Colombo et al. (1964), and Wahlman (1967) show that the maximum chip thickness which gives no screenings ranges from 3 to 5 mm depending upon the pulping conditions.

Empirical models describing the effect of chip dimensions on pulp properties have been developed by Hatton and Keays (1973) and by Akhtaruzzaman and Virkola (1979, 1980). Hatton and Keays derived a series of polynomial regression equations from their experimental data in which the screened yield, yield (yield in this paper refers to the total yield), rejects, kappa number, permanganate number, and effective alkali consumption are functions of chip length and chip thickness. Hatton and Keays used only one pulping condition so their results are limited.

Akhtaruzzaman and Virkola pulped chips of varying dimensions under a variety of conditions. In their study a series of polynomial regression equations were derived from their experimental data and give the kappa number, yield, screened yield, rejects, effective alkali consumption, pulp viscosity, fiber length, and paper strength properties as functions of chip thickness, chip length, initial effective alkali concentration, and H factor.

Hatton and Keays and Akhtaruzzaman and Virkola found that the effect of chip thickness on pulp properties is much more pronounced than the effect of chip length

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and that in chips thicker than about 4 mm the reaction rates are partially mass transfer limited.

The effect of chip thickness on pulp properties has been theoretically modeled by Johnsson (1971). Johnsson solved the differential equations describing the combined mass transfer and reaction kinetics in a pulp chip during a kraft cook.

Johnsson's model predicts reasonably well the cumulative kappa number distribution of a pulp produced in an industrial continuous digester. Subsequent kinetic studies have shown, however, that the kinetic equations used by Johnsson are too simple to give acceptable results. For example, Johnsson uses one delignification equation for all three reaction periods. In this equation the delignification rate is first order in alkali concentration and zero order in the sulfide concentration. Johnsson's equation is not consistent with experimental kinetic measurements (Norden and Teder, 1979), and his alkali consumption equation fails to predict the residual alkali data of Aurell and Hartler (1965).

Johnsson's assumption that the diffusivity in wood is a function only of temperature is incorrect. The results published by Hartler (1962) show that the diffusivity of a solute in wood is a strong function of pH and yield.

Tyler (1981) modeled the combined diffusion and kinetic problem for chips pulped in laboratory scale digesters. Only bulk period kinetics were used in Tyler's rate equation. The model was empirically fit to the data of Hatton and Keays (1973) and Akhtaruzzaman and Virkola (1979, 1980) by adjusting the alkali diffusivity and the reaction rate constants.

From this brief review it is evident that improvements in modeling the kraft pulping process can be made. Kinetic equations for all three reaction periods are available. The diffusivity in wood may be expressed as a function of temperature, pH, and yield. With good kinetic and diffusivity equations it should be possible to predict, a priori, the lignin content, carbohydrate content, and alkali concentration at each point within the chip at any time during a cook. If the lignin content and carbohydrate content throughout the chip are known, kappa numbers, yields, screen yields, and reject values for a given set of cooking conditions may be predicted. This paper discusses the development of an improved model, the model predictions, and some of the interesting phenomena illuminated by the model.

Model Development

The kraft pulping of a wood chip is a very complex phenomenon; therefore, simplifying assumptions are needed to model the process mathematically. The assumptions that are made in the model development and justification for them are the following.

(1) The liquor penetration rate is infinite. The liquor penetration is complete about the time the temperature reaches 140 °C during a typical kraft cook (Hartler, 1962), and at this low temperature the delignification reactions are still slow.

(2) The chips are isothermal. The characteristic time for heat transfer is much less than other characteristic times of the pulping process. Furthermore, the heats of reaction of pulping reactions are essentially zero.

(3) The pulp chips are one-dimensional. In the previous section, literature was presented which shows that chip thickness is the critical dimension. Pulp chips have a length to thickness ratio of about five to one. In alkaline pulping the diffusivities in the three primary directions are not significantly different (Rydholm, 1965a; Stone, 1957; Hartler, 1962). We anticipate, therefore, that chip thickness is the critical dimension.

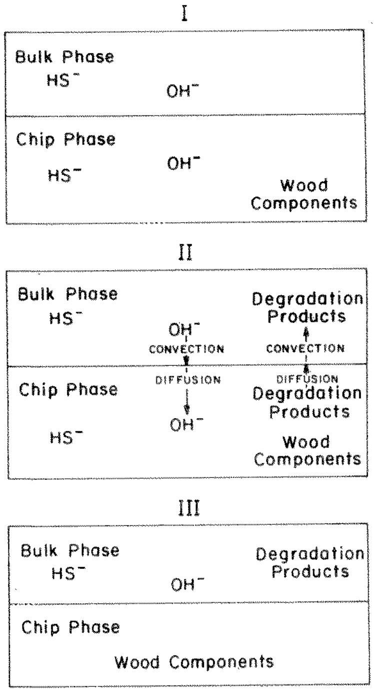

Figure 1. Schematic of kraft pulping process.

(4) The bulk phase is homogeneous and well stirred. The digester is modeled as a CSTR in which the mass transfer coefficient from the bulk phase to the chip phase is assumed to be infinite. These are good assumptions for modeling a laboratory scale digester and will be relaxed when modeling the industrial scale digester.

(5) Wood is divided into lignin, carbohydrate, and acetyl. Combining the carbohydrates into one category is justified because in softwoods the relative degradation rates of different carbohydrates are not significantly altered by normal changes in pulping conditions (Aurell and Hartler, 1965; Yllner et al., 1957). The acetyl groups are considered as a separate component (they are actually a component of the galactoglucomannans) because they consume a small, but significant, amount of alkali in a well-characterized fashion. Their inclusion, therefore, improves the alkali consumption rate equation. The other major wood component, the extractives, is assumed to be dissolved out of the wood before pulping begins (Olm and Tistad, 1979).

(6) Pulping reactions are irreversible. Condensation reactions occur when the cooking liquor lignin concentration is high and the alkali concentration is low (Hartler, 1978). The condensation reactions occur, therefore, at the end of a cook and at the center of thick chips. No accounting is made, in the model, for the condensation reactions because the knowledge of these reactions is too limited. Condensation reactions at the center of thick chips will be discussed later.

With these assumptions, the pulping process is modeled as shown in Figure 1. At the beginning of the cook, diagram I, it is assumed that the chip phase is full of cooking liquor and the alkali and sulfide concentrations are uniform throughout. As the digester heats up, pulping reactions begin, diagram II, that produce degradation products that neutralize alkali as they diffuse out of the wood. Alkali is transported from the bulk phase to the chip surface and then diffuses into the chip to replace the alkali consumed by the degradation products. The wood degradation and the alkali consumption and diffusion are described by eq 1–6. The sulfide concentration is assumed to remain constant (see later section entitled Alkali and

Sulfide Consumption), and therefore it does not diffuse into the chip. (Note that both the sulfide ions and hydrosulfide ions are regarded as the sulfide. This is done because [S] in the bulk delignification rate equation (eq 11) is the total sulfide sulfur concentration (Lemon and Teder, 1973). At the end of the cook, and after the pulp has been washed, diagram III, all that remains in the pulp are the bound wood components.

A mass balance on the chip, with the above assumptions, gives the following equations.

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left(D_i\frac{\partial C_i}{\partial x}\right) - Ra_i \qquad (1)$$

$$\frac{\partial C_i}{\partial x} = 0 \quad \text{(chip center)} \qquad (2)$$

$$D_i\frac{\partial C_i}{\partial x} = k_i(C_{i,\text{bulk}} - C_i) \quad \text{(chip edge)} \qquad (3)$$

$$C_i = C_{i0} \quad (t = 0) \qquad (4)$$

C_i = concentration of the i species, C_{i0} = initial concentration of the i species, $C_{i,\text{bulk}}$ = concentration of the i species in the bulk liquid phase, D_i = diffusivity of species i, k_i = mass transfer coefficient for species i, Ra_i = reaction rate of species i, t = time, and x = distance from the chip center. A mass balance on the bulk phase gives the following equations.

$$\frac{\mathrm{d}C_{i,\text{bulk}}}{\mathrm{d}t} = -D_i\frac{\partial C_i}{\partial x}\left(\frac{V_c}{CT\cdot V_b}\right) \qquad (5)$$

$$C_{i,\text{bulk}} = C_{i,\text{bulk},0} \quad (t = 0) \qquad (6)$$

V_c = volume of the chip, V_b = volume of the bulk liquid phase, CT = one-half the chip thickness, and $C_{i,\text{bulk},0}$ = initial bulk phase concentration of species i.

To solve the differential equations, expressions for the kinetics and the diffusivities of the lignin, carbohydrate, acetyl, hydroxyl, and sulfide are needed. As stated in assumption 4, the mass transfer coefficients, k_i, are assumed to be effectively infinite.

Kinetics

The foundation of a pulping model is the set of kinetic equations. Many kraft pulping kinetic studies have been done, but few provide data from which kinetic equations may be derived. Often in these kinetic studies the cooks are nonisothermal, or the liquor to wood ratio is low so the effective alkali concentration changes throughout the cook, or the chips are unscreened so the reaction rates are partially diffusion controlled. The kinetic equations selected for the model are derived from the best available data and are generally of a form that is consistent with the wood chemistry of softwoods. The lignin, carbohydrate, and acetyl kinetics are presented first and are followed by the alkali and sulfide kinetics.

Lignin, Carbohydrate, and Acetyl Kinetics. The kinetics of kraft pulping is divided into three periods: initial, bulk, and residual (Kleppe, 1970; Kleinert, 1966; Norden and Teder, 1979). (Typically these three periods are referred to as phases, but to avoid confusion, we restrict the term phase to distinguish between the bulk liquid phase and the chip phase.) The initial period is characterized by rapid delignification, significant hemicellulose degradation, and large alkali consumption. The only study on initial period kinetics is the one recently published by Olm and Tistad (1979). The delignification expression derived from their data is given by

$$\mathrm{d}L/\mathrm{d}t = 36.2T^{1/2}e^{(-4807.69/T)}L \qquad (7)$$

L = lignin content, % on wood, T = temperature, K, and t = time, min.

The lack of alkali or sulfide dependence in eq 7 can be explained by the initial period chemistry. Initial period delignification is attributed to the cleavage of phenolic α- or β-aryl ether groups. Work with model compounds (Gierer, 1980) shows that this cleavage readily takes place at pulping temperatures provided the pH is above 12.

The carbohydrate reaction rate for each period is a linear function of the lignin reaction rate (Aurell and Hartler, 1965; Kleinert, 1966; Olm and Tistad, 1979). This may be attributed to the chemical links between the carbohydrates and the lignin (Kleinert, 1966; Eriksson et al., 1980), and the similarity of the reaction mechanism of carbohydrate peeling and lignin degradation (Gierer, 1980). Olm and Tistad (1979) show that the constant relating the lignin reaction rate and the carbohydrate reaction rate in the initial period is independent of the sulfide concentration but dependent upon the alkali concentration. From their data eq 8 is derived for the initial phase carbohydrate degradation rate.

$$\frac{\mathrm{d}C}{\mathrm{d}t} = 2.53[\mathrm{OH}]^{0.11}\frac{\mathrm{d}L}{\mathrm{d}t} \qquad (8)$$

L = lignin content, % on wood, C = carbohydrate content, % on wood, [OH] = effective alkali concentration, M, and t = time, min.

Finally, Olm and Tistad show that the acetyl groups are removed from the hemicellulose very quickly and are neutralized completely by the NaOH in the initial period.

The transition from the initial period to the bulk period in kraft pulping takes place at a lignin content of about 22% on wood and is independent of temperature, sulfide concentration, and alkali concentration (Olm and Tistad, 1979; Rekunen et al., 1980).

Most of the lignin is removed in the bulk period. Carbohydrate degradation continues in this period as well, although at a much lower rate than in the initial period. The bulk delignification kinetics have been the subject of many studies (Kleinert, 1966; Wilder and Daleski, 1965; Daleski, 1965; Lemon and Teder, 1973). The results of Wilder and Daleski's study (1965) and Lemon and Teder's study (1973) are used in the derivation of the bulk delignification kinetic equation for the model.

In the Wilder and Daleski study the bulk delignification rate of Loblolly Pine chips was measured at 142, 150, 160, and 170 °C with liquor compositions ranging from 20 g/L of soda liquors to 60 g/L of active alkali, 100% sulfidity kraft liquors. The form of the rate equation they assumed is given by

$$\frac{\mathrm{d}L}{\mathrm{d}t} = (k_1[\mathrm{OH}] + k_2[\mathrm{S}]^n)L \qquad (9)$$

where L = lignin content, % on wood, [OH] = effective alkali concentration, M, [S] = sulfide sulfur concentration, M, and t = time, min.

This form should not be used because it does not predict a zero reaction rate as the alkali concentration approaches zero. Furthermore, the values of the constants k_1 and k_2 are such that at typical pulping conditions $k_2[\mathrm{S}]^n \gg k_1[\mathrm{OH}]$. This implies that the reaction is independent of the alkali concentration, which is incorrect.

Lemon and Teder measured the bulk regime delignification rate of Scots pine at 170 °C. The form of the rate equation they derived is given by

$$\mathrm{d}L/\mathrm{d}t = (k_1[\mathrm{OH}] + k_2[\mathrm{OH}]^{0.5}[\mathrm{S}]^{0.4})L \qquad (10)$$

(The terms have been defined in preceding equations.)

Equation 10 is used in this study. It predicts a zero reaction rate as the hydroxyl concentration goes to zero and reduces to the soda cooking rate as the sulfide concentration goes to zero. The dependence of eq 10 upon the hydroxyl and sulfide concentration is consistent with the chemistry of non-phenolic *β-o*-aryl ether cleavage (Gierer, 1980).

The temperature dependence of the constants k_1 and k_2 in eq 10 is taken from Wilder and Daleski's study. This is legitimate, provided the activation energies are not functions of caustic or sulfide concentration, since the rate constants in the two studies are derived in the same way. With this correction the bulk delignification rate expression used in the model is

$$\mathrm{d}L/\mathrm{d}t = [e^{(35.19-17200/T)}[\mathrm{OH}] + e^{(29.23-14400/T)}[\mathrm{OH}]^{0.5}[\mathrm{S}]^{0.4}]L \quad (11)$$

T = temperature, K.

The carbohydrate reaction rate in the bulk period is proportional to the lignin reaction rate and the constant of proportionality is independent of pulping conditions (Kleinert, 1966; Aurell and Hartler, 1965; Yllner et al., 1957). The constant of proportionality used in the model is derived from Rekunen's (1980) data, and the carbohydrate reaction rate is given by

$$\frac{\mathrm{d}C}{\mathrm{d}t} = 0.47\frac{\mathrm{d}L}{\mathrm{d}t} \quad (12)$$

The lignin content at the transition from the bulk period to the residual period is dependent upon temperature (Kleinert, 1966) and sulfidity (Norden and Teder, 1979), but the available data are insufficient to predict the transition point given the pulping conditions. The lignin content of the pulp at the transition point may vary from 2.5% on wood (Rekunen et al., 1980) to 1.1% on wood (Kleinert, 1966). The value used in the model is taken from experiments run at conditions closest to those being simulated. The value of the bulk to residual period transition point is input to the model.

The residual period is characterized by very slow delignification, significant carbohydrate degradation, and significant alkali consumption. The form of the residual delignification rate equation is taken from Norden and Teder's paper (1979), and the value of the rate constant is calculated from Kleinert's (1966) data. The expression used in the model is shown in eq 13.

$$\frac{\mathrm{d}L}{\mathrm{d}t} = e^{(19.64-10804/T)}[\mathrm{OH}]^{0.7}L \quad (13)$$

The carbohydrate reaction rate for the residual period is derived from Rekunen's (1980) data and is shown in eq 14.

$$\frac{\mathrm{d}C}{\mathrm{d}t} = 2.19\frac{\mathrm{d}L}{\mathrm{d}t} \quad (14)$$

The reaction rates presented above will not apply for all species, even among the softwoods, under all conditions. Both Wilder and Daleski (1965) and Lemon and Teder (1973) found that the bulk delignification rate changes significantly with the conditions used in the initial period. The bulk delignification rate measured for spruce (Kleinert, 1966) is about 20% higher than the value measured for pine (Wilder and Daleski, 1965; Lemon and Teder, 1973). Similar comments apply to the delignification rates in the other periods and to the carbohydrate reaction rates as well. It is important to note that because the form of the rate equations is consistent with the wood chemistry for softwoods, differences in the kinetics between species may be accounted for by adjusting the rate constants. If the data are available, the above kinetic equations will be modified to account for species differences. For the most part, however, the model results should be viewed as representative results rather than as predictions of specific behavior.

Alkali and Sulfide Consumption. A thorough study on the rate of consumption of alkali in kraft pulping has not been done. In fact, it is difficult to know the alkali concentration in kraft liquor. From the thermodynamic work that has been done with kraft liquors (Teder and Tormund, 1973), it is generally assumed that the effective alkali is the best measure of the alkali concentration. However, it is difficult to measure the true effective alkali concentration in the liquor because of the organics in the liquor. Lemon and Teder (1973) show that quite different values for the effective alkali concentration in kraft liquor may be obtained by changing the choice of end point, even with the addition of barium chloride.

Estimates of the amount of alkali consumed by reaction products have been made by Rydholm (1965b) and by Brauns and Grimes (1939). These estimates predict reasonable values for the total consumption of alkali during a cook but cannot accurately predict the shape of the alkali concentration vs. time curves.

To estimate the alkali reaction rate, it is assumed that the alkali consumption can be expressed as a linear function of the acetyl, lignin, and carbohydrate degradation rate. It is assumed that roughly one mole of effective alkali is consumed per mole of acetyl group liberated (Rydholm, 1965b). To calculate the amount of alkali consumed by the lignin and by the carbohydrate, the data of Rekunen et al. (1980) are used. Rekunen presents the carbohydrate content and the effective alkali concentration as linear functions of the lignin content for both the initial and bulk periods during a kraft cook. This gives two linear equations which can be used to solve for the two unknowns, namely, the moles of effective alkali consumed per gram of lignin and per gram of carbohydrate liberated from the chip. Equation 15 is the alkali reaction rate calculated in this manner.

$$\frac{\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = \left(1.87 \times 10^{-2}\frac{\mathrm{d}Ac}{\mathrm{d}t} - 4.78 \times 10^{-3}\frac{\mathrm{d}L}{\mathrm{d}t} + 1.81 \times 10^{-2}\frac{\mathrm{d}C}{\mathrm{d}t}\right)\rho/\epsilon \quad (15)$$

where Ac = acetyl content, % on wood, ϵ = void fraction in the chip, and ρ = wood density.

It will be shown later that eq 15 predicts the data well for a wide range of conditions, but it probably has little physical significance. Note, for example, the negative coefficient of the lignin term. Equation 15 does predict the well-known fact that most of the alkali is consumed in the neutralization of saccharinic acids.

The concentration of sulfide is assumed to be constant throughout the cook. Reactions which produce thiolignin and other sufur-containing compounds consume about 5–10 g of sulfur/kg of wood (Rydholm, 1965c). Because of this low consumption of sulfur and because of the low delignification dependence on sulfur (eq 11), the assumption that the sulfide concentration is constant is a good one, provided the initial sulfide concentration is above a value corresponding to about 20% sulfidity.

Diffusion. The diffusivities of the carbohydrate and the lignin are zero since these species are bound in the wood. The diffusivity of the sulfide is unimportant because the sulfide concentration is held constant. The reaction products of delignification and carbohydrate peeling diffuse out, of course, but we are not concerned with the rate because the pulping reactions are assumed to be irreversible, assumption 6, and because the lignin and carbohydrate contents of the *washed* pulp are the variables of interest.

To estimate the diffusivity of alkali for use in the model, three relevant studies were used. The first is McKibbins' work (1960), in which he measured the diffusivity of sodium in kraft cooked chips. McKibbins measured the diffusivity by immersing the cooked chips in distilled water and comparing the measured chip sodium concentration vs. time curves to those predicted by unsteady-state diffusion theory. This was done for a variety of temperatures and the results yielded

$$D = 3.4 \times 10^{-2} T^{1/2} e^{(-4870/RT)} \qquad (16)$$

where D = diffusivity, cm^2/min, T = temperature, K, and R = gas constant (cal/mol K).

Because McKibbins' work was done with cooked chips, eq 16 needs to be corrected with respect to pH and lignin content. Equation 16 was corrected with respect to pH and lignin content with the effective capillary cross-sectioned area (ECCSA) data published by Hartler (1962). The corrected diffusivity is given by

$$D = 5.7 \times 10^{-2} T^{1/2} e^{(-4870/RT)} [-0.02L + 0.13[\mathrm{OH}]^{0.55} + 0.58] \qquad (17)$$

The constant, 5.7×10^{-2}, was calculated by requiring the diffusivities from eq 16 and 17 to be equal when the alkali concentration and lignin content of the chips used in McKibbins' study are put into eq 16.

Solution Method

The differential equations (1)–(6) are solved with a modified version of Finlayson's program Reacol (Finlayson, 1980). Reacol uses the orthogonal collocation method to reduce the partial differential equations to a system of ordinary differential equations. The ordinary differential equations are then integrated numerically with the GEARB (Hindmarsh, 1974) integration package.

The orthogonal collocation forms for eq 1, 3, and 5 are shown in eq 18, 19, and 20, respectively.

$$\mathrm{d}C_j/\mathrm{d}t = \sum_{i=1}^{N+1} A_{ji}\alpha_i \sum_{i=1}^{N+1} A_{ji}C_i + \alpha_j \sum_{i=1}^{N+1} B_{ji}C_i - Ra_j \qquad (j = 1, 2, ..., N) \quad (18)$$

$$\sum_{i=1}^{N+1} A_{N+1,i}C_i = B_{\mathrm{W}}(C_{\mathrm{bulk}} - C_{N+1}) \qquad (19)$$

$$\frac{\mathrm{d}C_{\mathrm{bulk}}}{\mathrm{d}t} = -\alpha_{N+1} \sum_{i=1}^{N+1} A_{N+1,i}C_i(V_{\mathrm{C}}/V_{\mathrm{B}}) \qquad (20)$$

where A_{ji} = first derivative collocation matrix, B_{ji} = second derivative collocation matrix, N = number of collocation points, $BW = kCT/D$, $\alpha = Dt_f/CT^2$ and t_f = final cooking time. The boundary condition represented by eq 2 is satisfied identically by the A and B matrices.

Verification of the Model

The accuracy of the model is checked by comparing the model predictions with published literature data. It should be emphasized that all the predictions are a priori. Occasionally, however, the kinetic equations presented earlier are slightly modified to accommodate differences in the pulping rates of different species. It will be noted in the discussion where these modifications have been made.

The accuracy of the kinetic equations was checked by comparing the model predictions with the data of Aurell and Hartler (1965) and Matthews (1974), none of which were used in the development of the kinetic equations. These two studies were chosen because they present the lignin content and the carbohydrate content vs. time curves for chips cooked under typical pulping conditions. Aurell and Hartler's data also include the alkali consumption.

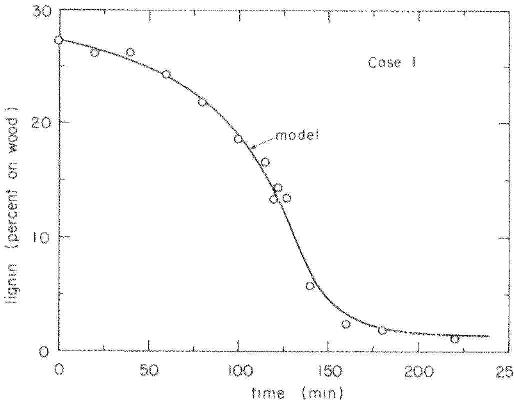

Figure 2. Model prediction and Aurell and Hartler's (1965) lignin content data.

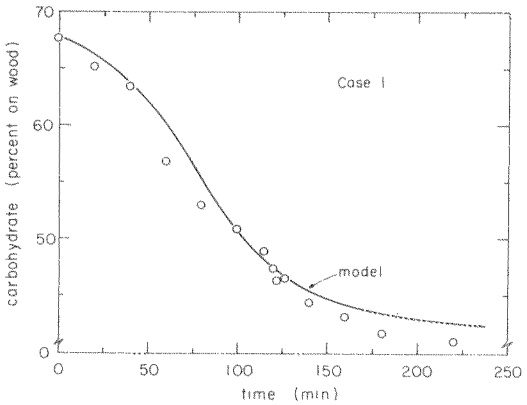

Figure 3. Model prediction and Aurell and Hartler's (1965) carbohydrate content data.

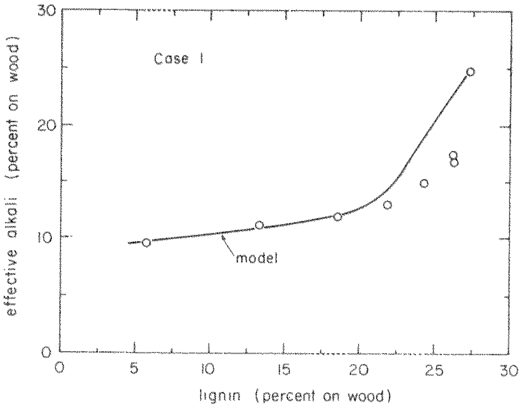

Figure 4. Model prediction and Aurell and Hartler's (1965) effective alkali concentration data.

The cooking conditions used by Aurell and Hartler are given in Table I, and Figures 2 through 7 compare the model predictions with the experimental results. Case 1 corresponds to the 25% effective alkali cook and case 2 the 15.75% effective alkali cook. These two experiments are a good test for the model because the alkali concentrations are at the extremes used in commercial pulping. The comparison is seen to be very good.

To compare the model predictions with Matthews' data, the bulk period carbohydrate reaction rate was adjusted to $0.20 \times (\mathrm{d}L/\mathrm{d}t)$. The value 0.20 was derived by fitting

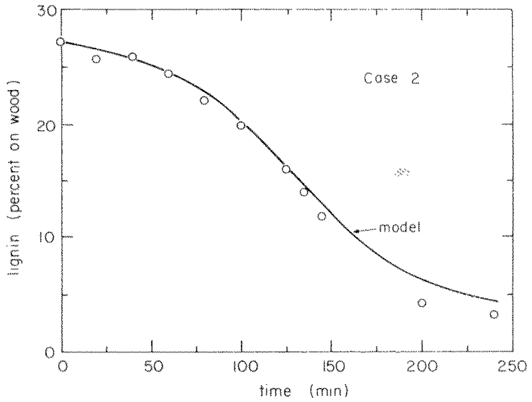

Figure 5. Model prediction and Aurell and Hartler's (1965) lignin content data.

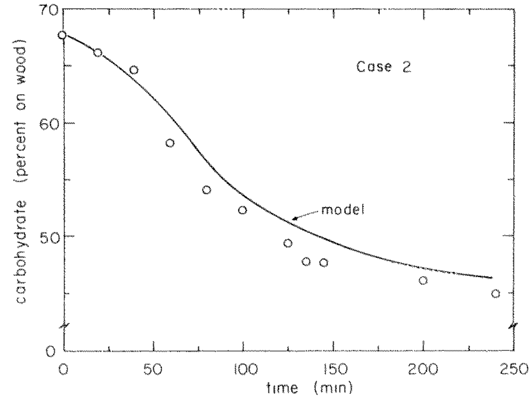

Figure 6. Model prediction and Aurell and Hartler's (1965) carbohydrate content data.

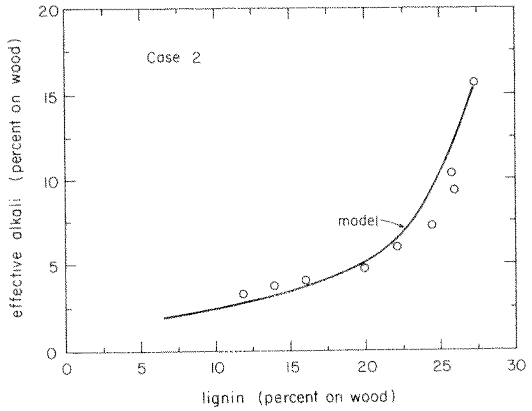

Figure 7. Model prediction and Aurell and Hartler's (1965) effective alkali concentration data.

Table I. Cooking Conditions Used by Aurell and Hartler (1965)

	case 1	case 2
effective alkali concentration	25% on wood as NaOH	15.75% on wood as NaOH
sulfidity	25%	25%
heating time	120 min	120 min
cooking time	240 min	240 min
liquor/wood ratio	4 L/kg	4 L/kg
cooking temperature	170 °C	170 °C
lignin content	27.3% on wood	27.3% on wood
carbohydrate content	67.7% on wood	67.7% on wood
acetyl content	1.3% on wood	1.3% on wood
species	*Pinus silvestris*	

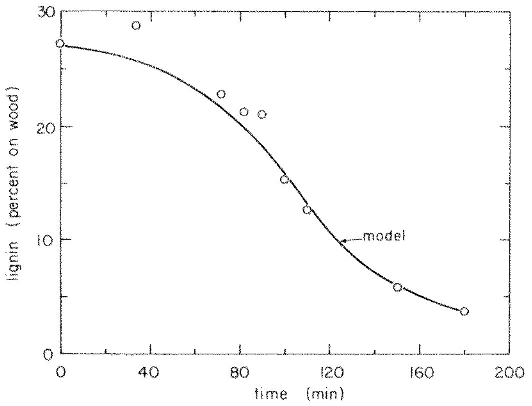

Figure 8. Model prediction and Matthews' (1974) lignin content data.

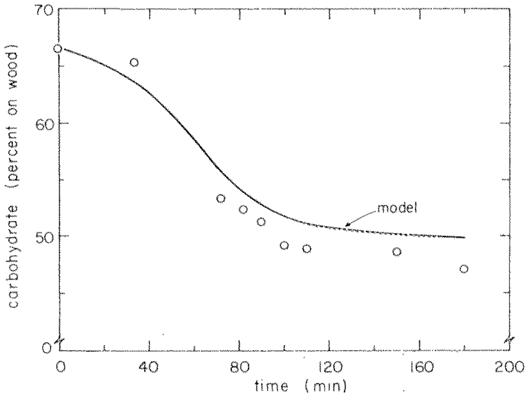

Figure 9. Model prediction and Matthews' (1974) carbohydrate content data.

Table II. Cooking Conditions Used by Matthews (1974)

effective alkali concentration	18.4% on wood as NaOH
sulfidity	22%
heating time	90 min
cooking time	180 min
liquor/wood ratio	5 L/kg
cooking temperature	170 °C
lignin content	27.2% on wood
carbohydrate content	66.5% on wood
acetyl content	1.3% on wood
species	*Pinus elliottii*

a line through Matthews' bulk period lignin content vs. carbohydrate content data. The difference between Matthews' value of 0.20 and Rekuner's (1980) value of 0.47 results from species differences in the two studies. The model predictions of Matthews' data are shown in Figures 8 and 9. The cooking conditions used by Matthews are shown in Table II. The comparison is again seen to be good.

Figures 2–9 illustrate that the kinetic equations used in the model are very good; however, there are some differences between the model predictions and experimental results which should be noted. In comparing the lignin vs. time curves with the carbohydrate vs. time curves, it can be seen that the lignin vs. time predictions are more accurate. This difference reflects the fact that the delignification kinetics have been much more thoroughly studied and are therefore better understood than the carbohydrate kinetics. In Figures 4 and 7 it can be seen that the model predictions of the alkali concentration during the initial period are high. This discrepancy is unimportant because the initial period kinetics are essentially independent of alkali concentration.

The model's ability to predict the effects of chip thickness was tested next. For this test the data of Akhtaruzzaman and Virkola (1979, 1980) and the data of Hatton and Keays (1973) were used.

Table III. Cooking Conditions Used by Akhtaruzzaman and Virkola (1979, 1980)

	case 1	case 2	case 3
effective alkali concentration	19% on wood (NaOH)	22% on wood (NaOH)	25% on wood (NaOH)
sulfidity	30%	30%	30%
heating time	60 min	60 min	60 min
cooking time	120, 211, 301 min	120, 211, 301 min	120, 211, 301 min
liquor/wood ratio	4 L/kg	4 L/kg	4 L/kg
cooking temperature	170 °C	170 °C	170 °C
lignin content	27% on wood	27% on wood	27% on wood
carbohydrate content	67.7% on wood	67.7% on wood	67.7% on wood
acetyl content	1.3% on wood	1.3% on wood	1.3% on wood
species	*Pinus silvestris*		

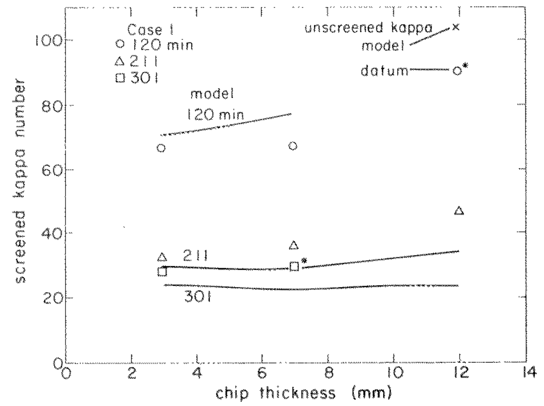

Figure 10. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) screened kappa data.

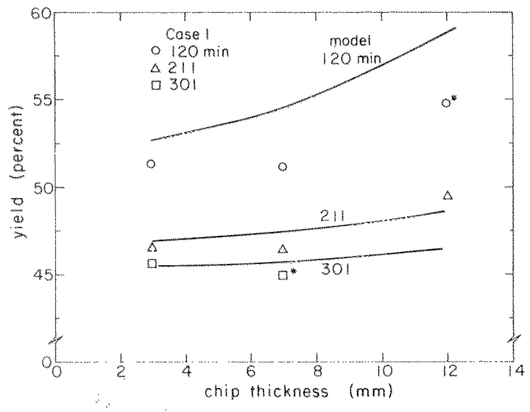

Figure 11. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) yield data.

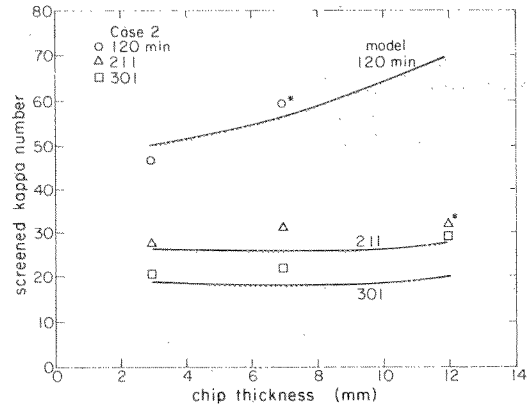

Figure 12. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) screened kappa data.

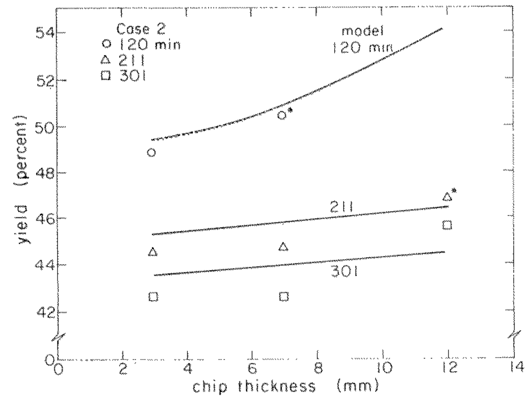

Figure 13. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) yield data.

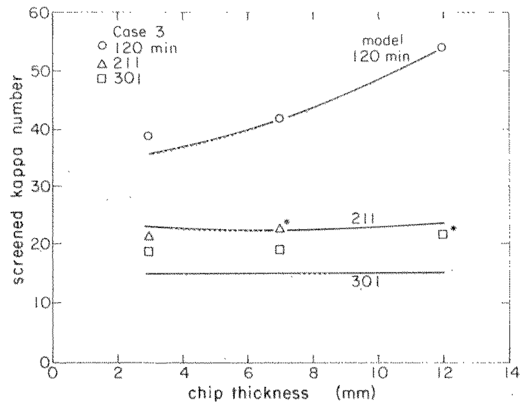

Figure 14. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) screened kappa data.

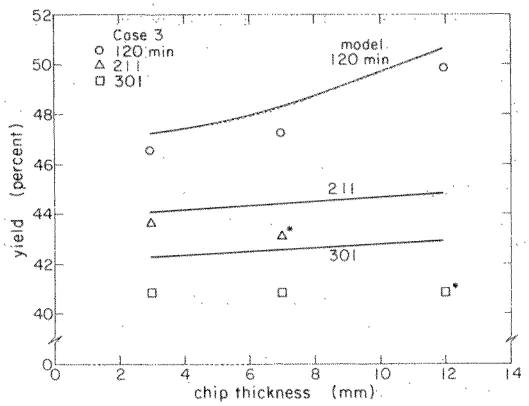

Figure 15. Model predictions and Akhtaruzzaman and Virkola's (1979, 1980) yield data.

The cooking conditions used by Akhtaruzzaman and Virkola are given in Table III. Figures 10 through 15 show the model predictions and data of screened kappa number vs. chip thickness and of yield vs. chip thickness for the three pulping conditions studied. The difference in these three pulping conditions is the effective alkali concentration. Akhtaruzzaman and Virkola ran one other experiment on chips 12 mm thick and 33 mm long with the pulping conditions shown in Table III except with a 28%

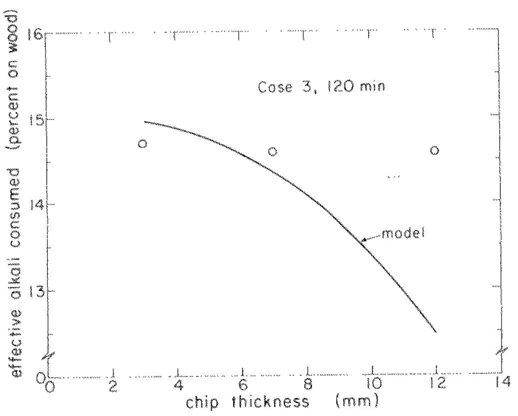

Figure 16. Model prediction and Akhtaruzzaman and Virkola's (1979, 1980) effective alkali concentration data.

effective alkali charge. The results from this experiment are anomalous and are not consistent with their other experimental results, and therefore they were not used to check the model.

The starred (*) points in Figures 10–15 are results of experiments with chips 33 mm in length corrected to 24 mm using the correlation equations of the authors, which lower the kappa numbers by 2.8 and the yield by 0.69. The rest of the points are data for chips 24 mm in length. The model screened kappa numbers are calculated from the lignin content of the modeled "chip" excluding the area in the center of the chip whose weight equals the experimental reject value. The kappa numbers are calculated by dividing the weight percent of the lignin on the accept pulp by 0.15. It can be seen that the model generally predicts the experimental results well.

The model predicts that the effect of chip thickness on kappa and yield is negligible at long cooking times, but the data show that this is not true for all pulping conditions (see Figures 10–13). There are two possible explanations for the difference. First, Akhtaruzzaman and Virkola state that the thicker chips have a higher percentage of knot wood than the thin chips, and they speculate that the thicker chips contain more compression wood and tension wood than the thin chips. These types of wood pulp slower than normal wood. It is not surprising, therefore, that the model, which assumes that the chips are uniform in composition, predicts kappa numbers and yields that are lower than the values measured in thick chips at long cooking times. Second, the conditions at the center of the chip are suitable for condensation reactions to take place. Work published by Hartler (1978) shows that lignin condenses when the cooking liquor lignin concentration is high and the alkali concentration is low.

High lignin concentration and low alkali concentration in the cooking liquor exist at the center of a thick chip during pulping. For example, the model predicts that in 12-mm chips pulped in 19% effective alkali liquor to an H factor of 540, the center effective alkali concentration is only 0.02 M while the concentration in the bulk phase is 0.68 M. At this same time all the initial regime lignin has reacted, and because the diffusivity of lignin oligomers in wood is certainly low, we can expect the cooking liquor lignin concentration at the chip center to be high. The presence of condensed lignin will result in a higher lignin content than predicted by assuming that all the delignification reactions are irreversible.

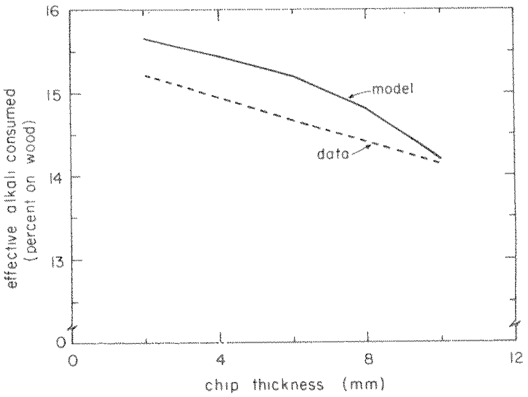

Figure 17. Model prediction and Hatton and Keays' (1973) effective alkali concentration data.

Table IV. Cooking Conditions Used by Hatton and Keays (1973)

effective alkali concentration	22% on wood as NaOH
sulfidity	25%
heating time	135 min
cooking time	210 min
liquor/wood ratio	4.6 L/kg
cooking temperature	170 °C
lignin content	27.8% on wood
carbohydrate content	70.0% on wood
acetyl content	1.0% on wood
species	*Tsuga heterophylla*

The model does not predict the experimental result that the consumption to effective alkali is independent of chip thickness (Figure 16). This result is surprising and is not substantiated by other studies on the effect of the chip thickness (Hatton and Keays, 1973; Colombo et al., 1960) (see Figure 17). Furthermore, Akhtaruzzaman and Virkola found that when chips of different dimensions are pulped together, higher rejects, higher yields, and lower screened kappa numbers are obtained than are predicted from the data obtained by pulping the chips individually. The authors explain this result, and we think correctly, by saying that when chips of different dimensions are pulped together, the smaller chips consume alkali at the expense of the larger chips. As a result, in mixtures, the small chips are overcooked and the large chips are undercooked as compared to what they would be if pulped individually. This consequence is inconsistent with the experimental result that the alkali consumption is independent of chip thickness but is consistent with the model prediction shown in Figure 16. The difference between the model prediction and the experimental result shown in Figure 16 may therefore be attributed to the difficulty in measuring the effective alkali concentration in black liquor as mentioned earlier.

Hatton and Keays (1973) measured the effect of chip thickness on hemlock and spruce pulp properties. To test the model on Hatton's data, an adjustment in the bulk delignification reaction rate was made. Hatton's data show that spruce and hemlock have equal reaction rates, and Kleinert's kinetic study (1966) on spruce shows that the bulk delignification reaction rate in spruce is greater than eq 11 predicts. The adjustment, then, was simply to increase the bulk delignification reaction rate term, eq 11, by 20% so that it predicts Kleinert's data.

The cooking conditions used by Hatton are shown in Table IV. Figures 17–19 are plots of alkali consumption, screened kappa, and yield vs. chip thickness for the hemlock experiments. The experimental results are for chips 41.4 mm in length. In Figures 18 and 19 the actual data are presented. These data were obtained from Ludden's Ph.D. thesis (1977). In Figure 17 Hatton's correlation of the data is shown. The correlation coefficient, R^2, for Hatton's regression line is only 0.58, which reflects the

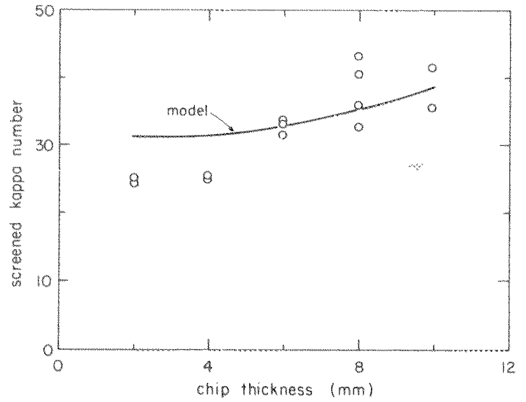

Figure 18. Model prediction and Hatton and Keays' (1973) screened kappa data.

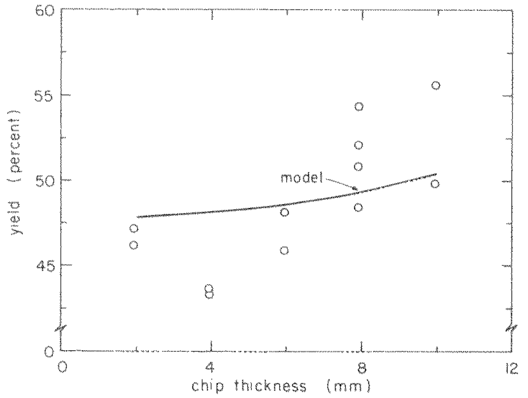

Figure 19. Model prediction and Hatton and Keays' (1973) yield data.

Table V. Pulp Properties of Spruce and Hemlock Pulps, Chip Length of 41.4 mm, Reported by Hatton and Keays (1973)

	hemlock			spruce		
chip thick, mm	screen kappa	yield, %	screen rejects, %	screen kappa	yield, %	screen rejects, %
2	24.3	46.65	0.2	23.0	47.4	0.1
4	24.35	43.55	0.3	30.3	49.4	1.0
6	31.67	47.3	3.6	35.0	54.0	10.3
8	37.03	51.28	9.15	37.0	58.4	19.0
10	37.25	52.55	12.3	39.0	61.1	22.8

difficulty in measuring alkalinities in the pulping liquor. Hatton's data are variable for thicker chips and are sometimes inexplicable (for example, the three point drop in yield in going from 2 mm to 4 mm of chips shown in Figure 19). Therefore, it is difficult to know the accuracy of the model predictions. It can be seen from Figures 17–19 that the model predicts very close to or within the range of all the experimental data except for the 2-mm and 4-mm screened kappa data, and even here the difference between the experimental data and model predictions is only six points.

The model failed to predict Hatton and Keays's spruce results, and this failure can be explained by reference to Table V. The 10-, 8-, and 6-mm spruce chips had high yields and high rejects with low screened kappa numbers compared to the hemlock chips. This means that the lignin profile in the thick spruce chips is very sharp.

The most sensible explanation of Hatton's spruce data is that the impregnation of the chips is poor. The penetration in spruce has been shown to be slow (Stone, 1956). Furthermore, Hatton and Keays used laboratory cut chips, which have been shown to yield higher rejects than commercial chips (Colombo et al., 1964), presumably because of the enhanced penetration in the highly fissured commercial cut chips. The assumption of good impregnation incorporated in the model may not be appropriate for the laboratory cut spruce chips.

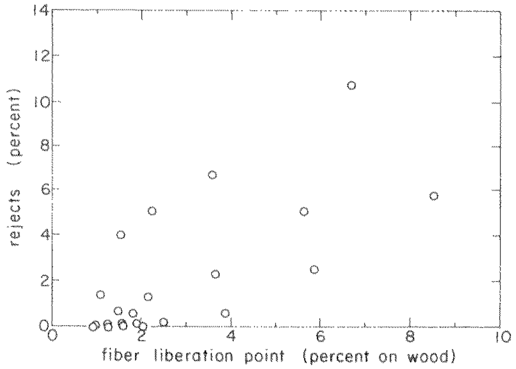

Figure 20. Correlation between the reject data of Akhtaruzzaman and Virkola (1979, 1980) and the fiber liberation point.

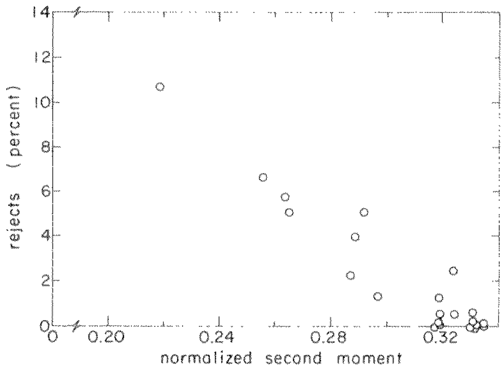

Figure 21. Correlation between the reject data of Akhtaruzzaman and Virkola (1979, 1980) and the normalized second moment.

Rejects from Oversized Chips

In pulping of oversized chips it is generally believed that those fibers whose lignin content is above a critical level, called the fiber liberation point, will not be liberated from the chip and will form a screening reject. Values of the fiber liberation point typically are about 9% on wood (Tyler, 1981).

When simulating the data of Akhtaruzzaman and Virkola (1979, 1980) and Hatton and Keays (1973), it was noted that the fiber liberation point is not constant. Figure 20 is a plot of reject values measured experimentally by Akhtaruzzaman and Virkola vs. the fiber liberation point predicted by the model with the assumption that the reject is the area in the center of the chip whose weight equals the experimental reject value. It can be seen that the range of fiber liberation points is quite large and the values for the fiber liberation points are lower than expected. This same conclusion is evident in Tyler's (1981) predictions of screen rejects with a fiber liberation of kappa 98.

It was suggested by Ricker (1981) that the normalized second moment (NSM) of the lignin profile in the chips might correlate with rejects. The NSM is defined as

$$\mathrm{NSM} = \int_0^1 L\chi^2 \, d\chi \Big/ \int_0^1 L \, d\chi$$

which L is the lignin content and χ is the dimensionless distance from the chip center. The second moment of a distribution is equivalent to the variance of a Gaussian distribution and as such the smaller the NSM, the steeper

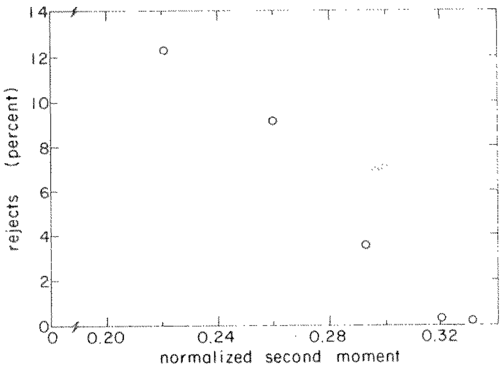

Figure 22. Correlation between the reject data of Hatton and Keays (1973) and the normalized second moment.

the lignin profile. A plot of the lignin NSM vs. the experimental reject level measured by Akhtaruzzaman and Virkola is shown in Figure 21. It can be seen that the correlation is very good, $R^2 = 0.90$. Hatton and Keays reject data give similar results (Figure 22).

At first it seems strange that the reject levels depend not on the absolute value of lignin content at the chip center, but on the profile of the lignin content in the chip. The physical explanation for the good correlation between the NSM and the reject levels may relate to what was said earlier about condensation reactions. Those chips with the lowest NSM, and thus the steepest lignin profiles, have had during the cook a time when the alkali concentration is low and the liquor concentration of lignin is high at the center of the chip. Thus, it is those chips with the lowest NSM in which lignin has been condensing. The condensing lignin may increase the bonding between fibers, thus lowering the fiber liberation from that value observed in the absence of condensation reactions. Experiments will have to be performed to confirm if the condensed lignin increases the fiber liberation point.

Summary

A theoretical model of the kraft pulping process has been developed and has been shown to be able to predict, a priori, with good accuracy, the pulping behavior of softwoods cooked under a variety of conditions. In the development of the model, kinetic and diffusion rate equations were derived from literature data. These equations were used in the partial differential equations describing the combined kinetics and diffusion of chemicals within a pulp chip. The differential equations were solved numerically.

The model predictions were compared with kappa number, yield, and residual alkali data from cooks in which the pulping rates were kinetically controlled and in which the pulping rates were partially mass transfer controlled. In general the comparison is good.

Results of the model show that the fiber liberation point cannot be used to predict reject level, but the normalized second moment (NSM) of the lignin profile correlates very well with reject levels. The good correlation is suggested to be a consequence of the relationship between the NSM and the condensation of lignin at the center of thick chips.

Experimental work is now being done to improve the expression used for the alkali diffusivity and to relax the perfect impregnation assumption. The model is being modified to accommodate a distribution of chip thickness and digester temperature gradients. Because the model makes a priori predictions, it will be used with a pattern search program to optimize the pulping conditions. The alkali and temperature vs. time curves will be adjusted to maximize, or minimize, objective functions such as the production rate at a given kappa number, the carbohydrate to lignin selectivity at a given kappa number for a given production rate, and the reject levels at a given kappa number for a given production rate. The optimization will be done for various chip thickness distributions. The model will also be used to investigate the potential performance of novel digester configurations.

Literature Cited

Akhtaruzzaman, A. F. M.; Virkola, N.-E. *Pap. Puu* **1979**, *61*, 578, 629, 737, 805.
Akhtaruzzaman, A. F. M.; Virkola, N.-E. *Pap. Puu* **1980**, *62*, 15, 70, 297.
Aurell, R.; Hartler, N. *Svensk Papperstidn*. **1965**, *68*, 59.
Bailey, R. N.; Maldonado, P.; McKibbins, S. W.; Tarver, M.-G. *Tappi* **1969**, *52*, 1272.
Brauns, F. E.; Grimes, W. S. *Pap. Trade J.* **1939**, *108*, 40.
Colombo, P.; Corbetta, D.; Pirotta, A.; Ruffini, G. *Svensk Papperstidn*. **1960**, *63*, 457.
Colombo, P.; Corbetta, D.; Pirotta, A.; Ruffini, G. *Svensk Papperstidn*. **1964**, *67*, 505.
Daleski, E. J. *Tappi* **1965**, *48*, 325.
Eriksson, O.; Goring, D. A. I.; Lindgren, B. O. *Wood Sci. Technol.* **1980**, *14*, 267.
Finlayson, B. A., "Nonlinear Analysis in Chemical Engineering"; McGraw-Hill: New York, 1980; Chapter 5.
Gierer, J. *Wood Sci. Technol.* **1980**, *14*, 241.
Hartler, N.; Onisko, W. *Svensk Papperstidn*. **1962**, *65*, 905.
Hartler, N.; Ostberg, K. *Svensk Papperstidn*. **1959**, *62*, 524.
Hartler, N. *Pap. Puu* **1962**, *44*, 365.
Hartler, N. *Svensk Papperstidn*. **1978**, *81*, 457.
Hatton, J. V. *Tappi* **1973**, *56*, 97.
Hatton, J. V.; Keays, J. L. *Pulp Pap. Mag. Can.* **1973**, *74*, 79.
Hindmarsh, A. C. "GEAR...Ordinary Differential Equation System Solver"; UCID-30001 Rev. 3; Lawrence Livermore Laboratory, Dec 1974.
Johnsson, L. *Acta Polytech. Scand. Math. Comput. Mach. Ser.* **1971**, *22*, 1.
Kerr, A. J. *Appita* **1970**, *24*, 180.
Kerr, A. J.; Uprichard, J. M. *Appita* **1976**, *30*, 48.
Kleinert, T. N. *Tappi* **1966**, *49*, 53.
Kleppe, P. J. *Tappi* **1970**, *53*, 35.
Lemon, S.; Teder, A. *Svensk Papperstidn*. **1973**, *76*, 407.
Lightfoot, R. G.; Premont, P. *Pulp Pap. Mag. Can.* **1962**, *63*, T141.
Ludden, J. Ph.D. Thesis, University of Washington, Seattle, WA, 1977.
Matthews, C. H. *Svensk Paperstidn*. **1974**, *77*, 629.
McKibbins, S. W. *Tappi* **1960**, *43*, 801.
Norden, S.; Teder, A. *Tappi* **1979**, *62*, 49.
Olm, L.; Tistad, G. *Svensk Papperstidn*. **1979**, *82*, 458.
Rekunen, S.; Jutila, E.; Lahteenmaki, E.; Lonnberg, B.; Virkola, N.-E. *Pap. Puu* **1980**, *62*, 80.
Ricker, N. L. Personal Communication, University of Washington, 1981.
Rydholm, S. "Pulping Processes"; Wiley: New York, 1965a; p 630.
Rydholm, S. "Pulping Processes"; Wiley: New York, 1965b; p 603.
Rydholm, S. "Pulping Processes"; Wiley: New York, 1965c; p 586.
Smith, C. C. Ph.D. Thesis, Purdue University, Lafayette, IN, 1975.
Stone, J. E. *Pulp Pap. Mag. Can.* **1956**, *57*, 139.
Stone, J. E. *Tappi* **1957**, *40*, 539.
Teder, A.; Tormund, D. *Svensk Paperstidn*. **1973**, *76*, 607.
Tyler, D. B. M.S. Thesis, University of Idaho, Moscow, ID, 1981.
Vroom, K. E. *Pulp Pap. Mag. Can.* **1957**, *58*, 228.
Wahlman, M. *Pap. Puu* **1967**, *49*, 107.
Wilder, H. D. Daleski, E. J. *Tappi* **1965**, *48*, 293.
Yllner, S.; Ostberg, K.; Stockman, L. *Svensk Papperstidn*. **1957**, *60*, 795.

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