Dynamic modeling of kraft pulping of southern pine based on on-line liquor analysis

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ABSTRACT

A nonlinear dynamic model of kraft pulping of southern pine, based on real-time liquor analysis, has been developed. The liquor analysis method eliminates the difficulty of having to withdraw pulp samples under high-pressure and -temperature cooking conditions. Effective alkali, sulfide concentration, total solids, and the lignin content of the cooking liquor are measured on-line using conductivity, ion chromatography, refractive index, and ultraviolet absorbance analysis. A material balance model is used to predict the wood composition every 5 minutes from the liquor analysis data.

Kraft cooking experiments with several initial effective alkali and sulfidity levels were conducted in a laboratory digester on screened softwood (southern pine) chips. The model parameters identified from the experimental data are comparable with the literature values and are within the parameter range for kraft pulping. The validity of the mathematical model was tested, and the model was found to be in good agreement with experimental data. This lumped-parameter model, in conjunction with liquor analysis, can be used in process monitoring, estimation, and control applications.

Application:

This model, in conjunction with liquor analysis, can be used in process monitoring, estimation, and control of a kraft digester.

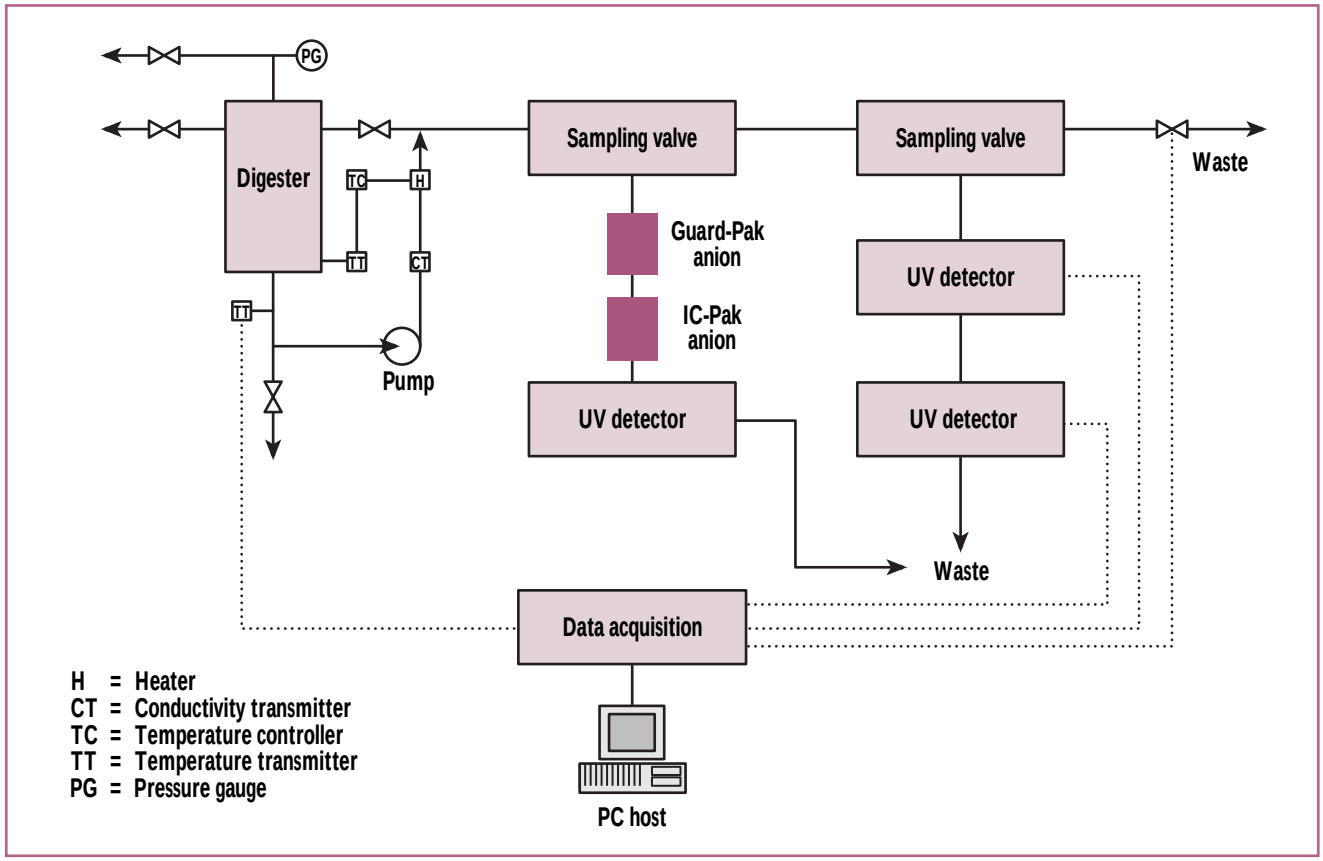
THE DIGESTER IS ONE OF THE major unit operations in the chemical pulping process, and its proper control is essential to produce uniform and quality paper products at minimum cost. In addition, environmental concerns and regulations in the paper industry necessitate better monitoring and control of pulping processes to achieve extended delignification. Better control of pulping results not only in improved pulp quality but also in reduced toxic effluent from bleach plants and increased energy savings.

Many kraft pulp mills presently use open-loop, feed-forward control strategies using *H*-factor analysis *(1)*, with or without some empirical models. The empirical models are inefficient in controlling the kraft process, and as a result, there is wide variation in kappa number and yield. Several empirical models are available in the literature correlating the rate of delignification with process variables *(2, 3)*. Studies on the development of these models generally have used wood meal or wood shavings and very high liquor-to-wood ratios to avoid the problems associated with diffusion of chemicals into the wood chips and to maintain the liquor composition at a constant value during the cook. Furthermore, these studies address only the bulk-phase delignification.

One of the frequently used empirical models *(3)* relates the pulp yield/kappa number with *H*-factor and effective alkali charge. This model correlates selected softwood and hardwood delignification data over a limited range of kappa number and yield. The parameters involved in this model depend on the wood species used. The theoretical model developed by Gustafson *(4)* involves solving partial differential equations for the combined diffusion and kinetic effects within a wood chip. In this model, the alkali consumption is assumed to be linearly related to the delignification rate, and the sulfide concentration is assumed to be constant throughout the cook. The rates of lignin and carbohydrate dissolution are modeled in the initial, bulk, and residual phases.

The success of any of these models for control purposes depends on prior knowledge of the feed composition. This is one of the major difficulties encountered in the industry, since the feedstock quality is not well defined. Moreover, these models are capable of providing simple feed-forward control only, keeping the control loop open. The control problem is further complicated by the difficulty involved in on-line measurement of the controlled variable, kappa number. To provide closed-loop control, it is necessary to monitor the extent of reaction with time, but chip analysis from the digester is impractical, and blow-line pulp analysis has an unacceptable time delay for control purposes.

An alternative and practical method is to monitor the liquor composition for the extent of reaction. The on-line measurement of liquor properties, in conjunction with a dynamic model, can be used to estimate the key states and parameters of the system. Such a system has the capability of compensating for the unknown feedstock variations that occur from batch to batch. Use of such a sampling method requires a kinetic model based on measurable liquor properties. This paper addresses the development of a dynamic model for kraft pulping based on liquor analysis.



1. Schematic of the experimental setup

EXPERIMENTAL METHODS

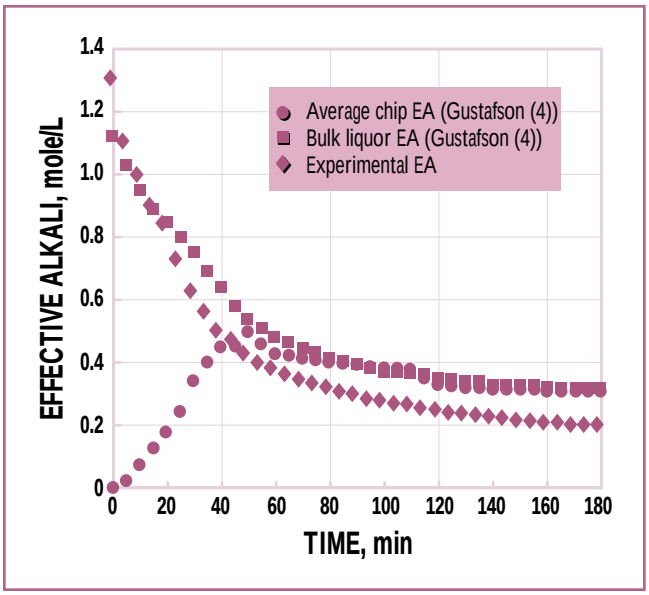
Figure 1 shows the experimental setup and the associated liquor analysis system used in data collection for kinetic modeling *(5)*. The experimental setup consists of a 6.5-L batch digester equipped with a liquor recirculation pump. The temperature in the digester is maintained by an independent controller, and the warmup rate can be varied by changing the setting in the controller. The recirculation line is equipped with a Rosemount series 78S platinum RTD temperature sensor, a Micro Motion Model D25 density/mass flowmeter, and a Rosemount 222 toroidal flow-through electrodeless conductivity sensor.

In addition to the above *in-situ* measurements, the setup is equipped with an on-line liquor sampling and analysis system. The liquor sampling system consists of two sample injection valves of 1-µL volume that extract liquor samples from the recirculation line every 5 min. One of the samples is diluted with water and injected into a Waters Model 481 Lambda-Max spectrophotometer (UV, λ=280 nm) and a Waters Model 410 differential refractometer (RI). The samples are diluted with water prior to injecting to avoid saturation of the measurement signal. Another sample is injected into an ion chromatographic (IC) column consisting of an anion packing using sodium borate/gluconate as eluent. The IC analysis is done using a Waters Model 440 dual-channel UV absorbance detector. The data collection from the *in situ* sensors, as well as from the extractive liquor sampling and analysis system, is done through a Keithley 570 data acquisition system and a Zenith 286 host computer. The extractive liquor sampling and analysis system permits determining total solids content, lignin content, and sulfide concentration. The repeatability of the analysis system is excellent, with typical variability being less than 1% of the reading in the operating range. All these analyses take less than 5 min for completion.

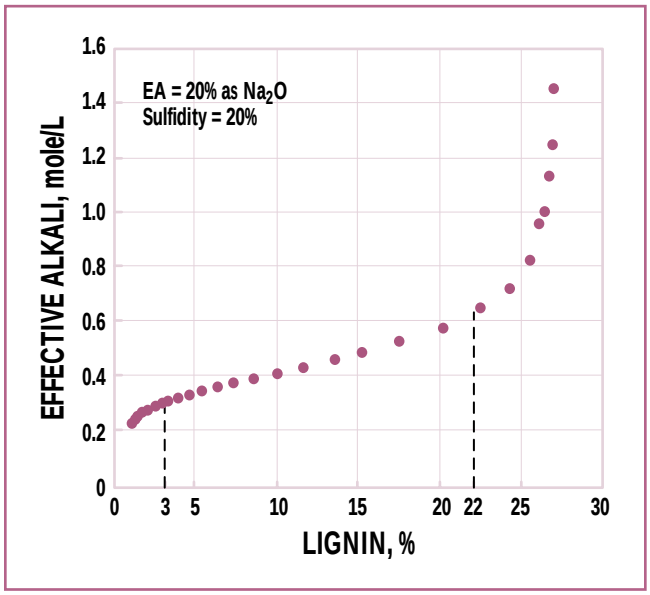
Batch cooks were carried out using screened southern pine chips of 3–5-mm thickness. The chips were loaded into the digester along with the pulping liquor at a liquor-to-wood ratio of 5.5:1. Synthetic white-liquor effective alkali concentrations (NaOH + 1/2 Na_2S) were varied between 14% and 20% as Na_2O based on ovendry (o.d.) wood, and the sulfidity varied from 20% to 30%. The sulfidity here is defined as the ratio of sodium sulfide to active alkali (NaOH + Na_2S), expressed as a percent on Na_2O basis. The digester was heated to the pulping temperature and held there for the appropriate period of time. The cooking temperature was reached in approximately 40 min. After completion of the cook, the chips were taken out, washed thoroughly, and analyzed for yield and kappa number.

LIQUOR ANALYSIS

Liquor analysis techniques provide



2. Comparison of bulk liquor EA and average chip EA concentrations during a kraft cook (EA = 18%, S = 24%, temp. = 170°C)



3. Effective alkali vs. lignin percent, showing the transition between different delignification periods

us with information on extent of delignification, effective alkali and sulfide consumption, and total dissolved solids concentration in the liquor during pulping in real time. The available kinetic models in the literature describe the degree of delignification based only on off-line analysis of pulp samples. Hence the availability of an on-line liquor analysis technique can greatly enhance the monitoring of the pulping process. In this study, conductivity, ion chromatography, refractive index, and UV absorbance analysis are directly correlated to measure the effective alkali, sulfide concentration, total solids, and lignin content of cooking liquor, respectively. The relevant equations relating the measurements to pulp and liquor properties are discussed in detail elsewhere *(6)*.

MATERIAL BALANCE MODEL

The material balance model previously developed *(7)* is used to calculate the lignin content and yield of pulp at any time during the cook. The material balance model essentially relates the liquor property measurements to chip composition inside the digester. The pulp yield can be found from the dissolved wood substance concentration (as indicated by the RI measurement) and the mass of wood chips charged. The pulp lignin content at any time during the cook can be found from the lignin concentration in the liquor and the initial lignin content of wood.

There are two parameters in the material balance model that vary with wood species and pulping conditions. These parameters are the ultraviolet-absorption calibration factor and the refractive-index reaction products weighting factor. The parameters are identified so that they minimize the deviation between measured and estimated yield and kappa number. The identification of these parameters involved generating on-line measurement data by performing several cooks with different cook end times. The material balance model parameters do not change drastically (±0.2%) with cooking conditions used in this study. The identified parameters are then used to determine the chip composition during a cook from the on-line liquor analysis values.

MODEL DEVELOPMENT

The kraft pulping of wood chips is a complex phenomenon. To model the reactions based on liquor composition, simplifying assumptions are needed. The assumptions made in the development of this model are given below:

- The liquor is in pseudo-equilibrium with the chips. Thus, the liquor composition can be used to infer chip composition.
- The chips used in this study had a length-to-thickness ratio of 5:1. In alkaline pulping, diffusion of inorganics takes place in all three directions in the chip at almost equal rates *(8)*; hence, it is assumed that chip thickness is the critical dimension. Furthermore, in this study (chip thickness 3–5 mm), it was found that diffusion effects were pronounced only in the initial phase of delignification. This was confirmed by simulating the Gustafson model *(4)* for the chip size used. The concentration profile with time for (a) bulk liquor effective alkali (EA), (b) average EA concentration inside the chip obtained from the Gustafson model, and (c) experimental bulk liquor EA concentration obtained during a typical kraft cook is shown in **Fig. 2**. This figure shows that diffusion effects are pronounced only in the initial heating period and are negligible

in the bulk and residual periods (i.e., bulk liquor EA concentration is the same as inside the chips). The liquor phase is assumed to be homogeneous and well stirred in all subsequent delignification periods. The digester is considered to be a continuously stirred tank reactor (CSTR) system, with the mass-transfer coefficient from the bulk phase to the chip phase being infinite.

- The time for heat transfer is considered to be much less than other characteristic times of the pulping process, and hence no temperature gradients exist within the chips.
- The major components of wood are lignin, carbohydrates, and extractives. This assumption is justified by the fact that the relative degradation rates of different carbohydrates are not altered significantly by normal changes in pulping conditions *(9, 10)*. Presently there are no on-line analytical techniques for determining different carbohydrate fractions; hence, they are treated as a single component in wood.
- Pulping reactions are irreversible. This assumption eliminates the need to model the condensation reactions at the end of the cook, when the lignin concentration in the liquor is high and the alkali concentration is low.
- The sulfide present in the cooking liquor completely hydrolyzes to hydrosulfide. It has been reported that the hydrosulfide ion rather than the sulfide ion is the primary reactant in the blocking reaction *(11)*.
- Extractives and other rapidly reacting components of the wood are assumed to dissolve immediately on contact with the cooking liquor *(12)*. This is apparent from an immediate reduction in alkali concentration at the start of the cook.

DELIGNIFICATION KINETICS

Alkaline delignification is divided into three phases: initial, bulk, and residual. The complex structural nature of lignin results in sharp rate transitions during kraft pulping *(8)*. These sharp transitions form the basis for the different phases of delignification. Each of the delignification phases has different rate constants with respect to the concentration of cooking chemicals. The initial phase is characterized by rapid delignification and large alkali consumption. During the bulk phase, most of the lignin is removed with higher selectivity. The point of transition from initial to bulk phase occurs at a lignin content of 20–22%. The rate of delignification during the residual phase is much lower than in the bulk phase *(13)*.

The point of transition from initial to bulk and bulk to residual delignification is defined as the intersection between two straight-line portions of a plot of alkali concentration vs. lignin yield. The transitions from the initial to the bulk phase and from the bulk to the residual phase were chosen as 22% and 3% lignin on wood, respectively, and were obtained from experimental data, as shown in **Fig. 3**. The reaction rates in all the phases are first order with respect to the lignin content, expressed as percent on original o.d. wood *(14)*.

The initial phase is characterized by the cleavage of α- and β-aryl ether bonds. Initial-phase delignification depends only on diffusion and does not depend on the effective alkali concentration and sulfidity *(12)*. The rate of delignification is dependent only on temperature, provided that the liquor pH is greater than 12 *(15)*. Under typical kraft cooking conditions, the pH is always greater than 12 during the initial phase, and hence a model similar to that developed by Olm and Tistad *(12)* can be applied for the initial phase. Thus, the initial phase delignification can be represented as follows:

$$-\frac{dL}{dt} = A_i \sqrt{T}\, e^{(-E_i / RT)}\, L \qquad (1)$$

where

L = lignin content, % on wood
T = temperature, K
t = time, min
A_i = frequency factor in the initial phase, $min^{-1}\ K^{-1/2}$
E_i = activation energy in the initial phase, cal/g·mole
R = gas constant, cal/g·mole K.

Bulk-phase delignification is generally modeled as first order with respect to lignin *(16, 17)*. The driving force for delignification reactions are the bulk liquor effective alkali and hydrosulfide concentrations. In Gustafson's model *(4)*, the sulfide concentration was assumed to be constant throughout the cook, due to its low consumption and low dependence of delignification on sulfide content under the conditions applicable to the model. But in a more detailed kinetic model developed at Purdue *(18)*, the dependence of delignification on hydrosulfide ion concentration has also been accounted for and was found to fit all the data used in their study. In this study, the data obtained using ion chromatographic techniques indicate a noticeable influence of hydrosulfide ions on bulk delignification. Hence, a form similar to the Purdue model was chosen for the bulk phase and is represented as:

$$-\frac{dL}{dt} = \left\{ A_{b,1} e^{\left(-E_{b,1}/RT\right)} [OH] + A_{b,2} e^{\left(-E_{b,2}/RT\right)} [OH]^{0.5} [HS]^{0.5} \right\} \quad (2)$$

where

$A_{b,1}$= first frequency factor in the bulk phase, min^{-1} $(mole/L)^{-1}$

$A_{b,2}$= second frequency factor in the bulk phase, min^{-1} $(mole/L)^{-1}$

$E_{b,1}$= first activation energy in the bulk phase, cal/g·mole

$E_{b,2}$= second activation energy in the bulk phase, cal/g·mole

[OH]= bulk liquor effective alkali concentration, mole/L

[HS]= bulk liquor hydrosulfide ion concentration, mole/L.

Residual-phase delignification is characterized by a rate much slower than that in the bulk phase. The model expression used in this phase is the same as in the Gustafson model. It is adopted from Norden and Teder *(14)* and is given as:

$$-\frac{dL}{dt} = A_r e^{\left(-E_r/RT\right)} [OH]^{0.7} L \quad (3)$$

where

A_r= frequency factor in the residual phase, min^{-1} $(mole/L)^{-0.7}$

E_r= activation energy in the residual phase, cal/g·mole.

CARBOHYDRATE KINETICS

The carbohydrate reaction rate is a linear function of the lignin reaction rate *(9, 13)*. The initial-phase carbohydrate reaction is modeled as a lumped-parameter system based on the bulk liquor effective alkali concentration. The expression is:

$$-\frac{dC}{dt} = q_i [OH]^{0.11} \frac{dL}{dt} \quad (4)$$

The carbohydrate reaction rates in both the bulk and residual phases are modeled as a linear function of the lignin reaction rate. The general model expression is:

$$-\frac{dC}{dt} = q_b \frac{dL}{dt} \quad (5)$$

and

$$-\frac{dC}{dt} = q_r \frac{dL}{dt} \quad (6)$$

where

C = carbohydrate, % on wood

q_i, q_b, q_r = the proportionality constants in the initial, bulk, and residual phases.

EFFECTIVE ALKALI CONSUMPTION

Effective alkali is consumed by both lignin and carbohydrate as well as by extractives and acetyl groups present in the wood. Effective alkali drops rapidly during the initial phase due to consumption by extractives and acetyl groups and due to dilution by wood moisture. The drop in alkali concentration during the initial warmup period is also due to carbohydrate reactions, which are rapid even at 100°C. The effective alkali consumption in the initial phase was modeled as a function of lignin, and the expression is given as:

$$-\frac{d[OH]}{dt} = b_{i,OH} L \quad (7)$$

where

$b_{i,OH}$= constant relating effective alkali concentration to lignin.

The rate of change of EA concentration in the bulk and residual phases is related to the rate of reaction of the wood components. After the initial-phase delignification, lignin and carbohydrates are the only major wood components involved in pulping reactions. Hence, the alkali consumption can be represented by:

$$-\frac{d[OH]}{dt} = \left[b_{b,1,OH} \frac{dL}{dt} + b_{b,2,OH} \frac{dC}{dt} \right] \bullet \frac{1}{r_{L/W}} \quad (8)$$

where

$r_{L/W}$ = liquor-to-wood ratio

$b_{b,1,OH}$= consumption of effective alkali by lignin, mole/g

$b_{b,2,OH}$= consumption of effective alkali by carbohydrates, mole/g.

HYDROSULFIDE CONSUMPTION

The presence of sulfide in the liquor improves the rate of delignification and therefore the pulp quality. Sulfide is assumed to be consumed only by lignin. This assumption is justified by the fact that the lignin dissolution is accelerated with sulfide, while the carbohydrate removal is comparatively unaffected *(11)*. Rydholm has also shown that nearly all of the sulfide consumed in the kraft process is combined with dissolved lignin. The sulfide consumption in the initial phase is modeled as a function of lignin and is given as:

$$-\frac{d[HS]}{dt} = b_{i,HS} L \quad (9)$$

where

$b_{i,HS}$= constant relating hydrosulfide concentration to lignin.

In the bulk and residual phases, the hydrosulfide consumption by lignin is modeled as a linear function of the dissolution rate of lignin. This model

form has also been used in the Purdue model *(18)* and is represented as:

$$-\frac{d[\mathrm{HS}]}{dt} = b_{\mathrm{b,\,HS}} \bullet \frac{dL}{dt} \bullet \frac{1}{r_{\mathrm{L/W}}} \qquad (10)$$

where

$b_{b,HS}$= consumption of hydrosulfide by lignin, mole/g.

PARAMETER IDENTIFICATION

The kinetic parameters to be identified in the model are the various activation energies, the frequency factors, and the stoichiometric coefficients representing the carbohydrate degradation as well as the alkali and hydrosulfide consumption. The reaction orders from the published literature data were used in the model development; an attempt to identify the reaction orders through optimization always resulted in values close to published values *(14, 18)*. The on-line liquor analysis developed at Auburn University, along with a material balance model, provided the necessary information about the wood dissolution products and consumption of chemicals.

Since the experimental data for lignin, carbohydrate, effective alkali, and hydrosulfide concentrations were available every 5 min and the concentration difference between two data points was linear, the differential equations reduce to an algebraic form. This algebraic system of equations can be handled easily when compared with the original differential form. The objective was to minimize the least-square errors between the actual measurements and the model predictions. To provide physical limits on the parameters, constrained optimization was performed. The experimental data from different cooks were used to identify the parameters. The identified parameter values are given in **Table I.**

Parameters	Optimized value	Equation reference
A_i, E_i	36.07, 9431.57	(1)
$A_{b,1}$, $E_{b,1}$	1.913×10^{15}, 34,266	(2)
$A_{b,2}$, $E_{b,2}$	4.95×10^{12}, 28,196	(2)
A_r, E_r	3.394×10^{8}, 19,826	(3)
q_i	2.12	(4)
q_b	0.665	(5)
q_r	0.55	(6)
$b_{i,OH}$	7.5×10^{-4}	(7)
$b_{b,1,OH}$, $b_{b,2,OH}$	5×10^{-3}, 1.2×10^{-2}	(8)
$b_{i,HS}$	4.28×10^{-5}	(9)
$b_{b,HS}$	7.08×10^{-4}	(10)

I. Optimized parameter values for the kinetic equations

Parameters	Current study	Literature values
A_i, E_i	36.07, 9431.57	36.02, 9552.88 *(4)*
$A_{b,1}$, $E_{b,1}$	1.913×10^{15}, 34,266	1.9179×10^{15}, 34,176 *(4)*
$A_{b,2}$, $E_{b,2}$	4.95×10^{12}, 28,196	4.95×10^{12}, 28,613 *(4)*
A_r, E_r	3.394×10^{8}, 19,826	3.385×10^{8}, 21,467 *(4)*
q_i	2.12	2.53 *(4)*
q_b	0.665	0.47 *(4)*
q_r	0.55	2.19 *(4)*
$b_{b,1,OH}$, $b_{b,2,OH}$	5×10^{-3}, 1.2×10^{-2}	4.15×10^{-3}, 9.88×10^{-3} *(18)*
$b_{b,HS}$	7.08×10^{-4}	9.76×10^{-4} *(18)*

II. Comparison of parameters from current study and literature values

RESULTS AND DISCUSSION

To verify the model with experimental data, the model equations (1 through 10), expressing the lignin and carbohydrate kinetics, along with effective alkali and hydrosulfide consumption equations, are integrated using the Adams method. The temperature of the digester rises from the initial value to a maximum specified value (T_{max}) in a particular period of time (t_{rise}). The linear rise in temperature during the warmup period was simulated from the temperature response curve obtained for a typical cooking experiment and is given in **Fig. 4**. The temperature profile during the rise period is calculated using the temperature–time relationship:

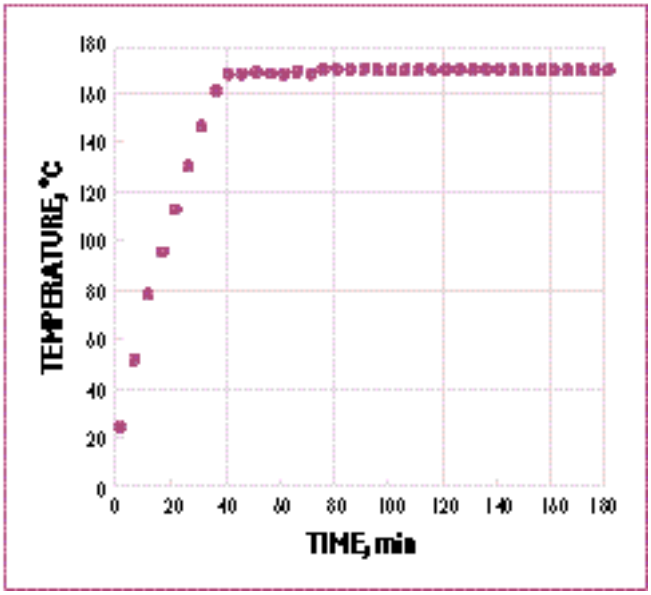
$$T = \begin{cases} 4.4035\,t + 29 & \text{for } 0 < t \le t_{\mathrm{rise}} \\ T_{\mathrm{max}} & \text{for } t > t_{\mathrm{rise}} \end{cases} \qquad (11)$$

where T is temperature in degrees Celsius and t is time in minutes. The accuracy of model predictions was compared with additional experimental data for lignin, carbohydrate, bulk liquor effective alkali, and hydrosulfide concentrations. The predicted and experimental values for different cases are presented in **Figs. 5–16**. The lignin predictions are good compared with the carbohydrate predictions. This is because the refractive index is a collective measure of all the dissolved solids in the liquor, while the lignin concentration was measured exclusively by the UV absorbance method. The predictions for the effective alkali and hydrosulfide concentration also fit the data well.

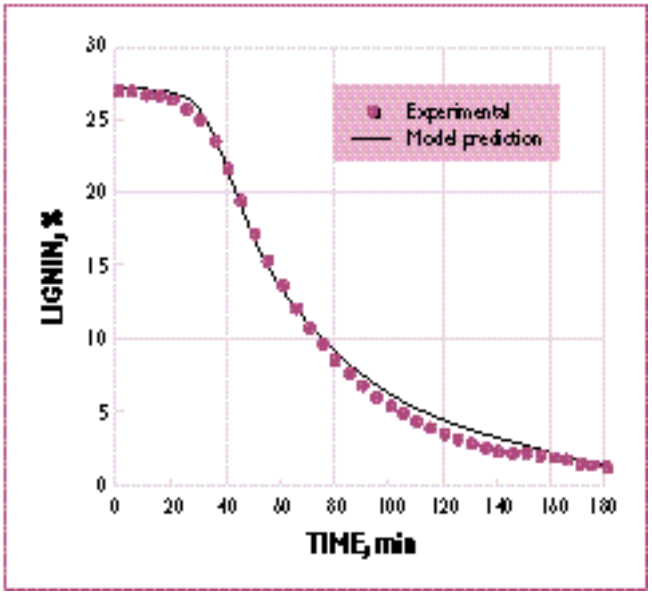
The delignification kinetic parameters obtained for the three delignification phases (initial, bulk, and residual) are comparable to the literature values and are within the

Description	EA=18% S=30% Model	EA=18% S=30% Exptl.	EA=20% S=20% Model	EA=20% S=20% Exptl.	EA=16% S=24% Model	EA=16% S=24% Exptl.
Kappa number	23.36	23.30	11.09	12.50	61.90	62.15
Yield, %	47.60	47.80	46.22	47.90	53.35	52.91

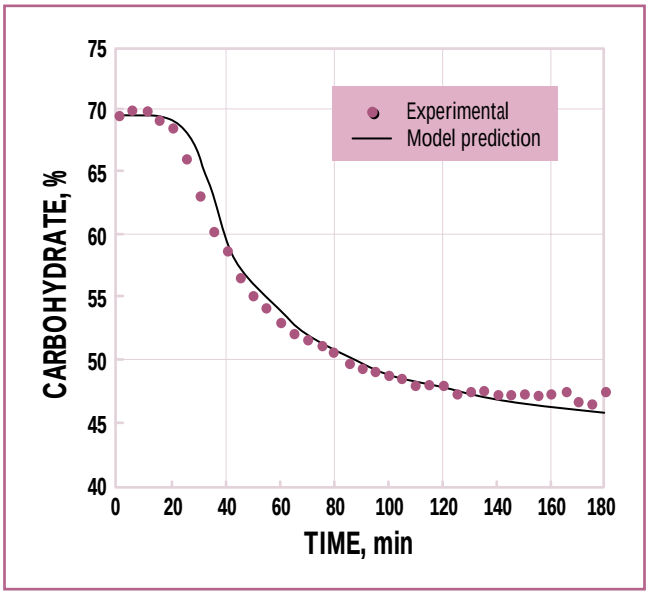
III. Experimental and predicted final pulp kappa number and yield



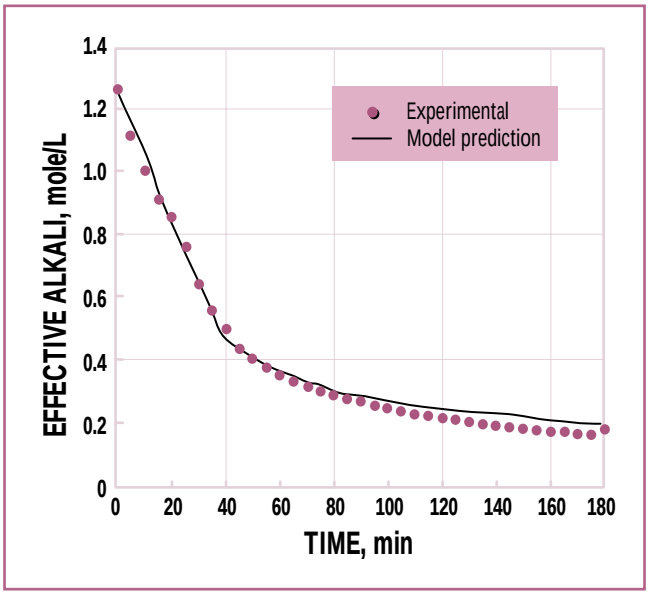
4. Temperature response curve for a typical cook



5. Model prediction and experimental lignin content (EA = 18%, S = 30%, temp. = 170°C)



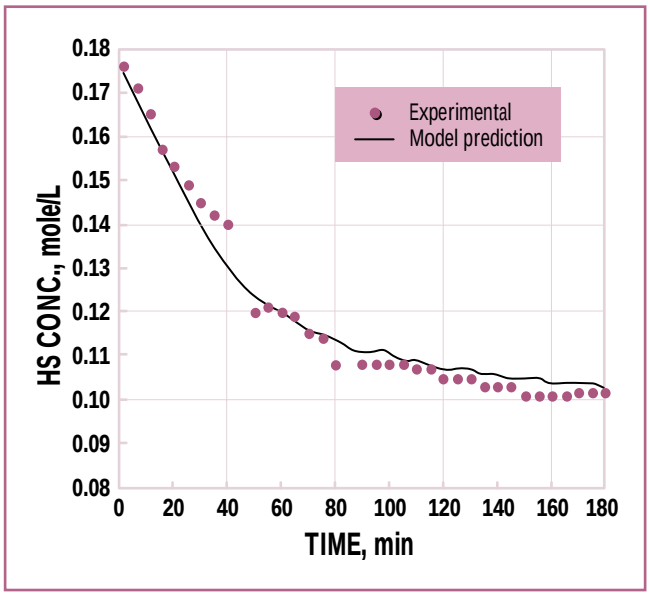
6. Model prediction and experimental carbohydrate content (EA = 18%, S = 30%, temp. = 170°C)



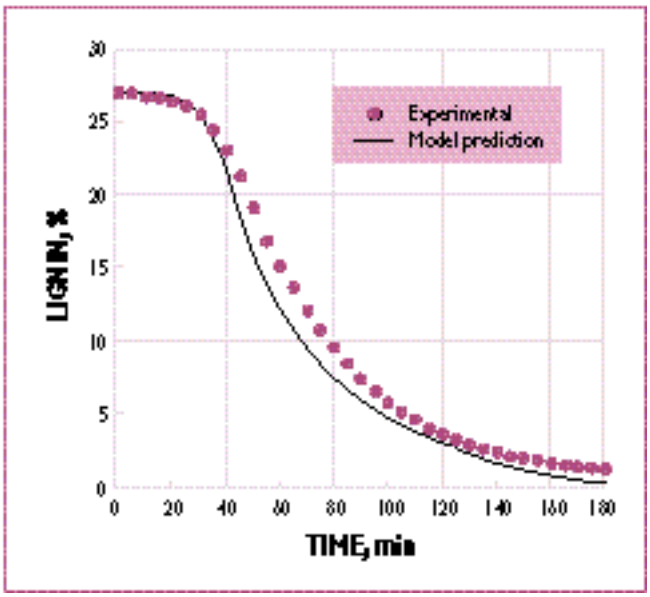
7. Model prediction and experimental EA concentration (EA = 18%, S = 30%, temp. = 170°C)

range of kraft pulping. For example, the bulk-phase activation energies in the present study are 34,266 and 28,196 cal/g•mole, respectively, while the Gustafson model values are 34,176 and 28,613 cal/g•mole. The carbohydrate kinetic parameters in the bulk and residual phases of delignification are also comparable to the published values. A comparison with published values of parameters in the initial phase of delignification is not possible, since the kinetics are modeled as a lumped-parameter system.

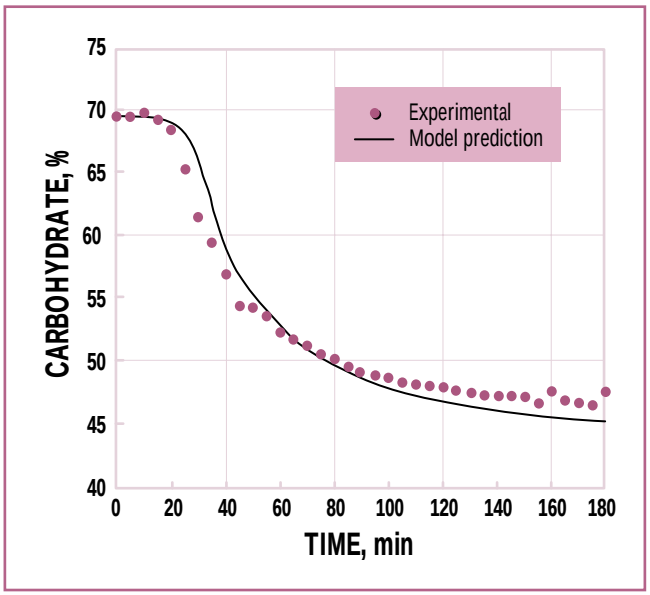
The consumption of effective alkali by lignin and carbohydrate in kraft cooks as reported by Rydholm



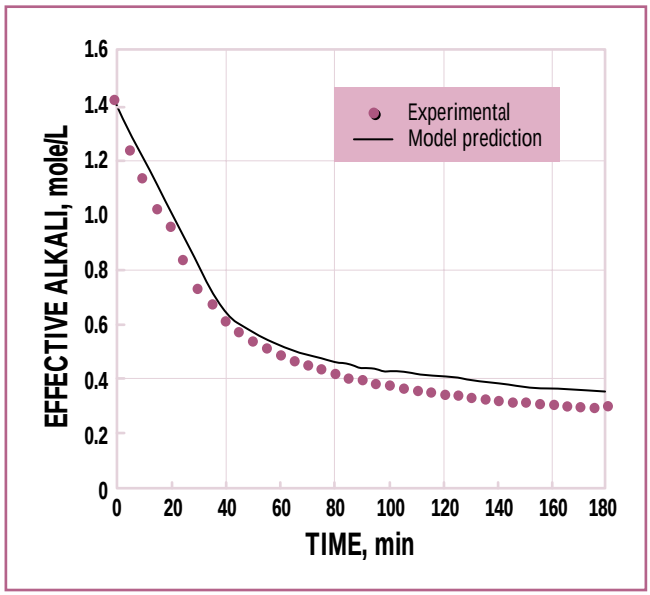
8. Model prediction and experimental HS concentration (EA = 18%, S = 30%, temp. = 170°C)



9. Model prediction and experimental lignin content (EA = 20%, S = 20%, temp. = 170°C)



10. Model prediction and experimental carbohydrate content (EA = 20%, S = 20%, temp. = 170°C)

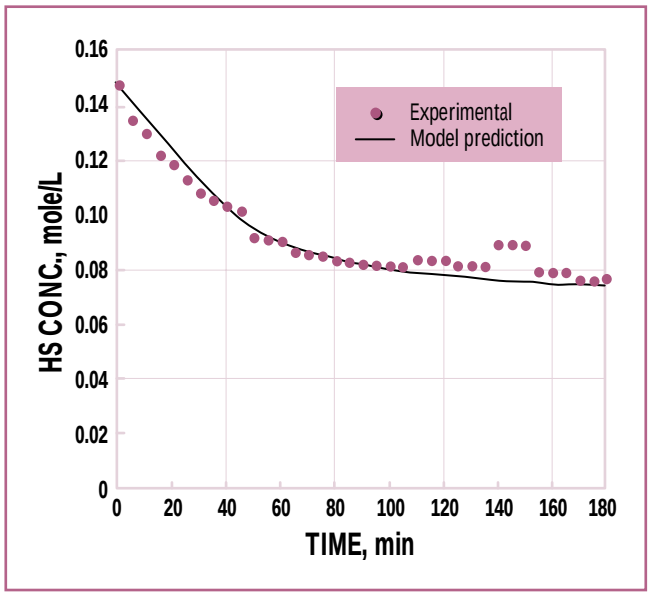


11. Model prediction and experimental EA concentration (EA = 20%, S = 20%, temp. = 170°C)

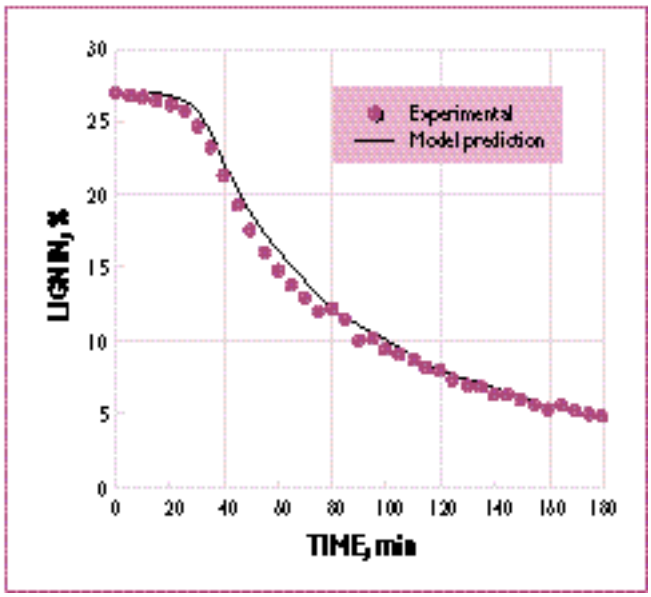
(11) is 0.04 kg for lignin and 0.095 kg for carbohydrates per kg o.d. wood used in pulping. The dissolved material at the end of a kraft cook consists of 0.24 kg of lignin and 0.24 kg of carbohydrate per kg o.d. wood. Hence, the consumption of NaOH by lignin and carbohydrate can be found as:

- Lignin: 0.04/0.24 = 0.166 kg NaOH/kg lignin
- Carbohydrate: 0.095/0.24 = 0.395 kg NaOH/kg carbohydrate.

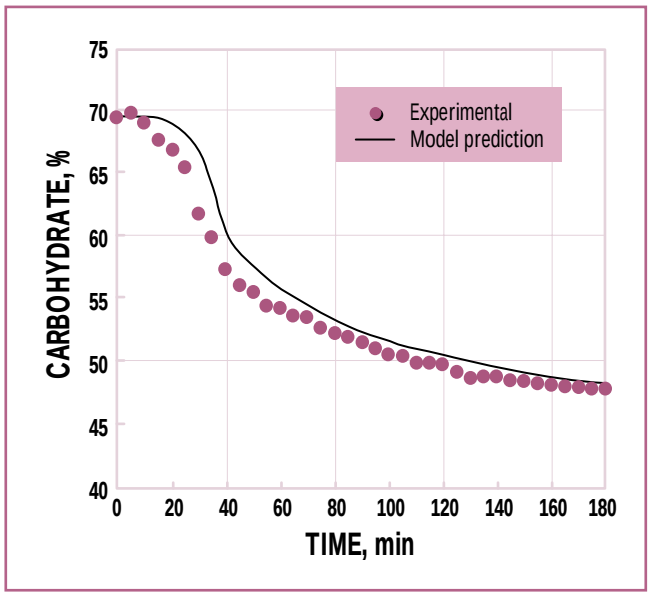
These values correspond to 4.15 x 10^{-3} and 9.88 x 10^{-3} mole/g, respectively, for lignin and carbohydrate. These values compare with those of 5 x 10^{-3} and 1.2 x 10^{-2} obtained from liquor analysis. Similarly, the consumption of hydrosulfide as obtained in this study of 7.08 x 10^{-4} mole/g is comparable to literature values of 9.76 x 10^{-4} mole/g. The parameters obtained are specific to the species under study. The differences in the kinetics between species can be accounted for by adjusting the parameters. A comparison of the parameters obtained in this study with literature values is presented in **Table II**.



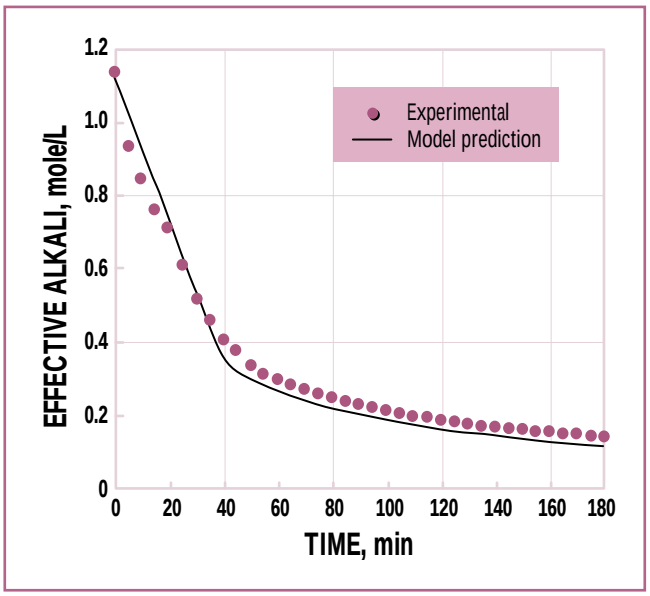
12. Model prediction and experimental HS concentration (EA = 20%, S = 20%, temp. = 170°C)



13. Model prediction and experimental lignin content (EA = 16%, S = 24%, temp. = 170°C)



14. Model prediction and experimental carbohydrate content (EA = 16%, S = 24%, temp. = 170°C)



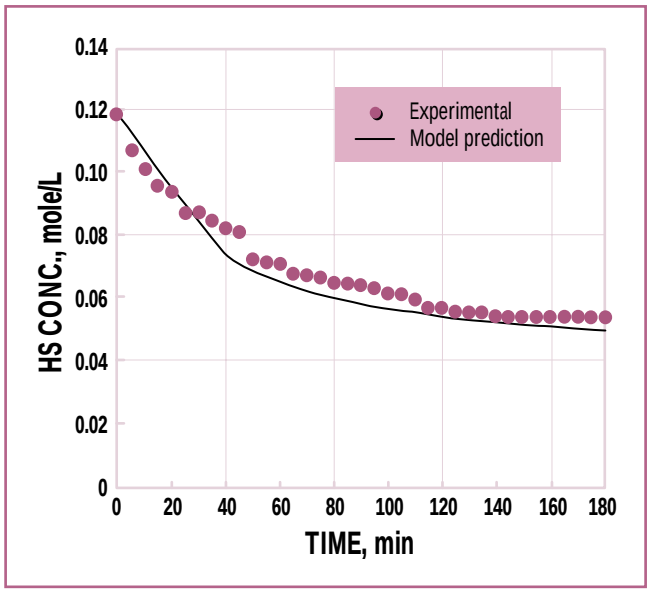
15. Model prediction and experimental EA concentration (EA = 16%, S = 24%, temp. = 170°C)

The experimental and model prediction values for final kappa number and yield for three cooks covering a range of EA and sulfidity are presented in **Table III**.

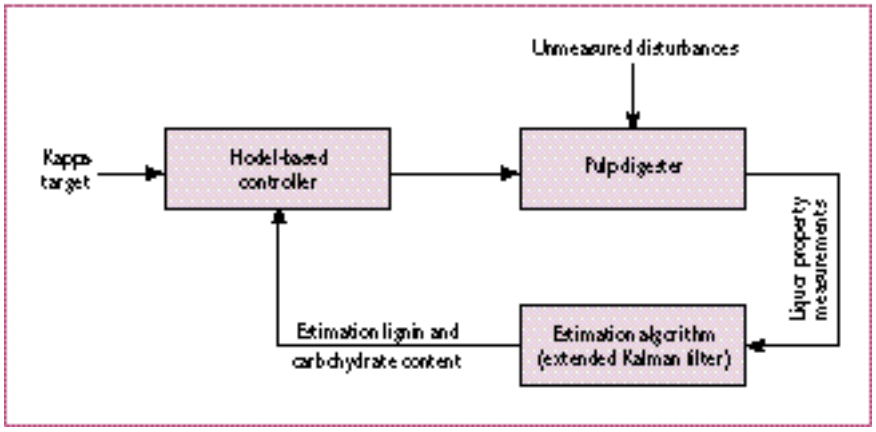
DIGESTER CONTROL

The developed kinetic model and liquor analysis technique can be used in on-line monitoring and control of a digester. The objective of digester control is to produce a consistent-quality pulp within a scheduled batch time. The control variable is the kappa number, which is a measure of residual lignin content in the pulp. Kappa number variability occurring in the pulp mills can essentially be attributed to variations in feedstock properties such as initial moisture content, wood composition, etc. The control problem is further complicated by the fact that kappa number is not measurable on-line.

The liquor analysis technique has the ability to detect any unmeasurable disturbances (feedstock properties) entering the digester, thus providing feedback information on wood dissolution products as well as effective alkali and hydrosulfide ion concentrations. Any stan-



16. Model prediction and experimental HS concentration (EA = 16%, S = 24%, temp. = 170°C)



17. Estimation-based batch digester control scheme

dard estimation techniques, such as extended Kalman filter, can be applied to estimate the lignin and carbohydrate contents during pulping by using the model in conjunction with the liquor analysis data as process measurements *(19, 20)*. The application of a kinetic model to the digester control problem requires that the initial conditions of the feedstock be known. In the absence of such *a priori* knowledge, as is often the case in pulp digesters, estimation techniques essentially provide an assessment of wood-dissolution-product concentrations from liquor measurement. The corrected concentration values can then be used in the kinetic model to predict the time and temperature profile needed to obtain a pulp of desired quality. **Figure 17** shows the block diagram for an estimation-based controller using the liquor property measurements.

CONCLUSION

A nonlinear dynamic model of kraft pulping of southern pine based on on-line liquor analysis has been developed. The model includes independent rate equations for delignification and carbohydrate dissolution as well as for effective alkali and hydrosulfide consumption. The kinetic model parameters have been identified from liquor analysis data. The model parameters obtained compare well with published literature values. The model was validated by comparing it with independent experimental data and was found to be in good agreement. The use of on-line liquor analysis has the potential of detecting unmeasurable disturbances, such as moisture content and feed composition, entering the digester as they affect the liquor properties. This inferential liquor analysis technique can be used in conjunction with the model for on-line monitoring, estimation, and control of the pulping process. **TJ**

KEYWORDS
Analysis, carbohydrates, chemical consumption, cooking liquor composition, delignification, dissolving, dynamics, effective alkali, hydrosulfides, kinetics, kraft pulping, mathematical models, on line measurement, parameters, southern pines.

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