Kraft delignification kinetics based on liquor analysis

Srinivasan Vanchinathan and Gopal A. Krishnagopalan

ABSTRACT: An inferential method uses a mathematical model with on-line liquor analysis to predict lignin content of pulp every 5 min. Conductivity, ion chromatography, refractive index, and UV absorbency analysis measure effective alkali, sulfide concentration, total solids, and the lignin content of cooking liquor. Experiments with several initial effective alkali and sulfidity levels used a laboratory digester with screened softwood chips to develop a model that incorporates initial and bulk delignification phases concentrating on regions of industrial importance.

KEYWORDS: Analysis, chemical reactions, cooking liquors, delignification, dynamics, kinetics, lignin content, mathematical models, measurement, mechanics, models, on line measurement.

The digester is a major piece of equipment in the chemical pulping process. It requires proper control to produce paper products with uniformly high quality at minimum cost. Despite the importance of good digester control, many kraft pulp mills use open-loop, feed-forward control strategies based on empirical models. Such models are inefficient in controlling the kraft process to produce a pulp at optimum kappa number and yield. The difficulty involved in the on-line measurement of kappa number—the control variable—further complicates the control problem.

Several empirical models are available in the literature correlating the rate of delignification with process variables. Studies on the development of these models often used wood meal or wood shavings and very high liquor to wood ratios. This avoided the problems associated with diffusion of chemicals into the wood chips and maintained the liquor composition at a constant value during the cook. These studies addressed only the bulk phase delignification.

Hatton *(1)* developed one empirical model that has had frequent use. It relates the pulp yield and kappa number with *H*-factor and effective alkali (EA) 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 require identification depending on the wood species used. A theoretical model with wide industry reference is the Gustafson model *(2)* that used published delignification data. This model assumes the alkali consumption relates linearly to the delignification rates, and the sulfide concentration is constant throughout the cook. The model provides rates of lignin and carbohydrate dissolution in the initial, bulk, and residual phases.

The success of using these models for control purposes depends on complete knowledge of the feed composition. Since the feed stock quality often does not have good definition, this is a major difficulty. In addition, the models can only provide simple feed-forward control keeping the control loop open. To provide closed-loop control, one must monitor the extent of reaction with time. Pulp analysis from digesters is impractical, however. A practical alternative would be to monitor the liquor composition for extent of reaction. Since the above models use pulp analyses, a model based on measurable liquor properties is necessary. This paper addresses the

Vanchinathan is graduate student and Krishnagopalan is associate professor at Department of Chemical Engineering, Auburn University, 236 Ross Hall, Auburn, AL 36849.

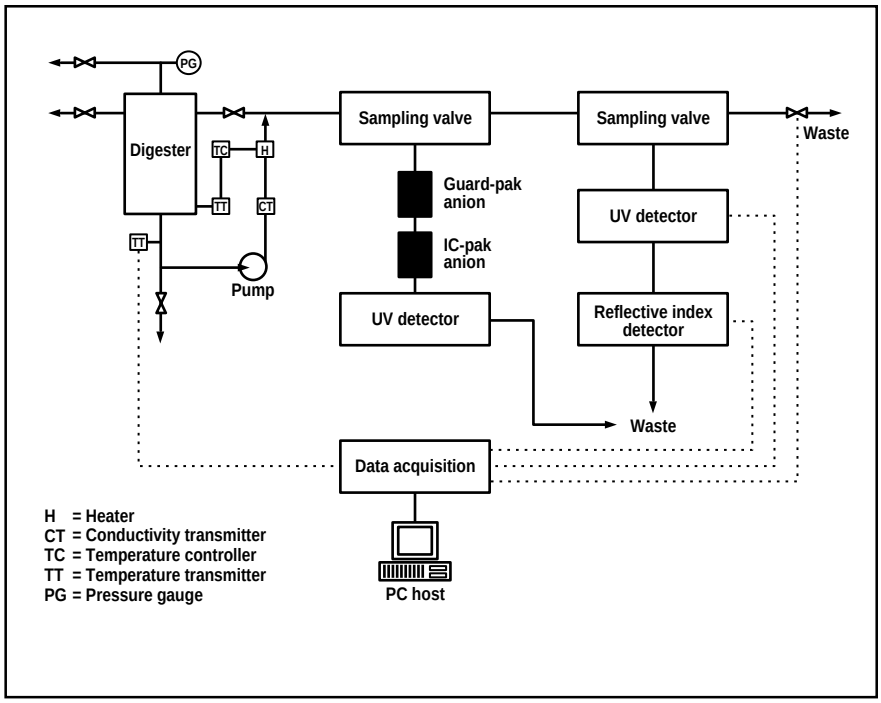
development of a kraft kinetic model based on liquor analysis with this goal in mind.

Experimental materials and methods

Figure 1 shows the schematic diagram of the experimental setup and the associated liquor analysis system used in data collection for kinetic modeling *(3)*. The setup consists of a 6.5 L batch digester equipped with a liquor recirculation pump. An independent controller maintains the temperature in the digester. Changing the setting in the controller can vary the heating rate. The recirculation line has a Rosemount series 78S platinum RTD temperature sensor, a Mirco Motion Model D25 density-to-mass flow meter, and a Rosemount 222 Toroidal flow-through, electrodeless, conductivity sensor.

Besides having the above in-situ measurements, the setup also has a liquor sampling and analysis system. The liquor sampling system consists of two sample injection valves of 1 µL volume that can extract liquor samples from the recirculation line every 5 min. One sample undergoes dilution with water and injection into a Waters Model 481 Lambda-Max spectrophotometer (UV) and a Waters Model 410 differential refractometer (RI). Another sample undergoes injection into an ion chromatographic (IC) column consisting of an anion packing using sodium borate and gluconate as eluent. The IC analysis uses a Waters Model 440 dual channel UV absorbency detector. The data collection from the in-situ sensors and from the extractive liquor sampling and analysis system uses a Keithley 570 data acquisition system and a Zenith 286 host computer. The extractive liquor sampling and analysis system provides the determination of total solids content, lignin content, and sulfide concentration. All these analyses take less than 5 min for completion.

1. Schematic diagram of the experiment



Batch cooks used screened southern pine chips of 3–5 mm thickness. Loading the chips into the digester occurred with the pulping liquor at a liquor to wood ratio of 5.5 to 1. After heating, the digester remained at the pulping temperature for the appropriate period. It took approximately 40 min to reach the cooking temperature. **Table I** shows the cooking conditions. The chips were removed after the completion of the cook, washed thoroughly, and analyzed for yield and kappa number.

Liquor analysis

Liquor conductivity with appropriate temperature corrections can directly measure white liquor EA *(4)*. For cooking liquor, additional correction factors are necessary to account for the dissolved wood substances in the measurement of EA using conductivity. The following is the correlation for cooking liquor conductivity and alkali concentration:

$$NaOH + 0.886\ Na_2S + 0.283\ Na_2CO_3 + 0.0694\ L_{280} = 4.048 \times 10^{-2}C + 2.9180 \times 10^{-5}C^2 \quad (1)$$

where

NaOH = sodium hydroxide, g/L as Na_2O

Na_2S = sodium sulfide, g/L as Na_2O

Na_2CO_3 = sodium carbonate, g/L as Na_2O

L_{280} = lignin concentration, g/L

C = conductivity (corrected to 170°C), mS/cm.

This equation rearranges to the following:

$$NaOH + 0.5\ Na_2S = 4.048 \times 10^{-2}C + 2.9180 \times 10^{-5}C^2 - 0.386\ Na_2S - 0.283\ Na_2CO_3 - 0.0694\ L_{280} \quad (2)$$

The left side of Eq. 2 provides a calculation for the EA, since all the terms on the right side are known.

Liaw and Krishnagopalan developed the measurement of sulfide concentration in white liquor and cooking liquor using an IC method *(5)*. Equation 3 gives the relationship between chromatogram area and sodium sulfide concentration for the case of white liquor:

$$Na_2S = 0.6969\ A_{254} + 0.1048\ EA \quad (3)$$

where

Na_2S = sodium sulfide concentration, g/L Na_2O

I. Experimental conditions used in model development

Experiment	*Cook no.*	*Temperature, °C*	*EA*, %**	*Sulfidity, %*
Effect of temperature	1	160	20	24
	2	170	20	24
	3	175	20	24
	4	180	20	24
Effect of EA with constant sulfide charge of 6.87% Na_2S on wood	5	170	16	29
	6	170	18	26.40
	7	170	20	24
	8	170	25	19.80
Effect of sulfide, with constant EA charge	9	170	20	20
	10	170	20	24
	11	170	20	26
	12	170	20	30

* As Na_2O on moisture-free wood

A_{254} = sulfide peak area measured at 254 nm

EA = EA from conductivity data, g/L as Na_2O.

For the cooking liquor, a modification of the white liquor calibration accounts for the dissolved lignin. The corrected relationship for cooking liquor is the following:

$$Na_2S = 0.7933 (A_{254} - A_{280}) + 0.0759 EA \quad (4)$$

where

A_{254} = chromatogram area of peak measured at 254 nm

A_{280} = chromatogram area of peak measured at 280 nm.

Using a typical cook, **Fig. 2** shows the hydroxide and sulfide concentrations in the cooking liquor with time. These are estimates from liquor conductivity and IC measurement.

The UV absorbance of the pulping liquor at 280 nm exhibits a linear relationship with dissolved lignin concentration. Equation 5 expresses this relationship:

$$C_L = UV/F_u \quad (5)$$

where

C_L = dissolved lignin concentration, g/L

UV = ultraviolet absorbance, AU

F_u = an adjustable constant.

The refractive index of the pulping liquor depends on total dissolved solids concentration. The contribution of each component dissolved in the pulping liquor to refractive index is linearly additive. The proportionality constants are not equal, however. Paulonis *(6)* developed the following relationship:

$$RI = 4.132 [NaOH + 1.364 Na_2S + 1.104 Na_2CO_3 + F_d(C_d)] \quad (6)$$

where

RI = differential refractive index, RIU

C_d = pulping reaction product con centration, g/L

F_d = an adjustable constant.

The C_d term incorporates the effect of many individual organic reaction products on RI.

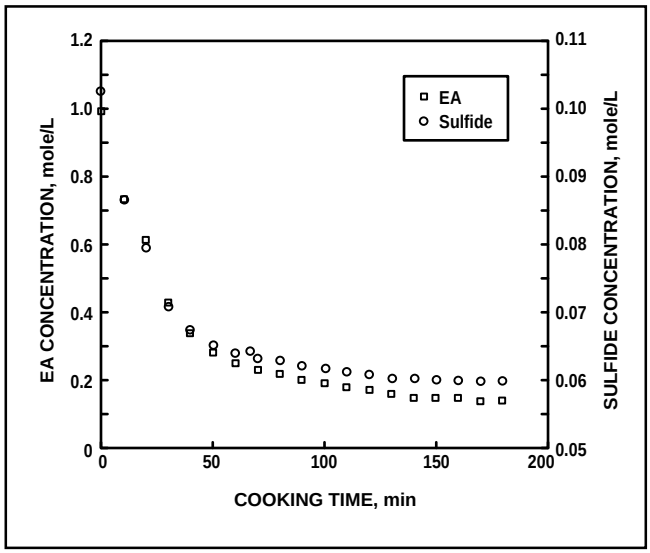
Material balance model

The material balance model of Paulonis *(6)* can calculate the lignin content and yield of pulp any time during the cook. The material balance model essentially relates the liquor property measurements to chip composition inside the digester. The pulp yield derives from the dissolved wood substance concentration as indicated by the RI measurement and the mass of wood chips charged. The pulp lignin content any time during the cook comes from the lignin concentration in liquor and the initial lignin content of wood. There are three parameters in the material balance model that vary with wood species and pulping conditions: UV absorption calibration factor, the kappa number to pulp lignin content calibration factor, and the refractive index reaction products weighting factor. Identification of these parameters can minimize the deviation between measured and estimated yield and kappa number.

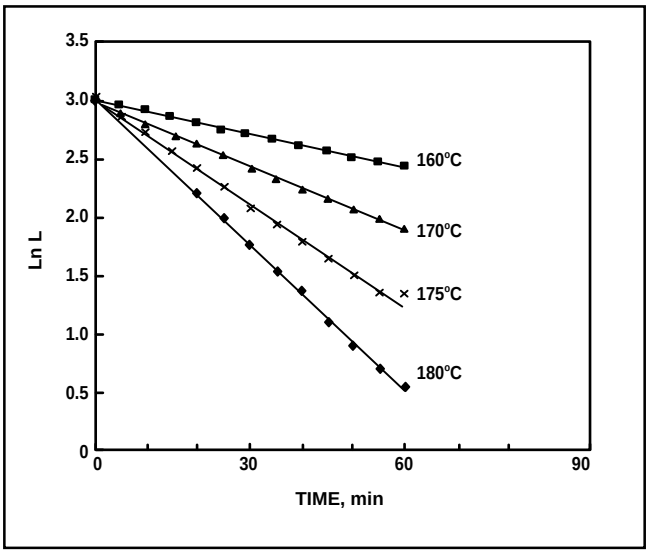
Model development

Alkaline delignification commonly divides into three phases: initial, bulk, and residual. Rapid delignification, significant carbohydrate degradation, and large alkali consumption characterize the initial phase. The bulk phase of delignification is the period for most lignin removal with higher selectivity. The residual phase has a delignification rate much lower than in the bulk phase. The transition from initial to bulk phase delignification takes place at a lignin content of about 20–22% on wood. It is independent of temperature, sulfide concentration, and alkali concentration *(7)*. In this study, we consider the initial and bulk phases of delignification for model development because of their importance to industry. We made the following assumptions in the development of the kinetic model:

2. EA and sulfide concentration profile in the cooking liquor



3. Bulk delignification kinetics at various temperatures



- The liquor is in pseudo equilibrium with the chips. Liquor composition therefore infers chip composition.
- The sulfide present in the cooking liquor completely hydrolyses to hydrosulfide.
- Pulping reactions are irreversible.

Initial phase

Cleavage of α- and ß-aryl ether bonds occurs during the initial phase delignification. Initial phase delignification depends only on diffusion. It does not depend on EA concentration and sulfidity *(7)*. The rate of delignification depends only on temperature, if the liquor pH is above 12 *(8)*. In a typical kraft cooking condition, the initial pH is always above 12. A model similar to that developed by Olm and Tistad *(7)* is therefore applicable for the initial phase. Equation 7 can then represent the initial phase delignification:

$$dL/dt = A_o(T)^{1/2}(e)^{-E/RT}(L) \qquad (7)$$

where

L = lignin content, % on wood

T = temperature, °K

t = time, min

A_o = constant

E = activation energy, cal/mole

R = gas constant.

Experimental data optimized the parameters involved in the above equation using the optimization tool box of the software. The optimized values for A and E/R were 40 and 4807, respectively.

Bulk phase

Bulk phase delignifications are first order with respect to lignin *(9)*. This allows for the following expression of delignification kinetics:

$$dL/dt = kL \qquad (8)$$

where

k = a constant that depends on temperature, alkali concentration, and sulfide concentration.

Integrating Eq. 8 for isothermal conditions and a constant chemical charge gives the following:

$$\ln L = kt \qquad (9)$$

The delignification will therefore result in a linear relationship between the logarithm of the lignin content (% on wood) and the reaction time. In this study, we assume the transition between the initial and bulk phase delignification occurs at a lignin content of 20% on wood. This assumption uses the experimental lignin data of different cooks. A power law model represents the bulk phase kraft delignification kinetics:

$$dL/dt = A(e)^{-E/RT}[OH^-]^a[HS^-]^b(L) \qquad (10)$$

where

$[OH^-]$ = EA concentration at the beginning of bulk phase, mole/L

$[HS^-]$ = hydrosulfide concentration at the beginning of bulk phase, mole/L

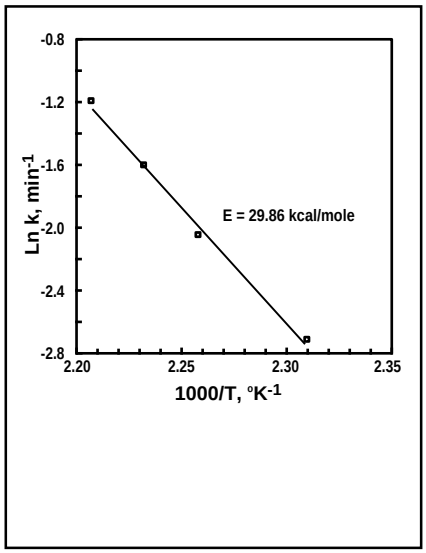
A = frequency factor

a = reaction order with respect to alkali concentration

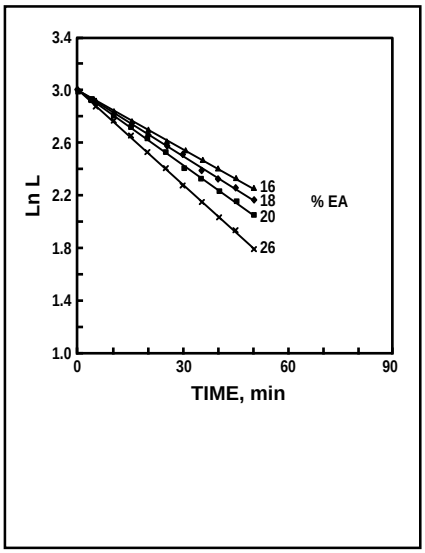
b = reaction order with respect to hydrosulfide concentration.

The values of E, A, a, and b come from experimental data. **Figure 3** shows the effect of temperature on bulk delignification kinetics for cooks 1–4. The slopes of the delignification curves give the rate constants, k. **Figure 4** is the Arrhenius plot of ln k vs. 1/T. The slope of this provides a measure of the activation energy as -E/R. The value of activation energy was 29,863 cal/mole. This is compa-

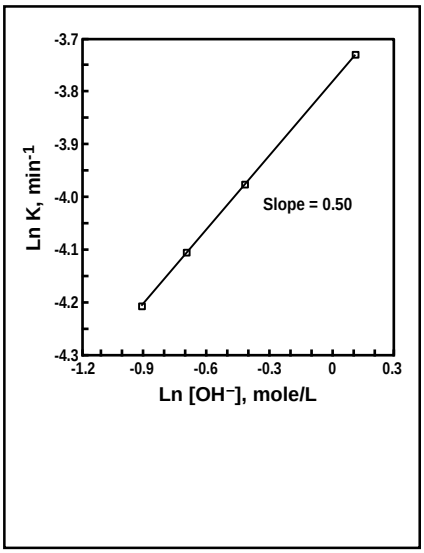
4. Arrhenius plot for kraft pulping



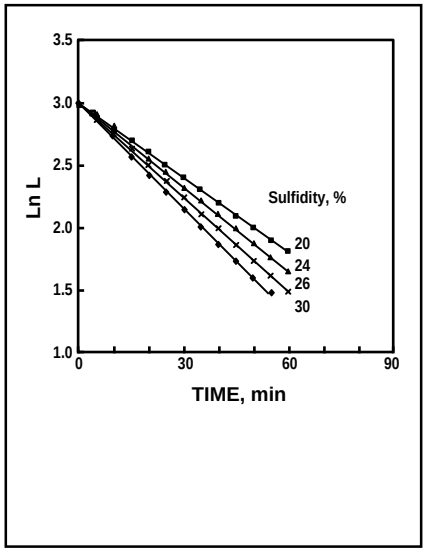
5. Dependence of delignification kinetics on EA



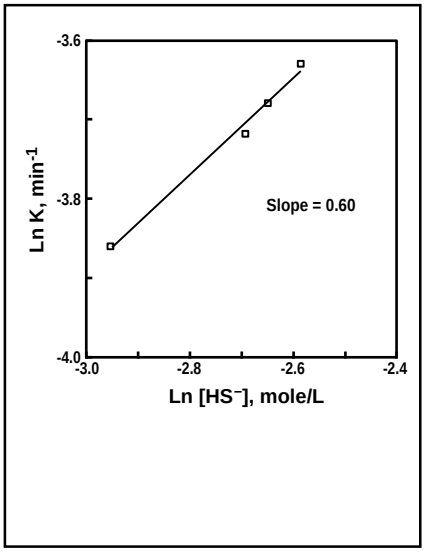
6. Delignification reaction order compared to EA concentration



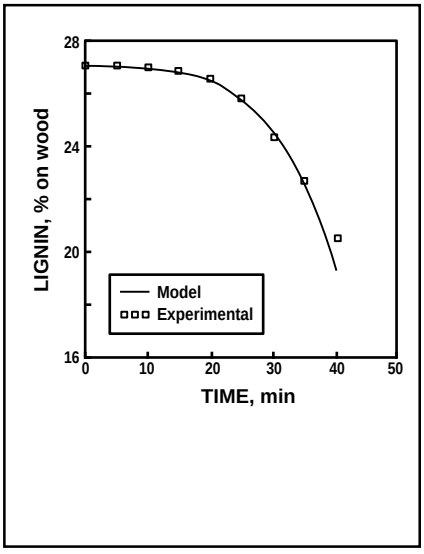
7. Dependence of bulk delignification kinetics on hydrosulfide concentration at 20% EA



8. Delignification reaction order compared to hydrosulfide concentration



9. Model prediction and experimental lignin data for initial phase delignification



rable to literature values. The intercept of Fig. 4 gives the value of the frequency factor, A.

Calculation of the reaction order with respect to the EA concentration came from keeping the hydrosulfide charge constant at 6.87% on wood and varying the initial EA charge. **Figure 5** shows a plot of ln L vs. time for cooks 5–8 where the sulfide charge remained constant. As the plot shows, the rate of delignification increases with increase in EA concentration. The slopes of these delignification lines represent the rate constants, k. **Figure 6** is a plot of ln k vs. ln [OH^-]. This is the EA concentration at the beginning of bulk phase. It shows a linear correlation with a slope of 0.5. This represents the value of exponent a in Eq. 10. The reaction order with respect to the hydrosulfide concentration derives similarly by plotting the bulk delignification rate with various sulfide charges at constant EA charge. **Figure 7** shows a plot of ln L vs. time with constant charge of EA and various sulfide charges for cooks 9–12. Again the slopes of the lines give the rate constants, k. **Figure 8** is a plot of ln k vs. ln [HS^-]. This is the hydrosulfide concentration at the beginning of bulk phase. The reaction order b in Eq. 10 comes from the slope of this plot. It is 0.60.

Equations 11 and 12 represent the final expressions for the initial and

bulk phase delignifications as follows:

$$dL/dt = 40(T)^{1/2}(e)^{-4807/T}(L) \quad (11)$$

$$dL/dt = 7.49 \times 10^{13}\,(e)^{-29863/RT}[OH^-]^{0.5}\,[HS^-]^{0.6}(L) \quad (12)$$

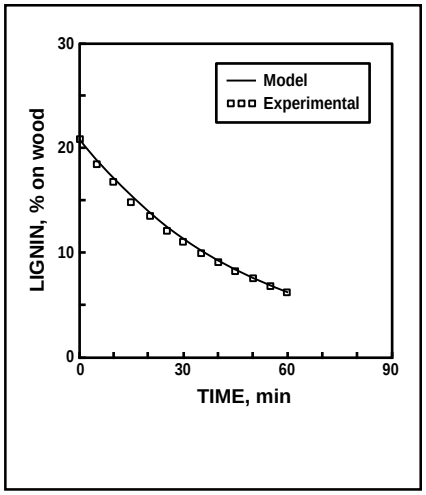
Model validation

Checking the validity of the model involved comparing the model predictions with experimental data by integrating the respective initial and bulk phase model equations. Using data from several cooks that were not in the model development verified the model. **Figure 9** shows the model prediction and experimental values of initial phase delignification. Since the initial phase model is independent of the EA concentration and sulfidity, there is only a typical case. **Figure 10** presents the validity of the bulk phase model for a cook that was not in the model development. **Figure 11** shows model prediction for a cook used in the model development. As these figures show, the predicted and experimental lignin values agree well.

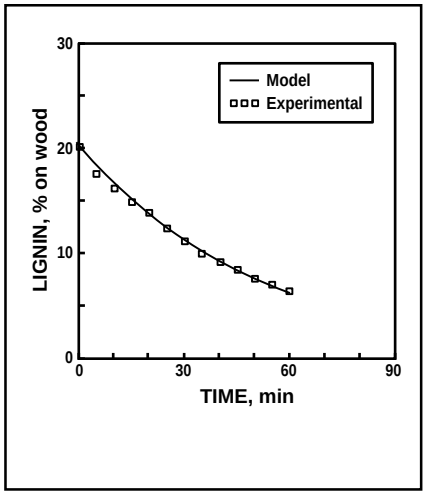
Conclusions

On-line liquor measurements provided a study of kraft delignification kinetics. This led to the development of kinetic models for both the initial and bulk phases of delignification. This inferential method eliminates the need to perform many cooks to determine the effect of cooking conditions on delignification. The study shows that it was appropriate to model the initial phase delignification independently of EA and sulfide concentrations under the kraft pulping conditions used. Bulk phase delignification kinetics used the conditions at the beginning of bulk phase. The EA and hydrosulfide concentrations at the beginning of bulk phase came from liquor analysis. The model predictions for delignification fit the experimental data over a range of cooking conditions of industrial importance. This is the first step toward closing the control loop using liquor based control strategy. Real-time data on the consumption of hydroxide and sulfide during a kraft cook can now develop a dynamic model for delignification.

10. Model prediction and experimental lignin data for bulk phase delignification for 18% EA and 30% sulfidity at 170°C



11. Model prediction and experimental lignin data for bulk phase delignification for 20% EA and 24% sulfidity at 170°C



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