

Ethanol–kraft pulping and papermaking properties of aspen and spruce

Part II: Delignification kinetics, activation thermodynamics, and pulping productivity

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KRAFT PULPING IN THE PRESENCE of a solvent shows promise as a means of improving pulp yield and increasing process efficiency. In an earlier report (1), a 4% gain in pulp yield and a 30% reduction in pulping time were achieved using an ethanol–kraft pulping process—with minimal changes in paper quality—for aspen and spruce wood chips. These results suggest that the reactivity of kraft delignification increases in the presence of an ethanol-reinforced reaction medium. The heightened reactivity is due to enhanced accessibility of lignin to the chemical agents, an increase in solution basicity, and greater ionic mobilities.

Kraft delignification in the alcohol–water binary liquor is a complicated process involving molecular solvation, lignin depolymerization, and solubilization processes. Addition of ethanol to the kraft delignification media can change the pulping rate. The objective of the present study was to investigate the kinetics of solvent–kraft delignification to develop and identify quantitative interrelationships among important pulping variables. A kinetic study would provide for a better understanding of the actual delignification reaction while providing new insight into the development of a mathematical model to simulate pulping productivity.

This kinetic study was limited to only the bulk delignification stage,

where the main dissolution of lignin takes place. Activation thermodynamics of solvent–kraft delignification was investigated based on the classical transition-state theory (2). A mathematical model simulating pulping in a continuous digester was developed to estimate the pulping productivity of a solvent–kraft process. Data for the model were obtained from laboratory cooks of aspen (*Populus tremuloides*) and Norway spruce (*Picea exelsa*) wood chips in a laboratory M/K digester at three different pulping temperatures (150°C, 160°C, 170°C).

RESULTS AND DISCUSSION

Kinetic rate law in solvent–kraft delignification process

The rate of a chemical reaction can generally be expressed as a function of several important kinetic variables, including the concentration of the reactants, reaction temperature, and the pressure at which the reaction occurs (2). If solvent–kraft delignification is represented by a single chemical reaction, the delignification rate would be primarily a function of the lignin content of the wood chips, the concentration of kraft ions, the pulping temperature, and the solvent composition of the cooking liquor at that particular pulping time:

$$-R_L = f[L, A, T, Xe] \quad (1)$$

where

ABSTRACT

The kinetics of solvent–kraft pulping was investigated for two tree species (aspen and spruce). Kinetic parameters were determined at three pulping temperatures (150°C, 160°C, 170°C) and four mole fractions of ethanol (0, 0.1, 0.2, 0.3). Activation thermodynamics of the solvent–kraft delignification process were investigated based on classical transition-state theory. A mathematical model was developed to estimate the pulping productivity of the solvent–kraft process in a continuous digester. The simulation shows a 50% increase in the reaction order of delignification and a 30% decrease in the activation energy of delignification with increasing ethanol mole fraction in the cooking liquor. Activation Gibbs' free energy of delignification increased steadily with ethanol content, while activation enthalpy and entropy of delignification showed dynamic behavior. Estimated pulping productivity increased by a factor of 2.5. The results suggest that addition of ethanol to conventional kraft pulping liquor increases pulping productivity through the combined effects of faster delignification, increased pulp yield, and a decrease in the activation energy of delignification.

Application:

A mathematical model of a solvent–kraft pulping process suggests that adding ethanol to kraft pulping liquor can increase pulping productivity by a factor of 2.5.

R_L = rate of lignin removal

L = residual lignin content

A = concentration of chemical agent

T = pulping temperature, K

Xe = mole fraction of ethanol in the kraft cooking liquor.

In applying Eq. 1, it is assumed that (a) the rate of delignification at constant pulping temperature and (b) a constant chemical and solvent

Aspen

$$\begin{aligned}\text{Control: } -dL/dt &= 1.2510^9 \exp(-21,648/RT)L^{1.19} \\ 0.1Xe: -dL/dt &= 7.92 \times 10^6 \exp(-17,364/RT)L^{1.55} \\ 0.2Xe: -dL/dt &= 7.87 \times 10^4 \exp(-13,452/RT)L^{1.71} \\ 0.3Xe: -dL/dt &= 1.14 \times 10^5 \exp(-13,845/RT)L^{1.80}\end{aligned}$$

Spruce

$$\begin{aligned}\text{Control: } -dL/dt &= 3.92 \times 10^{13} \exp(-31,106/RT)L^{1.00} \\ 0.1Xe: -dL/dt &= 1.54 \times 10^{12} \exp(-28,482/RT)L^{1.39} \\ 0.2Xe: -dL/dt &= 4.79 \times 10^{11} \exp(-27,364/RT)L^{1.47} \\ 0.3Xe: -dL/dt &= 2.06 \times 10^9 \exp(-22,912/RT)L^{1.64}\end{aligned}$$

* Xe = mole fraction of ethanol in kraft cooking liquor

Unit of activation energy = cal/mole-K

R = 1.987 cal/mole-K

T = absolute temperature

L = residual lignin content of pulp

I. Rate expressions for delignification in the solvent-kraft pulping and conventional kraft pulping of aspen and spruce*

concentration during pulping can be represented as being proportional to the residual lignin content raised to an arbitrary power. Thus the delignification rate can be expressed as an ordinary differential equation:

$$-R_L = -dL/dt = k_L L^\alpha \quad (2)$$

where the quantity k_L is referred to as the delignification rate constant and α is the reaction order of delignification. The delignification rate constant k_L , however, is not truly a constant, but is merely independent of the concentrations of the species involved in the pulping reaction. It is almost always strongly dependent on the pulping temperature (3). The quantity k_L and α can be determined directly from experimental data.

After taking the natural logarithm of both sides of Eq. 2, i.e.,

$$\ln(-dL/dt) = \ln k_L + \alpha \ln L \quad (3)$$

it can be found that the slope and the y-intercept of a plot of $[\ln(-dL/dt)]$ as a function of $(\ln L)$ represent the reaction order and the delignification rate constant, respectively, if the empirical concept of a power function is valid. To obtain the derivative term $(-dL/dt)$ in Eq. 3, the concentration-time data obtained from 150°C, 160°C, and 170°C isothermal solvent-kraft pulping of aspen and spruce were differentiated using a

nonlinear regression technique (4).

The delignification rate constant can be found in all cases to be well represented by Arrhenius law:

$$k_L = Ae^{-E_L/RT} \quad (4)$$

where

A = preexponential factor

E_L = activation energy of delignification, cal/mole

R = universal gas constant

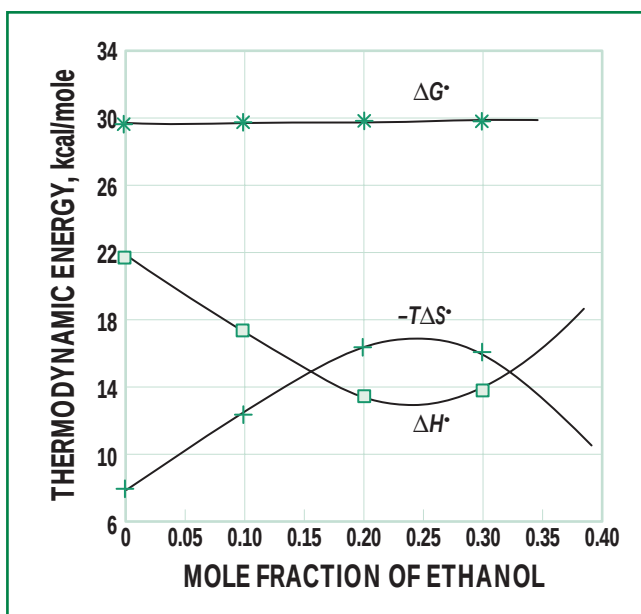
This expression has been verified empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges and is strongly suggested from various standpoints as being a reasonable first approximation of the true temperature dependency of a reaction (2,5). The activation energy of delignification can be calculated from the data collected at each temperature.

With the reaction order, preexponential factor, and activation energy for the delignification obtained from the kraft and solvent-kraft pulping of aspen and spruce, the rate expressions for delignification were formulated using Eqs. 2 and 4 and are summarized in **Table I**. Since no significant differences in reaction order were observed among the three different temperatures, each reaction order of delignification was taken as an average. However, the reaction order of delignification increases significantly—while the activation energy of delignification decreases—with increasing ethanol addition in the kraft cooking liquor for both wood species. The reductions in activation energy imply that the temperature dependency of delignification could be

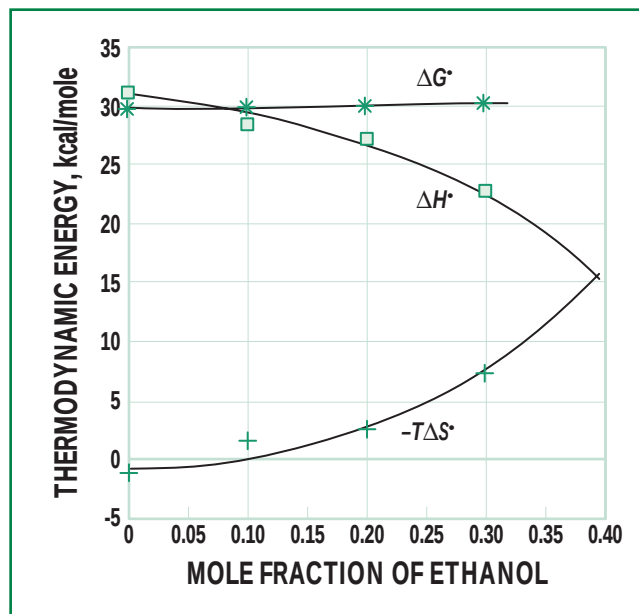
decreased with the addition of ethanol to the kraft cooking liquor.

According to Kleinert (6), bulk delignification could occur by rapid fragmentation of the lignin macromolecule through rupture of intermolecular ether bonds by both chemical attack and thermal softening of lignin. In the postulated mechanism (involving cleavage of the alpha- and beta-aryl lignin-lignin ether bonds followed by dissolution of the liberated lignin), the increased reaction order of delignification by addition of ethanol to liquor may be due to (a) the greater chemical driving force to break additional chemical bonds and (b) the dissolution of lignin in the liquid phase.

Delignification rates for aspen and spruce pulps were compared with their orders of reaction. The reaction order of delignification was significantly higher at a given level of ethanol in aspen pulping than in spruce pulping. It is generally accepted that the rate of delignification for hardwoods is faster than for softwoods. This trend is mainly due to the lower amount of lignin in hardwood species and to the syringyl units formed in hardwood lignins (7). Sarkanen *et al.* (8) reported that the rate of delignification of hardwoods was directly proportional to the ratio of syringyl to guaiacyl content. Chiang *et al.* (9) demonstrated that the structure rather than the amount of hardwood lignin is the major factor responsible for the fast rate of hardwood delignification. Researchers also have reported that lignin fragments may react with each other to form lignin condensation products (10). The major condensation reaction in alkaline pulping occurs at the unoccupied C-5 position of phenolic units. The presence of a high percentage of syringyl units in hardwood lignin means that fewer reactive sites are available for carbon-carbon condensation reaction compared with coniferous lignin,



1. Activation parameters for delignification reaction plotted as a function of ethanol mole fraction in kraft cooking liquor—aspens pulps



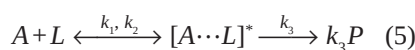
2. Activation parameters for delignification reaction plotted as a function of ethanol mole fraction in kraft cooking liquor—spruce pulps

where the aromatic units are mainly of the guaiacyl type (unoccupied C-5). Therefore, the relative difficulty of pulping softwood by both kraft pulping and solvent-kraft pulping could be explained by assuming that softwood lignin tends to repolymerize after partial degradation more readily than hardwood lignin.

Activation thermodynamics of solvent-kraft delignification

The influence of solvent addition to the kraft cooking liquor on delignification rates can be understood in terms of the Arrhenius theory of activation thermodynamics, which is also known as the classical transition theory (5). Considering the delignification process, it can be postulated that the kraft chemicals and wood lignin would combine to form unstable intermediates, which then decompose spontaneously into the final reaction products. The unstable intermediates of reactants are called the activated complex.

Assuming the elementary reversible reaction for the delignification process, we have the following conceptual scheme:



where

A = kraft chemical

L = lignin molecule

$[A \cdots L]^*$ = chemical-lignin activated complex

P = reaction product

In classical transition-state theory, it is assumed that (a) an equilibrium exists between reactants and activated complex at all times and (b) the rate of decomposition of activated complex is the same for all reactants. The rate is given by kT/h , where $k = 1.38 \times 10^{-16}$ erg/K is the Boltzmann constant and $h = 6.63 \times 10^{-27}$ erg·s is the Planck constant (3). Therefore, the equilibrium constant K_{eq}^* at the transition state of the delignification process can be expressed as:

$$K_{eq}^* = k_1/k_2 = C_{[A \cdots L]^*}/C_A C_L \quad (6)$$

and

$$k_3 = kT/h \quad (7)$$

where

$C_{[A \cdots L]^*}$ = concentration of chemical-lignin activated complex

C_A = concentration of kraft chemical

C_L = residual lignin content

The equilibrium constant K_{eq}^* at transition state is connected with activation thermodynamic data, viz., the activation enthalpy of delignification ΔH^* and the activation entropy of delignification ΔS^* :

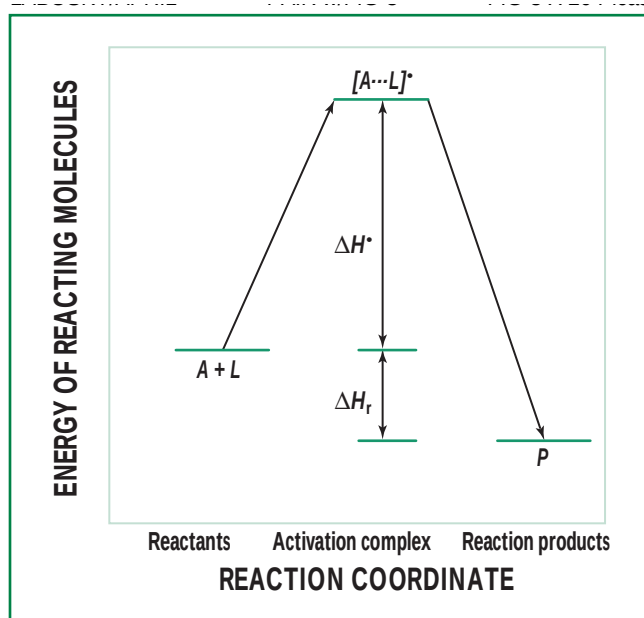
$$-RT \ln K_{eq}^* = \Delta H^* - T\Delta S^* = \Delta G^* \quad (8)$$

where ΔG^* is the change in the activation Gibbs' free-energy of delignification. Equation 8 can be written in a van't Hoff equation form:

$$\ln K_{eq}^* = -(\Delta H^*/RT) + (\Delta S^*/R) \quad (9)$$

which describes the temperature dependence of the equilibrium constant K_{eq}^* at the transition state of the delignification process. The observed rate of delignification is then

$$\begin{aligned} -R_L &= k_3 C_{[A \cdots L]^*} \\ &= (kT/h) C_{[A \cdots L]^*} \\ &= (kT/h) K_{eq}^* C_A C_L \end{aligned} \quad (10)$$



3. Visualization of the energies involved in the delignification process (A = kraft chemical, L = lignin in wood, P = delignification product, $[A\cdots L]^*$ = chemical-lignin activation complex, ΔH^* = activation enthalpy of delignification, ΔH_r = reaction enthalpy of delignification)

Substitution of Eq. 9 into Eq. 10 gives:

$$-R_L = (kT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}C_A C_L \quad (11)$$

Therefore, the reaction rate constant of delignification is:

$$k_L = (kT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R} \quad (12)$$

By taking natural logarithms on both sides of Eq. 12, we obtain:

$$\ln k_L = -(\Delta H^*/RT) + (\Delta S^*/R) + \ln(kT/h) \quad (13)$$

A plot of $\ln k_L$ vs. $1/T$ should yield a straight line of slope $-\Delta H^*/R$ and intercept $(\Delta S^*/R) + \ln(kT/h)$. Theoretically, both ΔH^* and ΔS^* vary very slowly with temperature (5). Of the two exponential terms that make up the delignification rate constant in Eq. 12, the second term $e^{\Delta S^*/R}$ is much less temperature sensitive than the first term $e^{-\Delta H^*/RT}$. Since the magnitude of k/h is very large ($\approx 2 \times 10^{10}$), the temperature dependence of $\ln(kT/h)$ at temperatures ranging between 150°C and 170°C is negli-

ble. Therefore, we can take ΔH^* , ΔS^* , and $\ln(kT/h)$ to be constants. The activation entropy can be determined by subtracting $\ln(kT/h)$ from the intercept of each regression line and dividing this quantity by the universal gas constant, R . The activation Gibbs' free energy of delignification can then be calculated using Eq. 8. These data are presented in Figs. 1 and 2 for

aspen and spruce, respectively. Both figures show the behavior of the three principal activation parameters as a function of solvent composition in the kraft cooking liquor. The results indicate that while ΔG^* of delignification increased steadily with increasing ethanol content in aqueous ethanol binary cooking liquor, the component ΔH^* and $-T\Delta S$ of delignification showed dynamic behavior as a function of ethanol composition. The activation Gibbs' energy of delignification appears to slightly increase with increasing mole fraction of ethanol. Dissolution of lignin during chemical pulping is believed to occur through conversion of a relatively nonpolar molecule to an ion-pair-like transition state. Therefore, ΔG^* of delignification should increase steadily as the dielectric constant of the reaction media is reduced on going from water to ethanol. This type of monotonic behavior of ΔG^* is quite general when a chemical reaction takes place in alcohol-water binary mixtures and may permit a rough prediction of solvent effects on the transition-state equilib-

rium through linear free-energy relationships (11). From Eq. 8, it can be noted that an increase in ΔG^* of delignification indicates a decrease in the equilibrium constant of the transition state. Therefore, it is possible that the transition-state equilibrium may slightly shift to the left in the reaction pathways because of a slight increase in reverse reaction constant as the mole fraction of ethanol in liquor increases. However, this minute movement of transition-state equilibrium can be neglected if a much larger change in ΔH^* of delignification is taken into account.

A change in delignification rate constant as we change the ethanol composition in cooking liquor could be the result of a much larger change in ΔH^* and $-T\Delta S^*$ of the delignification process. These changes in thermodynamic parameters are the typical characteristics of chemical reactions involving changes of solvation in an ethanol-water binary mixture. According to the classical transition-state theory, solvents in a reaction medium can modify the activation enthalpy of delignification by differential solvation of the reactants and the activated complex (12). This classical transition-state theory is based on the assumption that the reactants have to overcome a potential energy barrier, ΔH^* , in order to be transformed into the delignification products, as illustrated in Fig. 3. Reaction rates are very sensitive to the height of the potential-energy barrier.

As can be seen from Figs. 1 and 2, ΔH^* of delignification decreased as a function of ethanol composition. A minimum point in ΔH^* for the delignification of aspen was observed at around 0.25 mole fraction of ethanol, whereas it appeared that the minimum in activation enthalpy of delignification of spruce exists at much higher mole fraction of ethanol. At 0.3 mole fraction ethanol, a drop of approximately 8 kcal/mole in ΔH^* of delignification was

observed for both wood species. Since a lower ΔH^* indicates that temperature has a limited effect on a reaction, it would be expected that as the mole fraction of ethanol in solvent–kraft cooking liquor increases, the temperature dependency of delignification would decrease. In addition, the lower ΔH^* for solvent–kraft delignification compared with kraft indicates that the differences in the delignification rates between the two pulping processes should be magnified with decreasing pulping temperature.

The activation entropy of delignification ($-T\Delta S^*$) increased—with some compensation effect with activation enthalpy of delignification (ΔH^*)—as the mole fraction of ethanol increased. Maxima in $-T\Delta S^*$ of delignification were observed at the same position of minima in ΔH^* of delignification. The fact that the activation entropy of delignification shows a similar type of behavior as ΔH^* indicates that the kinetic activation process of delignification is reflecting the solvent structural changes as the composition of the binary mixture in the kraft cooking liquor is varied. In view of this response, the behavior of $-T\Delta S^*$ of delignification could be used as an experimental tool for examining liquor structure at a given pulping temperature. The tendency of $-T\Delta S^*$ of delignification to increase with increasing mole fraction of ethanol clearly indicates that the solvation structure of reactants and the order of structure in the kraft cooking liquor could be decreased by addition of ethanol at a given pulping temperature. The temperature dependency of ethanol–water binary solvent systems was fully discussed in Part I of this work (1).

Productivity simulation model

The production rate (or pulping productivity) for a particular pulping process is largely governed by the delignification kinetics. Consequently, applying the delignification rate

equation for the pulping process to a simulation model of a digester could provide quantitative information on its pulping productivity. In an attempt to estimate the productivity of the solvent–kraft pulping process, a simulation model for a mill-scale continuous digester was developed through the use of a general material balance in a plug-flow reactor (2). The kinetic parameters obtained from a previous kinetic study (1) were inserted into the model.

Continuous digesters can be considered to consist of two separate zones: a preheating zone and an isothermal pulping zone (13). The simulation model for pulping productivity was based on the sum of retention time of fluid in the preheating zone and in the isothermal pulping zone of the continuous digester.

In the isothermal zone of a continuous digester, the composition of the fluid (including wood chips and cooking liquor) varies from position to position along a flow path. Therefore, the material balance for a reaction component, lignin, should be made for a differential element of digester volume dV . This approach assumes an isothermal delignification process. Figure 4 is a schematic diagram depicting the variables involved in a continuous digester. Thus for lignin, L , we obtain:

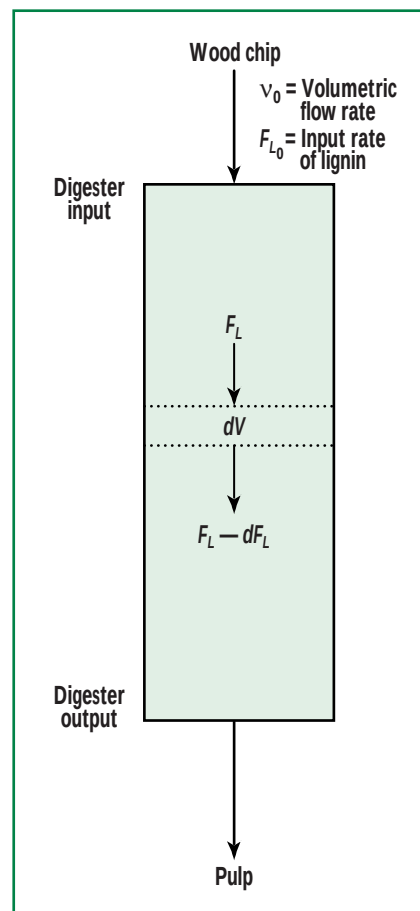
$$\begin{aligned} [\text{lignin input}] = \\ [\text{lignin output}] + [\text{lignin removed by reaction}] \end{aligned} \quad (14)$$

Referring to Fig. 4, we see that for volume dV

$$\begin{aligned} F_L &= \text{input of lignin (amount of lignin/time)} \\ F_L - dF_L &= \text{output of lignin (amount of lignin/time)} \\ R_L dV &= \text{disappearance of lignin by reaction (amount of lignin/time)} \end{aligned}$$

Introducing these three terms in Eq. 14, we obtain:

$$dF_L = -R_L dV \quad (15)$$



4. Schematic diagram showing variables involved in the isothermal pulping zone of a continuous digester

Noting that

$$dF_L = d[F_{L_0}(1-X_L)] = -F_{L_0} dX_L \quad (16)$$

and

$$dX_L = d[1-(L/L_0)] = -(dL/L_0) \quad (17)$$

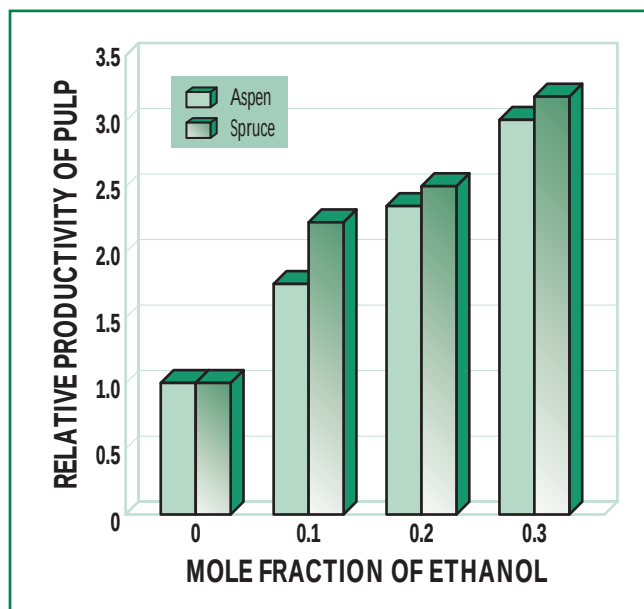
we obtain—on replacement of Eqs. 16 and 17 into Eq. 15—Eq. 18.

$$(F_{L_0}/L_0)dL = (-R_L)dV \quad (18)$$

or

$$\int_0^V (dV/F_{A_0}) = (1/L_0) \int_{L_0}^L (dL/-R_L)$$

This then is the equation accounting for lignin in the differential section of a continuous digester having a fluid volume of dV . Now F_{L_0} , the feed rate of lignin, and L_0 , the lignin content of wood chips at isothermal



5. Effect of mole fraction of ethanol in kraft cooking liquor on the estimated relative productivity of solvent-kraft pulping of aspen and spruce in a mill-scale continuous digester

pulping time zero, are constants, but $-R_L$ is certainly dependent on the concentration of residual lignin in wood chips. Thus, grouping the terms accordingly, we obtain Eq. 19.

$$V = (F_{L_0}/L_0) \int_{L_0}^L (dL/-R_L) \quad (19)$$

where V is the total volume of the isothermal zone in the continuous digester. If we define the overall retention time of fluid in the digester as τ , then we obtain Eq. 20.

$$\tau = \tau_1 + \tau_{II} = \tau_{II} [1 + (\tau_1/\tau_{II})] \quad (20)$$

where

τ_1 = retention time of fluid in the non-isothermal preheating zone

τ_{II} = retention time of fluid in the isothermal pulping zone

The retention-time ratio, τ_1/τ_{II} , of the right-hand side of Eq. 20 can be expressed in terms of the heatup time t_1 and the isothermal pulping time t_{II} in a batch digester as:

$$\tau_1/\tau_{II} = t_1/t_{II} \quad (21)$$

The retention time of fluid in the isothermal pulping zone τ_{II} can also be expressed in terms

of the flow rate of fluid through the continuous digester:

$$\tau_{II} = V/v_0 \quad (22)$$

where v_0 is the flow rate of fluid through the digester. The volumetric flow rate of fluid, v_0 , can also be expressed as:

$$v_0 = \frac{m}{Y} \left(\frac{Z}{W} + \frac{1}{\rho_w} \right) \quad (23)$$

where

m = mass of pulp produced in time τ

Y = fractional total pulp yield

Z/W = liquor-to-wood ratio

ρ_w = density of wood

On replacement of Eqs. 21–23 into Eq. 20, we obtain Eq. 24.

$$\tau = \frac{F_{L_0} Y \left(1 + \frac{t_1}{t_{II}} \right)}{L_0 m \left(\frac{Z}{W} + \frac{1}{\rho_w} \right)} \int_{L_0}^L \frac{dL}{-R_L} \quad (24)$$

The production rate of pulp in the continuous digester should be inversely proportional to the retention time of wood chips in the digester. If we designate the production velocity of pulp as P , we obtain:

$$P = \frac{A}{\tau} = \frac{AL_0 m \left(\frac{Z}{W} + \frac{1}{\rho_w} \right)}{F_{L_0} Y \left(1 + \frac{t_1}{t_{II}} \right)} \left[\int_{L_0}^L \frac{dL}{-R_L} \right]^{-1}$$

$$= B \left[\frac{Y}{L_0} \left(1 + \frac{t_1}{t_{II}} \right) \int_{L_0}^L \frac{dL}{-R_L} \right]^{-1} \quad (25)$$

where A and B are proportionality constants. Noting that the unknown constant B is independent of the type of pulping process, it may be convenient to consider the relative productivity of a solvent-kraft pulping process, P_r as:

$$P_r = \frac{P_s}{P_k} = \frac{L_{0s} Y_k \left[1 + \left(\frac{t_1}{t_{II}} \right)_k \right] \int_{L_0}^L \frac{dL}{-R_{Lk}}}{L_{0k} Y_s \left[1 + \left(\frac{t_1}{t_{II}} \right)_s \right] \int_{L_0}^L \frac{dL}{-R_{Ls}}} \quad (26)$$

where

P = pulping productivity

L_0 = lignin content at inlet of isothermal zone

Y = total pulp yield at lignin content L

(t_1/t_{II}) = retention-time ratio

R_L = delignification rate

and where the subscripts k and s represent kraft and solvent-kraft pulping, respectively. By assigning a value of unity to the pulp production rate of a kraft pulping process at 170°C cooking, a relative productivity can be assigned to a solvent-kraft pulping process by substituting each delignification rate equation, the initial lignin content at the isothermal pulping time zero, and the average total pulp yield at the final lignin content L into Eq. 26.

The relative productivity of solvent-kraft pulping at 170°C was determined using Eq. 26 for aspen and spruce pulping. The average total pulp yields at kappa no. 15 and at kappa no. 30 were used for aspen and spruce pulps, respectively. The relative productivity of the solvent-kraft pulping process was

KEYWORDS

Ethanol, populus, picea, delignification, thermodynamics, modified kraft process, kraft pulping, reaction kinetics, temperature, solvents, mathematical models, activation.

plotted against ethanol content in the cooking liquor, as seen in **Fig. 5**. The relative pulping productivity of bleachable grades increased considerably with increasing ethanol addition to the kraft cooking liquor for both wood species. It is striking to note that with an addition of 0.3 mole fraction of ethanol, the pulping productivity in the continuous digester was increased by a factor of approximately three for both aspen and spruce solvent-kraft pulping compared with the kraft pulping process. Higher productivity was achieved in softwood pulping than in hardwood pulping using the solvent-kraft process. These results strongly suggest that a solvent-kraft pulping process could increase pulping efficiency throughout the pulp and paper industry.

CONCLUSIONS

The delignification kinetics and activation thermodynamics of the solvent-kraft pulping process were studied by pulping aspen and spruce wood chips at 150°C, 160°C, and 170°C. These results were then applied to a model of a continuous kraft digester to evaluate the pulping productivity of solvent-kraft pulping.

- The reaction order of delignification increased significantly as the molar concentration of ethanol in the solvent-kraft cooking liquor increased from zero to 0.3 for both wood species.
- Activation Gibbs' free energy of delignification steadily increased with increasing ethanol content, and activation entropy increased dynamically. Activation enthalpy decreased dynamically with increasing ethanol content in the kraft cooking liquor.

- For kraft pulping liquors containing 0.3 mole fraction of ethanol, the activation enthalpy of delignification dropped approximately 8 kcal/mole for both aspen and spruce. This implies that ethanol considerably reduces the temperature dependency of delignification during kraft pulping.
- A model simulating a mill-scale continuous digester showed that addition of 0.3 mole fraction of ethanol to the kraft cooking liquor increased pulping productivity by a factor of close to three for both aspen and spruce wood chips.
- At lower levels of ethanol addition (0.1 mole fraction), pulping productivity was increased by a factor of two. The enhanced productivity is due to the combined effect of faster delignification, increased pulp yield, and a decrease in the activation energy of delignification.

EXPERIMENTAL

Aspen (*Populus tremuloides*) and Norway spruce (*Picea exelsa*) wood chips were subjected to isothermal solvent-kraft digestions at three different pulping temperatures (150°C, 160°C, and 170°C). Ethanol mole fraction level was varied from zero to 0.3. The time-at-temperature for pulping ranged from zero to 2 hours. Pulping conditions and analysis procedures were the same as those described in Part I of this work (1). TJ

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LITERATURE CITED

1. Yoon, S-H., Labosky, P., Jr., and Blankenhorn, P. R., *TAPPI J.* 80(1): 203(1997).
2. Fogler, H. S., *Elements of Chemical Reaction Engineering*, 2nd edn., Prentice-Hall, Englewood Cliffs, NJ, 1992, pp. 11-205.
3. Levenspiel, O., *Chemical Reaction Engineering: An Introduction to the Design of Chemical Reactors*, John Wiley and Sons, New York, 1962, pp. 25-28.
4. Neter, J., Wasserman, W., and Kutner, M. H., *Applied Linear Statistical Model*, Richard D. Irwin, Boston, 1990, pp. 315-348.
5. Laidler, K. J., *Chemical Kinetics*, 2nd edn., McGraw-Hill, New York, 1965, pp. 49-85.
6. Kleinert, T. N., *Tappi* 48(8): 447(1965).
7. Rydholm, S.A., *Pulping Processes*, Vol. 1, Interscience, John Wiley and Sons, New York, 1965, pp. 576-649.
8. Sarkanen, K.V., Hrutford, B. F., Johanson, L. N., et al., *Tappi* 53(5): 766(1970).
9. Chiang, V. L. and Funaoka, M., *Holzforchung* 44(2): 147(1990).
10. Sjostrom, E., *Wood Chemistry: Fundamentals and Applications*, Academic Press, New York, 1981, pp. 124-141.
11. Arnett, E. M., "Behaviour in highly aqueous binary solvents," in *Physico-Chemical Processes in Mixed Aqueous Solvents*, American Elsevier, New York, 1967, pp. 105-113.
12. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn., VCH, New York, 1988, pp. 121-129.
13. Casey, J. P., *Pulp and Paper Chemistry and Chemical Technology*, Vol. 1, 3rd edn., Wiley Interscience, New York, 1978, pp. 386-392.