

# Delignification and Degelation: Analogy in Chemical Kinetics\*

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## Synopsis

Structurally and kinetically, chemical pulping can be treated as a degelation process. Kinetics derived from the empirical power law is rejected on the grounds that lignin is a polymer. Using an extended version of the Flory–Stockmayer theory and a kinetic expression derived by Whittle, the delignification kinetics is expressed in terms of opposing unimolecular–bimolecular reactions. The quantity replacing lignin concentration is the “extent of reaction” defined in the theory. Parameters used in this reaction are estimated, and the time dependence of the undissolved lignin fraction can be calculated. The calculated delignification curve is shown to be in good agreement with experimental results.

## INTRODUCTION

Lignin is one of the major components in wood. For the simplest model, lignin in wood is regarded as acting like a glue that binds the cellulose fibers together. The removal of lignin by chemicals is known as delignification or chemical pulping. Treatments on this delignification process are supposedly based on the molecular structure of lignin. Unfortunately, this structure is so complicated that even one of the simplest molecular parameters, the molecular weight, has not been convincingly determined. Kinetic studies of delignification are, therefore, handled empirically, largely because of the urgent need in practical applications. Fruitful results on the reactions of model compounds appear to be shedding some light on the reactivity of functional groups or reactive sites. However, direct application of the kinetics of small molecules to delignification has resulted in a serious error as judged from the basic principles of polymer chemistry.<sup>1</sup>

Despite these difficulties, the treatment of delignification processes can be greatly simplified and clarified from the basic recognition that lignin is a polymer. Because its smallest structural unit is an aromatic C<sub>9</sub> unit with polyfunctional groups, the resultant lignin or its degraded products contains branched polymers. According to Flory's theory of polyfunctional polymerization,<sup>2</sup> branched polymers are characterized by a broad molecular weight distribution (MWD) and by a transition from sol (the soluble fraction) to gel at high conversion.

By considering these two characteristics, Szabo and Goring<sup>3</sup> were the first to propose that lignin in wood or the insoluble fraction be treated as a gel or three-dimensional network. Since the simple equations of Flory's theory had been available, Szabo and Goring were able to provide a theoretical basis for delignification by treating it as a degelation process. Subsequent applications

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of Flory's theory to delignification were made by Bolker and Brenner,<sup>4</sup> Bolker et al.,<sup>5</sup> and Yan and Johnson.<sup>6</sup>

The MWD aspect of branched polymers has been elaborated by many authors with elegant mathematics.<sup>7-11</sup> It must be pointed out, however, that in delignification, Flory's theory is applicable for the range beyond the gel point,<sup>6</sup> while most of the theories<sup>7-11</sup> treat the polymerization in the pregel stage. The broad MWD of degraded lignin in the sol fraction has been confirmed in many experiments.<sup>3,5,6</sup> However, Goring<sup>12</sup> has recently questioned the naive nature of this direct application. Of the questions raised, the infinite weight-average molecular weight at the gel point<sup>2,7</sup> appears to be in contradiction with the observation that lignosulfonate particles, and perhaps even lignin in wood, are of finite dimensions.<sup>12</sup> This is not a serious objection, because the infinite weight average degree of polymerization (DP) is a mathematical definition of a gel, while the chemical definition is that a gel is insoluble in good solvents at a given temperature.<sup>2,6</sup> The finite-sized lignin particles in wood, as speculated by Goring,<sup>12</sup> are also insoluble and, therefore, can be safely regarded as a gel.

It is well recognized that Flory's theory was formulated with the "equal reactivity" (of functional groups) and "ring-free" assumptions. These amount to a tree-like structure of the branched polymers.<sup>8-11</sup> Obviously, these are simplified assumptions, but the qualitative aspect of this theory has been reaffirmed many times during the last three decades.<sup>13</sup> Even in applications to complicated natural branched polymers, the MWD aspect of this theory has been proved successfully in amylopectin and glycogen,<sup>14</sup> and antibody-antigen reaction,<sup>15</sup> as well as the gas-liquid transition of water.<sup>16</sup> In a previous communication, we have demonstrated the application of the Flory-Stockmayer (F-S) distribution to the MWD of lignin sol.<sup>6</sup> We also pointed out that the kinetic scheme proposed by Szabo and Goring<sup>3</sup> was written somewhat arbitrarily without conforming to the F-S theory.

The F-S distribution does have a unique *overall* kinetic scheme in terms of  $\alpha$  (the "extent of reaction"—see Appendix for symbols used here). This is demonstrated by Stockmayer.<sup>7</sup> Furthermore, Whittle<sup>10</sup> arrived at this distribution *kinetically*. In this report, we illustrate the kinetic aspect of this theory as applied to delignification.

## EMPIRICAL KINETICS

Before using the F-S theory to delignification, we first discuss the delignification kinetics as commonly practiced in the past. For example, the empirical kinetics associated with a reaction involving lignin L, alkali OH<sup>-</sup>, and anthraquinone AQ is usually written as a "power law" given by

$$-d(L)/dt = k(L)^a(OH^-)^b(AQ)^c \quad (1)$$

where the square brackets denote the concentrations;  $a$ ,  $b$ , and  $c$  are their respective orders of reaction.

As we have pointed out,<sup>1</sup> this kinetics is basically inadequate because it may hold for small molecules or model compounds of lignin, but it is entirely invalid for polymers (linear or branched). Conventional kinetics of delignification expresses the concentration of lignin (L) in weight units, without considering the time dependence of molecular weight. Knowledge of molecular weight in lignin

sol or gel is required to express (L) in correct units of mole or number of molecules per unit volume. Small molecules, such as  $\text{OH}^-$  and AQ in eq. (1), can be expressed either in weight or mole units because their molecular weights are fixed and can be incorporated into the rate constant  $k$ . Published studies of delignification kinetics have seldom been accompanied by molecular weight measurements.

Furthermore, even if (L) is expressed in correct units, it is unusual to write a polymerization or a depolymerization reaction in only one rate equation. Only an overall reaction can be derived which may be the sum of infinite sets of rate equations.<sup>1,7,10</sup> The overall reaction usually expresses the rate in terms of average properties such as average DP or the "extent of reaction." Polymerization always involves chain reactions. A polymeric intermediate with  $\text{DP} = x$  can be formed by species with  $\text{DP} = x - 1$  or less. It can also polymerize to DP greater than  $x$ . In its usual meaning, L in eq. (1) has not been identified as a polymeric intermediate, therefore, the kinetic scheme in this equation is highly questionable from the standpoint of polymer chemistry.

It is doubtful that polymerization kinetics can be formulated without proposing a theoretical model or scheme. The overall reaction thus obtained must be examined carefully to see if it furnishes the complete description of the polymerization or just a part of the process. One example is the rate of polymerization, measured by the rate of disappearance of the initial monomers.<sup>2</sup> This definition is useful in free-radical polymerization. Even there, the evaluation of the rate of polymerization alone does not constitute a complete description of the polymerization process but only the propagation step.

### DEGELATION KINETICS

Stockmayer considers the formation and disappearance of a polyfunctional  $x$ -mer by allowing the molecule to branch out like a tree.<sup>7-11</sup> The starting molecule is a monomer  $\text{RA}_n$  with  $n$  functional groups; the kinetics is

$$\frac{1}{k} \frac{dm_x}{dt} = \frac{1}{2} \sum_{s=1}^{x-1} (ns - 2s + 2)(nx - ns + 2x - 2s + 2)m_s m_{x-s} - (nx - 2x + 2)m_x \sum_{s=1}^{\infty} (ns - 2s + 2)m_s \quad (2)$$

where  $m_x$  denotes the number of  $x$ -mers in a given volume at a given temperature. The substitution of the variable  $x$  with 1, 2, 3, etc., results in the rate of formation and disappearance of monomers, dimers, trimers, etc. There are infinite numbers of rate equations because  $x \rightarrow \infty$ . Fortunately in many polymerization schemes, these result in a summable, rapidly convergent series from which the expression of MWD can be derived. In addition to the MWD expression, an overall kinetics in  $\alpha$  is also obtained<sup>7</sup>:

$$d\alpha/dt = (kN/4)(1 - \alpha)^2 \quad (3)$$

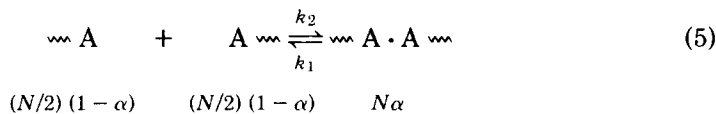
where  $N$  is the total number of functional groups.

This expression actually spells out the basic scheme of the F-S type of polycondensation: it takes two unreacted functional groups to form a crosslink. The number of reacted group at any instant is  $N\alpha$ , that of the unreacted group is  $N(1$

—  $\alpha$ ). Whittle considers a general case where depolymerization is also allowed.<sup>10</sup> The net rate is

$$d\alpha/dt = (k_2N/4)(1 - \alpha)^2 - k_1\alpha \quad (4)$$

which is a description of the reaction to the right-hand side of the following scheme:



The concentrations in terms of the number of reactive groups are written under the A groups. The dot between two As denotes a crosslink. This reaction obviously treats the functional groups as small molecules in their kinetics.

In a delignification process, the "cooking chemicals" react with both the polysaccharide and lignin components of wood. These can be considered as two competitive, parallel reactions. In the presence of excessive cooking agents under an isothermal cooking condition, we can treat the dissolution of lignin as a separate reaction.<sup>3,4</sup> Furthermore, it is believed that the porous structure of the polysaccharide portion of the cell wall plays an important role in the dissolution process of lignin.<sup>12</sup> This effect is also ignored in our treatment because the F-S theory implies a change in molecular size which in turn is partly controlled by the pore size of the cell wall.

Experimentally, the total number of reactive groups  $N$  can be made constant. Therefore, we can write  $k_2N/4$  as  $k_2$ . Furthermore, the effect of cooking chemicals, e.g.,  $\text{OH}^-$  and  $\text{AQ}$ , can be made fixed by adding constant and excessive amounts of these reactants. Therefore, for the delignification alone, we can write the kinetics as the reverse process of eq. (4):

$$d\alpha/dt = k_1\alpha - k_2(1 - \alpha)^2 \quad (6)$$

This equation is that of an opposing unimolecular-bimolecular (OUB) reaction and has the solution<sup>17</sup>

$$\tau + C = \frac{2}{B} \tanh^{-1} \frac{(r + 2 - 2\alpha)}{B} \quad (7)$$

where  $r = k_1/k_2$ ,  $\tau = k_2t$ ,  $B = (r(r + 4))^{1/2}$ , and  $C$  is the integration constant evaluated at  $\tau = 0$ ,  $\alpha = \alpha_0$ .

We also note that  $t \rightarrow \infty$ ,  $d\alpha/dt = 0$ ,  $\alpha = \alpha_c$ . This is the boundary condition under which an equilibrium is reached. We have, from eq. (6),

$$(1 - \alpha_c)^2/\alpha_c = k_1/k_2 = r \quad (8)$$

We identify the critical value  $\alpha_c$  as the extent of reaction at the gel point. This is a practical condition since we note that it takes a very long time to remove all the lignin in a cooking process. The complete removal of the lignin gel is described here as  $\alpha = \alpha_c$  with  $t \rightarrow \infty$ . Of course, there are still crosslinks in the soluble branched polymers that may be broken, but there is no gel at  $\alpha_c$ . These remaining crosslinks can be ignored in the degelation process.

Having identified the delignification kinetics by a direct appeal to the F-S theory, we now demonstrate the application with two numerical calculations. To allow for a greater flexibility, the F-S theory used here is the extended form,

applicable to the postgel stage.<sup>11,18</sup> First, we assume that primary linear chains are formed and that crosslinking then takes place between these chains. The DP of both the linear chains and the crosslinked molecules is expressed in terms of repeating units, with each unit containing one functional group capable of crosslinking. In delignification, of course, the crosslinking process is reversed. The primary chains are actually the ultimate chains into which lignin would degrade. However, to avoid excessive change in terminology, we shall still call them the primary chains.

The extended F-S theory allows both the average DP and MWD of primary chains to vary,<sup>11</sup> as opposed to the fixed number of functional groups ( $n$ ) in the original F-S theory. For our computation, we need the following postgel properties<sup>18</sup>:

The crosslinking index in the postgel stage is

$$\gamma = \lambda\alpha \geq 1 \quad (9)$$

The critical value of  $\gamma$  is unity at the gel point;  $\lambda = \bar{y}_w - 1$ , where  $\bar{y}_w$  is the weight-average DP of the primary chains. The weight fraction of the gel ( $w_g$ ) and that of the sol ( $w_s$ ) are given by

$$1 - w_g = w_s = (1 - \alpha)u + \alpha u^2 \quad (10)$$

where  $u$  is defined by Flory as the probability that a noncrosslinked group selected at random belongs to the sol fraction. Values of  $u$ , depending on the primary MWD, have been tabulated for both broad and narrow distributions.<sup>18</sup>

### ONE-GEL MODEL

Our model calls for an assumed weight average DP and MWD of the primary chains.<sup>6</sup> The value of  $\lambda$ , according to Bolker et al.,<sup>5</sup> is 17. The primary distribution, characterized by a dispersion ratio (the ratio of weight average to number

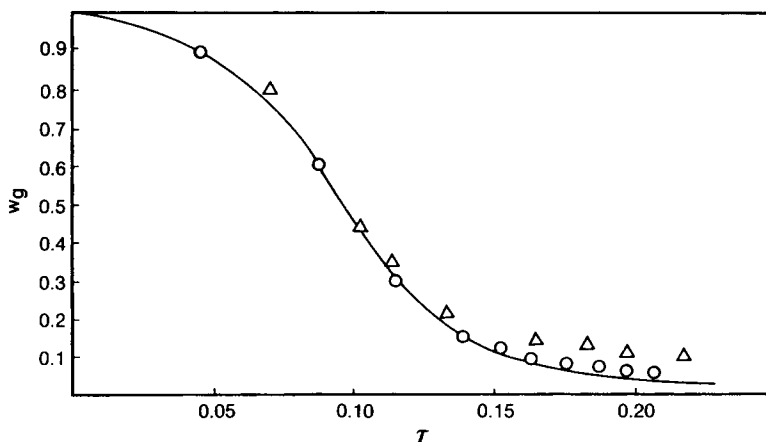


Fig. 1. Delignification curve as defined by plot of  $w_g$  vs.  $\tau$ . Solid curve is obtained by assuming a "most probable" distribution for the primary chains with  $\lambda = 17$ . Circle data points are obtained with a kraft process (suffidity 31%), triangles are from a soda process. Both cooking processes were carried out at 170°C.

average) of 2, is Flory's "most probable" distribution.<sup>6</sup> The identification of the MWD allows one to use the values of  $u$  given in Table 2 of ref. 18.

Next, we need an initial value of  $\alpha$  at  $t = 0$ . As did Szabo and Goring,<sup>3</sup> we use  $\alpha_0 = 1$ . The gel point is given by  $\alpha_c = 1/\lambda = 0.0588$ . From eq. (8), we obtain  $r = 15.06$ . With these parameters, the integration constant  $C$  in eq. (7) is found to be  $C = 0.1672$ . We can then calculate  $\tau$  as a function of  $\alpha$ , which, together with values of  $u$ , allows us to calculate  $w_g$  in eq. (10). A plot of  $w_g$  vs.  $\tau$  can then be made.

Using the estimated parameters for calculation, the result is shown in Figure 1, which can be considered as a delignification kinetic curve. The curve shape in this figure agrees well with that obtained by Hägglund.<sup>19</sup>

To compare the calculated curve with actual "cooking" data, we also use two sets of data obtained by Hägglund and Hedlund.<sup>20</sup> We arbitrarily chose the cooking time to reach  $w_g = 0.5$  to coincide with our calculated value of  $\tau$ . We can see that the general curve shape throughout the entire range is in excellent agreement with the data. In translating the cooking data to  $w_g$ , we use the relation  $w_g = \text{weight fraction of lignin in pulp} \times \text{fractional pulp yield/original fraction of lignin in wood}$ .

The curve shape in Figure 1 can be altered by changing the primary chain distribution. If a narrow (Poisson) distribution is assumed, the data fit the curve well at low  $\tau$  values. At high cooking time, the fit is much worse than the one shown in Figure 1. The curve obtained with a Poisson primary chain distribution is now shown in Figure 1 because the MWD argument does not support a predominantly narrow chain size distribution.<sup>6</sup>

The result in Figure 1 obviously has the required validity in the basic principles of kinetics. In kraft and soda pulping, it is usually claimed that both are first order with respect to the weight of lignin.<sup>21,22</sup> According to the "power law" in eq. (1), this claim amounts to the identification  $a = 1$ . We can easily see how this identification is arrived at, simply by plotting our calculated  $\log w_g$  vs.  $\tau$  as given in Figure 2. It is easy to define a portion of this curve as a straight line; thereby, one might conclude that the kinetics is first order in the weight of lignin. The range of linearity happens to be in the practical pulping range, or the range of "bulk" delignification.

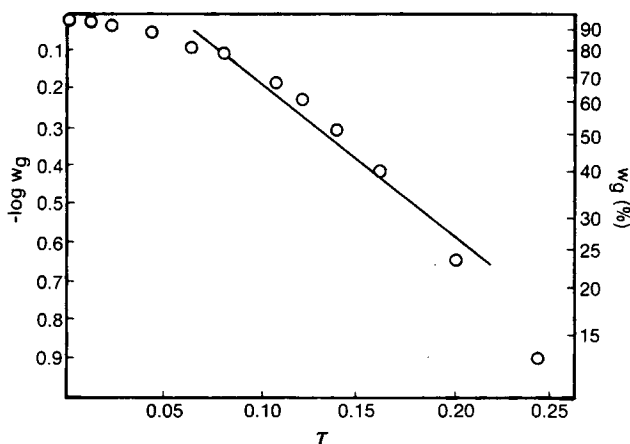


Fig. 2. Plot of  $\log w_g$  vs.  $\tau$  obtained from the theoretically calculated data.

If delignification involves anthraquinone in alkali, the reaction order in lignin has been claimed to be second order.<sup>23</sup> Again, using our theoretical curve to test this claim, we plot  $1/w_g$  vs.  $\tau$  in Figure 3. Here, we can also find a linear portion, and one might conclude that the reaction is second order.

### TWO-GEL MODEL

The delignification curve shown in Figure 1 contains three stages, namely, the "initial," "bulk," and "residual" delignifications. Again, this distinction of three stages agrees well with practical observation. However, the model suffers a major discrepancy because all kinetic schemes are formulated under an isothermal condition, whereas the actual cooking time is not corrected for the temperature difference in the course of the reaction. Conventionally, the cooking time can be converted to the effective time with the application of the "H" factor.<sup>24</sup> Unfortunately, the development of the "H" factor was based on the assumption of the validity of an activation energy, which in turn was derived from a questionable first-order kinetics in  $w_g$ .<sup>21,24</sup> Therefore, a fair comparison between the model and cooking data should be made by choosing experimental results obtained with rapid heating to a fixed temperature. Experimental data are indeed available for isothermal cooking.<sup>21,22</sup> Most of the data points, as fitted with a theoretical curve, are found to be located at lower time than that prescribed by the model. Isothermal cookings generally reduce the initial stage to a negligible proportion.<sup>22</sup>

Our model is therefore modified with a two-gel scheme. Szabo and Goring<sup>3</sup> used the argument of a topochemical difference to distinguish two forms of lignin gel, applicable to the lignins in the cell wall and middle lamella of wood. There

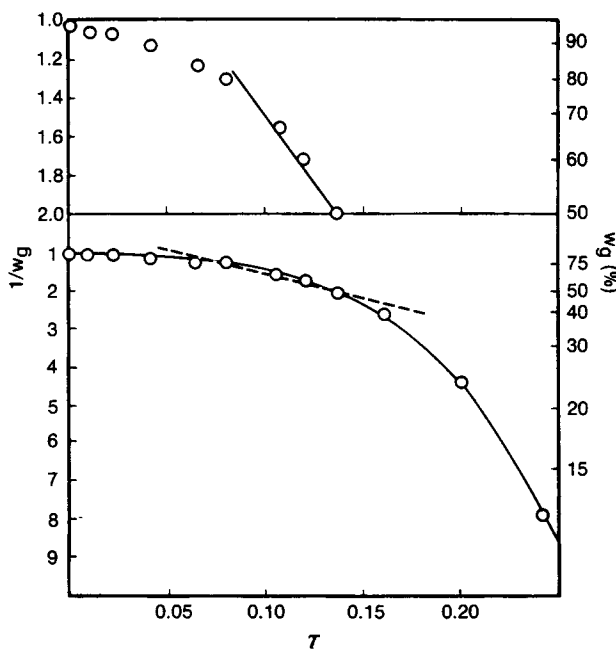


Fig. 3. Plot of  $1/w_g$  vs.  $\tau$ .

are two sets of rate constants for two lignin gels. The evidence of two gels can also be derived from the measurement of the MWD of dissolved lignin, as pointed out in our previous article.<sup>6</sup> The assignment of so many rate constants obviously complicates the calculation. However, in our model, the rate constants can be readily translated into molecular parameters such as the primary MWD and  $\lambda$ . With reasonable experimental evidence, we make the following assumptions for a two-gel model:

(1) Once a crosslink is broken, the free functional groups are equally reactive.<sup>2-7</sup> Therefore, the rate constant  $k_2$  is identical in the two forms of lignin gel.

(2) The bulk of lignin, located at the secondary cell wall is degraded into primary chains with a "most probable" distribution and weight average DP =  $\lambda' + 1$ .

(3) A smaller portion of lignin in the middle lamella has a Poisson distribution in the primary chains with weight-average DP =  $\lambda'' + 1$ .

A strong support for the last two assumptions is given in Figure 4. The variation of dispersion ratios with the dissolved fraction, measured for the dioxane lignin, cannot be accounted for with a single MWD of the primary chains.<sup>6</sup> However, if the separation of two gels is made according to assumptions (2) and (3), the dependence of this ratio on the dissolved fraction is in good agreement with the experimental data, as shown in Figure 4. In calculating the total fraction undissolved, we used the weight fractions estimated by Szabo and Goring<sup>3</sup>:

$$w_g = 0.7w_g' + 0.3w_g'' \quad (11)$$

where the prime and double prime signs refer to the properties of the gels in the cell wall and middle lamella, respectively.

In addition to the inclusion of two forms of gel, we also modify the boundary condition concerning the value of  $\alpha_0$ . This requires a deeper analysis of lignin structure. The crosslinks described here generally refer to  $\beta$ -aryl ether groups.<sup>3,6</sup> Once a crosslink is broken, a free phenolic hydroxyl group is liberated. Since the other free group generated is not a phenolic hydroxyl group, we actually start the reaction with a heterofunctional crosslink A-A' instead of the homofunctional one, A-A. There is no need, in this treatment, to assume a single type of functional group.

The introduction of the heterofunctional group does not alter the mathematics

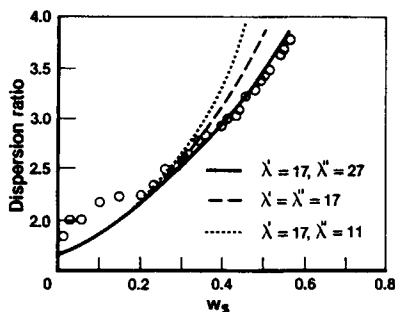


Fig. 4. Dispersion ratio in the lignin sol plotted against the soluble fraction, with  $\lambda'$  and  $\lambda''$  specified.



we use. The derivation of postgel properties has its origin in the consideration of the MWD of branched polymers.<sup>18</sup> The MWD of both heterofunctional and homofunctional crosslinking is governed by a general form of Lagrange distribution functions.<sup>13</sup> However, the consideration of a heterofunctional crosslinking requires a modification of the value of  $\alpha_0$ .

The number of free phenolic hydroxyl group per  $C_9$  unit in wood has been determined to be 0.2–0.25.<sup>25,26</sup> Since each free phenolic hydroxyl group (A) has associated with a pairing group (A'), the value of  $1 - \alpha_0$  should be twice this value; it therefore ranges from 0.4 to 0.5. The value of  $\alpha_0$  given by Bolker and Brenner is 0.28.<sup>4</sup> This value is too low because they fail to account for the factor of 2. When this factor is applied, we again obtain  $1 - \alpha_0 = 0.44$ .

In the two-gel model, the total number of functional groups is designated as  $N'$  and  $N''$  in the cell wall and middle lamella, respectively. The numbers of free A and A' groups at the beginning of reaction are  $(N'/2)(1 - \alpha_0')$  and  $(N''/2)(1 - \alpha_0'')$  in these two gels. Experimentally, it has been determined that  $N'(1 - \alpha_0')/N''(1 - \alpha_0'') = 2$  for spruce wood.<sup>26</sup> The numbers  $N'$  and  $N''$  are proportional to the weight fraction of cell wall and middle lamella lignins in wood and are estimated<sup>3</sup> to be  $N' = 0.7N$ ,  $N'' = 0.3N$ .

Following this argument, we can readily write down

$$N(1 - \alpha_0) = N'(1 - \alpha_0') + N''(1 - \alpha_0'')$$

$$\frac{(1 - \alpha_0')}{(1 - \alpha_0'')} = \frac{6}{7}$$

By assuming  $1 - \alpha_0 = 0.4$ , we obtain  $1 - \alpha_0' = 0.38$ ,  $1 - \alpha_0'' = 0.44$ . These values of  $\alpha_0'$  and  $\alpha_0''$  are used for our calculation in the two-gel model.

Using assumption (1), the time dependence of  $w_g$  on  $\tau$  (which is the same for both forms of lignin) can be calculated as in the one-gel model; the calculation uses only eqs. (7), (10), and (11), together with their boundary conditions. The evaluation of Flory's probabilities  $u'$  and  $u''$  can be found elsewhere.<sup>18,27</sup>

The result in Figure 4 suggests that the best fit is the one with  $\lambda' < \lambda''$ . This criterion is used in Figures 5 and 6 where the delignification curves are displayed in semilogarithmic plots. This type of plot allows an immediate comparison with experimental data obtained isothermally. It can be seen that the initial delignification stage is reduced to a smaller extent with a proper choice of  $\lambda'$  and  $\lambda''$ . In Figure 5,  $\lambda'$  is fixed at 17, with  $\lambda'' = 17$  and 27. The increase in the value of  $\lambda''$  does not result in a drastic change in the shape of the curves.

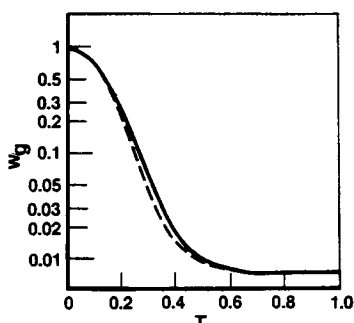


Fig. 5. Delignification curves obtained with the two-gel theory, with  $\lambda'$  fixed at 17. The insoluble fraction  $w_g$  is plotted in logarithmic scale. Solid curve  $\lambda'' = 17$ , dashed curve  $\lambda'' = 27$ .

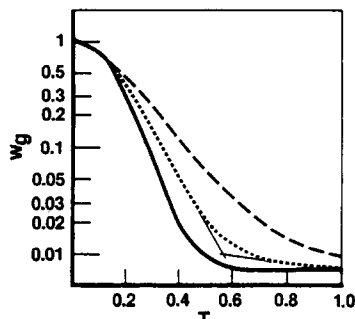


Fig. 6. Same as Fig. 5, except  $\lambda'' = 17$ ;  $\lambda' = 7$  (dashed curve), 11 (dotted curve), and 17 (solid curve).

On the other hand, we fix  $\lambda''$  at 17 in Figure 6. Here, the change of  $\lambda'$  has a greater effect on the curve shape. The one with  $\lambda' = 7$  gives an apparent straight line. The curve with  $\lambda' = 11$  starts to give two apparently straight lines intersecting at the beginning of residual delignification. This point of intersection is much lower than those found experimentally.<sup>22</sup> This may be due to the choice of the boundary condition given in eq. (8).

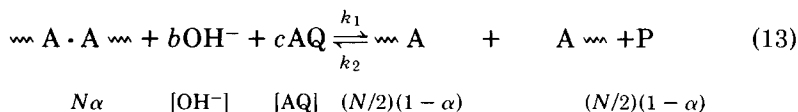
The argument against the empirical evaluation of the reaction orders still applies here, as in the case of the one-gel model. The two models differ only in the range of initial delignification, with the two-gel model being closer to the isothermal delignification. Further improvement with the two-gel model is also evident in Figure 4, which can be considered as a supplement to our previous argument on the MWD of lignin sol.<sup>6</sup> In either one-gel or two-gel model, the slope of a straight line portion in a plot of  $\log w_g$  vs.  $\tau$  or  $1/w_g$  vs.  $\tau$  does not seem to allow the evaluation of  $k_1$  or  $k_2$  in an OUB reaction model.

## DISCUSSION AND CONCLUSIONS

Our models consider only the kinetics on lignin alone. The effect of cooking chemicals, such as  $\text{OH}^-$ , AQ, or  $\text{HS}^-$ , can be incorporated into  $k_1$  in eq. (6). This requires another "power law" approach such as

$$k_1 = k'(\text{OH}^-)^b(\text{AQ})^c \quad (12)$$

The "power law" as applied here is now justifiable because the reactants involved are small molecules (or groups or species with constant molecular weights). The reaction can be written as



The concentrations written below the species are now in correct units. The symbol P denotes other products which may or may not be inert.

Our model suggests an OUB reaction, i.e., a delignification of first order in  $\alpha$  and an opposing second order, also in  $\alpha$ . The opposing reaction can be considered as a resistance to delignification. This resistance accounts for the extremely long time to remove all the lignin in wood. Phenomenologically, this resistance

is known as a "recondensation" of lignin.<sup>28</sup> In pulping experience, both kraft and soda-AQ processes are known to reduce the recondensation, more so than the soda process. This reduction in recondensation may be accounted for with higher values of  $k'$  such as  $k_1 \gg k_2$ . However, the value of  $k_2$  in any process, although very small, may still contribute significantly at the later stage of delignification.

Although we have formulated the delignification kinetics from the basic principles of polymer chemistry, there are also parallel studies in lignin chemistry, especially in kinetics of model compounds. The reaction given in eq. (13) suggests that if lignin is replaced with a dimeric model compound, with  $N\alpha$  molecules in the reaction vessel, the same kinetics should hold. In other words, the scheme in eqs. (6) and (7) should be also valid for a dimer containing one functional group. Indeed, reversible kinetics for a dimer has been proposed.<sup>29</sup> This reaction was carried out in a kraft cooking medium. With excessive amounts of cooking chemicals added, the opposing reaction is suppressed such that the second term in the right-hand side of eq. (6) becomes negligibly small. The first-order reaction thus derived is well justified because the model compound is a small molecule.

Our reaction model expresses the rate constants  $k_1$  and  $k_2$  in terms of the molecular parameter  $\lambda$ . The literature values of  $\lambda$  range from 2 to 17 for a uniform distribution,<sup>3-5</sup> 11 for a Poisson distribution,<sup>6</sup> and 27 for a most probable distribution.<sup>6</sup> Also, these values may vary in different cooking media. It is doubtful that such an intrinsic value of primary chains in lignin can be determined unequivocally soon. Fortunately, the range of  $\lambda$  is not large for a trial-and-error type of calculation,<sup>4</sup> which may not be tedious since only relative values of the rate constants are needed.

The largest estimated value of  $\lambda$  gives a maximum value of  $r$  of only about 25. This itself is not such a large number that the term  $(1 - \alpha)^2$  may be significant in comparison with  $r\alpha$ . This is to say that the complete suppression of the second term in the right-hand side of eq. (6) may not be feasible in the degelation kinetics.

From the arguments given above, we reach the following conclusions:

In accord with previous publications,<sup>3-6</sup> our model proposes that the delignification be treated as a degelation process. This proposal has been supported with both the MWD<sup>6</sup> and the kinetic aspects of data. Theoretical and empirical bases of this approach have been consistent with the principles of polymer chemistry.

The basic requirement of this model is the validity of the F-S theory itself. Since it is perhaps the only available quantitative theory on crosslinking and gelation, its application to natural and synthetic branched polymers has been very popular. Although the theory itself involves some simplified assumptions, its successful application to branched polymers appears to justify these assumptions. For delignification studies on MWD or kinetics, these assumptions are at least qualitatively correct.

We have not studied the dependence on the cooking chemicals for  $k_1$ , as given in eq. (12). Like the discussion on the MWD of degraded lignin,<sup>6</sup> we leave the more refined data fitting for future studies. It is sufficient to conclude that, judging from the success of the degelation theory, chemical pulping can be expected to progress on a sound molecular basis.

## APPENDIX

## Symbols

A	reactive functional group in polyfunctional monomer RA <sub>n</sub> or functional group in lignin <sup>6</sup>
A'	heterofunctional group crosslinks with A
B	$[r(r + 4)]^{1/2}$
AQ	anthraquinone
C	integration constant
L	lignin molecule
N	total number of functional groups in lignin
[ ]	concentration in moles per liter
a, b, c	reaction orders in eq. (1)
k, k', k <sub>1</sub> , k <sub>2</sub>	rate constants
m <sub>x</sub>	number of x-mers in eq. (2)
n	number of functional groups in RA <sub>n</sub>
r	k <sub>1</sub> /k <sub>2</sub>
s	running variable in eq. (2)
t	time
u	Flory's probability listed in ref. 18
w <sub>g</sub>	weight fraction of insoluble lignin (gel)
w <sub>s</sub>	weight fraction of soluble lignin (sol)
x	DP of branched polymers
$\bar{y}_w$	weight-average DP of primary chains
α	extent of reaction = fraction of reacted functional group
α <sub>c</sub>	critical value of α at the gel point
α <sub>0</sub>	initial value of α at t = 0
γ = λα	crosslinking index
λ = $\bar{y}_w - 1$	
τ = k <sub>2</sub> t	

## Abbreviations

DP	degree of polymerization; in lignin, DP is expressed as the number of functional groups in a molecule
MWD	molecular weight distribution
OUB	opposing unimolecular-bimolecular (reaction)

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