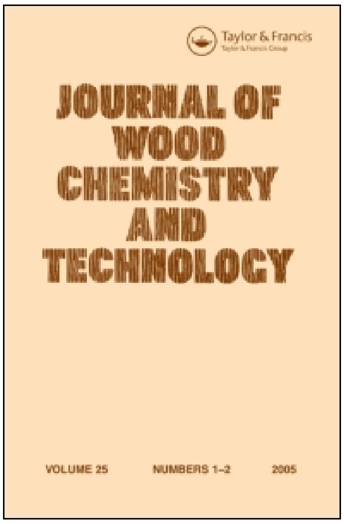

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THE GEL DEGRADATION THEORY, PART III
AN EXPERIMENTAL KINETIC VERIFICATION

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ABSTRACT

Yan and Johnson's kinetic model, which has been developed for the purpose of describing wood delignification, recognizes the polymer network structure of lignin. Their model is experimentally examined with a synthetic network polymer. The starting material was functionalized monodisperse polystyrene crosslinked to yield networks in which the parameters of the theoretical equations were known. By the hydrolytic random cleavage of the crosslinks, kinetic data for this model network degradation experiment was obtained.

Thus, the kinetics of this model degradation were found to be adequately described by the Yan and Johnson expressions, which furnish additional support for the gel degradation theory and the model examined herein.

INTRODUCTION

The elucidation of kinetics is of vital importance towards comprehending a chemical process, with wood delignification representing no exception.

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There are basically two approaches developed to kinetically treat the pulping of wood, which probably represents one of the oldest chemical processes known to mankind. Empirical kinetics and those based on the recognition of the polymeric nature of lignin[1]. The rather complex and controversial nature of lignin in wood has led towards the development of empirical kinetic expressions which have been useful in serving the industry despite the serious errors involved when they are judged from a polymer chemists viewpoint[1,2]. The advancing state of our knowledge with regard to the chemical nature of lignin points towards it being a three-dimensional crosslinked network[3-6]. Accordingly, one cannot apply simple homogeneous molecular kinetics to an inhomogenous macromolecular system.

The theoretical inadequacy of the empirical approach is apparent from an examination of typical master delignification curves. In these, concentration is never expressed in moles but rather in weight. The idea of a mole is of no significance when there is inadequate knowledge on the structure of lignin. Yan's admirable efforts[1,2,7-9] to establish delignification kinetics on a sound scientific basis using the principles of polymer chemistry and the gel degradation theory have provided the literature with a comprehensive handle on this intricate and mathematically involved subject.

The work described in this communication represents an experimental effort to test for the validity of the Yan and Johnson kinetic model[1]. Thus, an appropriate model network polymer has been synthesized[10] in which all parameters of the theoretical expressions are known. The hydrolytic degradation of this network, attempts to experimentally simulate an ideal delignification experiment. The kinetic data thus derived is compared with the Yan and Johnson model in an effort to shed more light in this controversial subject.

THEORY AND DISCUSSION OF RESULTS

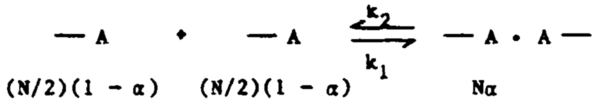
Bolker and Brenner[4], in their efforts to elucidate the structure of lignin arrived at a somewhat different picture for the network to that of Szabo and Goring[3]. They proposed that this naturally occurring network was one formed by the random crosslinking of primary monodisperse chains of DP = 18 and an average degree of crosslinking equal to 0.277. Our work undertook the testing of the primary assumption of reversibility of gelation both for the Szabo and Goring[12] and the Bolker and Brenner[10] pictures by synthesizing and then degrading model networks which fit their descriptions respectively. In both cases the basic premises of the gel degradation theory have been found to hold.

Yan and Johnson[1], in their efforts to treat chemical pulping as a degelation process, derived a kinetic model based on an extended version of the Flory-Stockmayer theory[13-15], and the kinetics of Whittle[16]. The Yan and Johnson model assumes the Bolker and Brenner description for lignin and it can be briefly summarized as follows: it takes two unreacted functional groups to form a crosslink. Thus, the number of reacted functional groups at any time is $N.\alpha$, where N is the total number of functional groups and α is the extent of reaction. Consequently, the number of unreacted groups will be $N(1 - \alpha)$. In a kinetic sense, the Flory-Stockmayer theory[14] implies Equation 1.

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

Whittle[16], however, considered a more general case by allowing for depolymerization, in which the net rate will be represented by Equation 2, which describes the process in Equation 3.

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



$$\underset{(N/2)(1-\alpha)}{—A} \quad + \quad \underset{(N/2)(1-\alpha)}{—A} \quad \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \quad \underset{N\alpha}{—A\cdot A—} \qquad (3)$$

The concentrations of the reactive groups A are written below them. The dot between two A groups represents a crosslink. Yan and Johnson assume that "experimentally the total number of reactive groups N can be made constant", thus $k_2N/4 = k_2$. The diffusion of lignin macromolecules through the porous structure of wood[17,18] is also ignored. For degelation, therefore, one may reverse the kinetic expression (2), giving Equation (4).

$$d\alpha/dt = k_1\alpha - k_2(1-\alpha)^2 \qquad (4)$$

For such an opposing unimolecular-bimolecular reaction, Margenau and Murphy[19] supply Equation (5) as the solution to Equation (4)

$$\tau + C = \frac{2}{B}\tanh^{-1}\frac{(r+2-2\alpha)}{B} \qquad (5)$$

where $r = k_1/k_2$

$\tau = k_2t$, dimensionless time

$B = [r(r+4)]^{\frac{1}{2}}$

$C =$ the integration constant for $\tau = 0$, $\alpha = \alpha_o$.

Yan and Johnson state that as $t \to \infty$, when equilibrium is reached, $d\alpha/dt = 0$, $\alpha = \alpha_c$ (α_c the degelation point). With such a boundary condition, Equation (5) can be transformed to Equation (6).

$$(1-\alpha_c)^2/\alpha_c = k_1/k_2 = r \qquad (6)$$

For the calculation, the model also requires certain postgel quantities. The crosslinking index, γ, in the postgel region is defined by Equation (7),

$$\gamma = \lambda\alpha > 1 \qquad (7)$$

γ_c = critical value = 1 at the critical point, and $\lambda = \bar{y}_w - 1$, where $\bar{y}_w$ is the weight average degree of polymerization of the primary chains (4). The quantities W_g and W_S are also required, and represent the weight fractions of gel and sol, respectively, remaining at any stage beyond the gel point. They can be obtained from Equation (8).

$$1 - W_g = W_S = (1 - \alpha)u + \alpha u^2 \tag{8}$$

Flory defined u as the probability of an uncrosslinked group selected at random from the system, belonging to the soluble fraction. The values of u depend on the molecular weight distribution of the primary chains, and for this purpose they have been tabulated by Yan[9] for the broad and narrow molecular weight distribution cases.

In accordance with the principles of the gel degradation theory[3-5], the random cleavage of crosslinks in a network would initially result in minute amount of material being freed from the network. The size and amount of the fragments, however, should increase as the crosslink cleavage proceeds. This is because the probability increases that the larger number of bond cleavages will have occurred that are required to detach larger fragments. Thus, in the latter stages of the degradation process the crosslink cleavage reactions become progressively more effective in freeing more soluble material. At this stage, fewer bonds need to be cleaved to free larger fragments from a less densely crosslinked network. Several concepts flow from this description which attempts to put into words the network-forming process in reverse.

One of the features of this description, in the context with the subject matter of this paper, is that the gel degradation theory predicts accelerated kinetics as the degradation point is approached. Our experiments, have monitored the quanity of material (W_S) detached from the network during degradation as a function of degradation time. In Figure 1, the two measurable quantities have been plotted and the qualitative correlation with the above description is obvious. In an effort to quantify the magnitude of the correlation the kinetic model of Yan and Johnson was applied to the results of Figure 1. The model kinetically treats the process of degelation of a crosslinked network formed by the random crosslinking of primary chains of known $\bar{y}_w$ and molecular weight distribution.

Thus, according to our starting polymer, the value of λ is 20. The initial value of $\alpha = \alpha_o = 1.0$ (representing a fully crosslinked network in which all functional groups have been used up) is in accordance with Szabo and Goring[3] and Yan and Johnson[1]. For the critical point Equation [9] gave:

$$\alpha_c = 1/\bar{y}_w - 1 = 1/19 = 0.0526 \qquad (9)$$

r was then evaluated from Equation (6) as being equal to 17.064. Consequently, the integration constant C of Equation (5) could then be evaluated by using $\tau = 0$, $B = 18.958$ (because $B = [r(r + 4)]^{\frac{1}{2}}$) and $\alpha = \alpha_o = 1$, giving $C = 0.1553$. Next, τ was calculated as a function of α from Equation (5). Finally, by using the values of u supplied in Table 2 of reference 9, for the case of a narrow Poisson primary chain distribution, the values of W_S were calculated through Equation (8). Relation (7) was used at this point so that the W_S values calculated would coincide with the values of γ tabulated by Yan[9]. This procedure allowed the theoretical plot (solid line) of W_S versus τ of Figure 2 to be made. Next the values of time t of the data of Figure 1 had to be transformed to dimensionless time τ so that the data could be compared with the model curve. This was done, as suggested by Yan and Johnson[1], by arbitrarily choosing the degradation time to reach $W_S = 0.5$ (from Figure 1). This time was 2.13 hours, and it was coincided with the τ value given

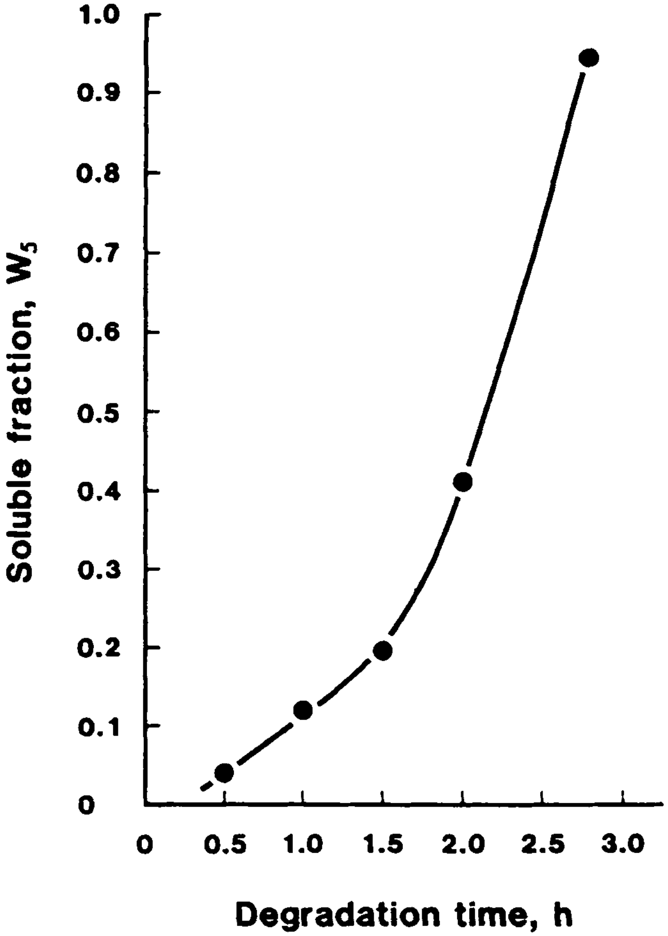


Figure 1. The plot of W_S versus degradation time as obtained by degrading a network whose primary monodisperse chains had a DP = 20 and a degree of crosslinking $\rho = 0.4$.

by the model at the same Ws value, i.e., $\tau_{0.5} = 0.218$. Some criticism as to this arbitrary scaling of the τ parameter could probably be made. Its use is an unavoidable necessity, however, because no information as to the value of k_2 is available.

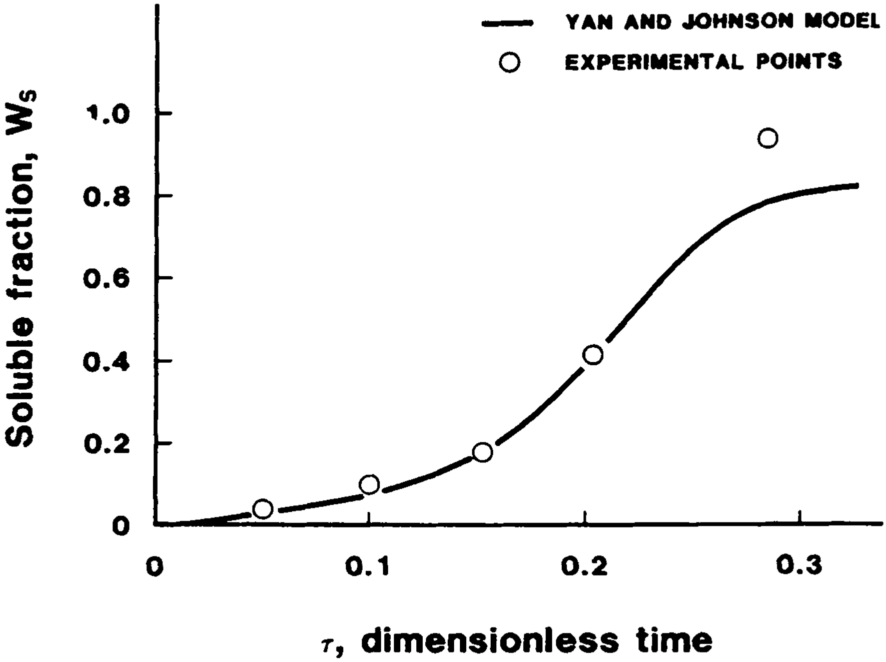


Figure 2. Comparison of the Yan and Johnson kinetic model with the experimental results calculated from the data of Figure 1.

Excellent agreement between the model and the experimental points (except one near the critical point) is shown in the plot of Figure 2. This confers considerable strength on the model because although it was developed to describe the process of wood delignification, it has now been tested with a model system. Its success in predicting the kinetics of degradation of the model network is comparable to that of an earlier effort by Yan and Johnson[1]. They compared their model delignification curve with actual wood delignification data as given by Hägglund and Hedlund[20,21] for the kraft process. When a narrow primary chain distribution was assumed, the Hägglund and Hedlund data fit the theoretical curve quite well at low τ values but not so well at higher τ values. The fit improved when the most probable primary chain distribution was assumed for the lignin network.

The discrepancy obtained at the high τ value in the plot of Figure 2 cannot be accounted for on the basis of the molecular weight distribution of the primary chains of the network because they were carefully chosen to be of a narrow distribution. The effect may be the consequence of experimental error because the discrepancy is very near the critical point ($W_S = 0.941$), a region susceptible to errors. Alternatively, the deviation may be due to the boundary condition $t \rightarrow \infty$, $d\alpha/dt = 0$, $\alpha = \alpha_c$ imposed by Yan and Johnson. This is a practical condition because it takes very long time to remove all the lignin from wood during the delignification process. It is thus probable that this deviant point is more representative of the model process under study, because it has been observed that infinite time is not required for degelation to be effected in any of the experiments of this work.

In any event, the excellent correlation between the Yan and Johnson model and the experimental results of degrading a synthetic network supplies ample evidence of the applicability of the model. Thus the correlation provides theoretical and experimental justification of the validity of the gel degradation theory.

EXPERIMENTAL

The Preparation of the Model Network

Monodisperse polystyrene ($\bar{M}_w/\bar{M}_n < 1.06$, $\bar{M}_n$=1990 g·mole^{-1}, $\bar{M}_w$=2100 g·mole^{-1} ±5%) was randomly carboxylated on its para-position by the synthetic route described elsewhere[11]. Its –COOH content was then determined by three independent techniques[11] to be 40 mole %. The polymer was finely pulverized in a mortar and carefully dried by standing over phosporous pentoxide in a vacuum desiccator (10^{-3} mm Hg) until constant weight.

Ten grams of this material (accurately weighed) were thoroughly mixed and repulverized with 2.86 g of dry 1,10–

decamethylene glycol (DMG) (Reg. No. 112-47-0). The powdered, homogeneous mixture was quantitatively transferred to a 100-mL round-bottomed flask. It was then sealed with a rubber septum and its air was replaced by a slow dry nitrogen stream. The needles used for introducing the nitrogen were removed and the flask was immersed in an oil bath at 140°C. At this temperature, both components melted and the flask was turned to facilitate the mixing of the melt. After about 15 minutes, the temperature of the bath was increased to 160°C and was kept at that level for an additional 12 hours. More frequently at this time, and especially prior to gelation, the flask was again turned uniformly to facilitate mixing. The septum was also punched with a needle occasionally so that the liberated vapour would escape. In order to make sure that the reaction proceeded smoothly to its limiting conversion value, care was taken to remove all liberated water, and this was done in stages. On occasions the flask was wiped clean and, while hot, was placed in a desiccator over KOH under high vacuum overnight. This ensured removal of the water formed, and the reaction was continued to its next stage. After sufficient heating at 160°C, the theoretical amount of water had been evolved (0.575 g H_2O). A further 2 hour period of heating and drying verified the completion of the reaction.

To the hard mass of material thus formed 50 mL of distilled THF was added. The polymer was allowed to swell and soften overnight in the solvent. It was then easily scraped and poured out of the flask. The swollen gel was filtered from the solvent and then Soxhlet-extracted for 48 hours with THF. Next it was transferred into a 250-mL beaker (Pyrex USA No. 1000) and pulverized, in its swollen state, and, finally, dried in air for 24 hours, at 55°C overnight in a vacuum oven and by storage in a vacuum desiccator over KOH at 10^{-3} mm Hg over a period of two weeks.

Network Degradation

An accurately known weight of sol-free, pulverized network (~1.0 g) was mixed with 25 mL of pure THF in a 100 mL beaker.

The beaker was covered with aluminium foil followed by wax paper surrounded by a rubber band so as to prevent evaporation of the solvent. Network swelling was allowed to proceed overnight under mild stirring with the aid of a small magnetic follower. The addition of 10 mL sodium methoxide solution, 0.183 M (prepared by dissolving pure sodium in methanol under nitrogen), would commence network degradation. Throughout the experiments reported in this paper, the same batch of MeONa solution was used. The extent of degradation from sample to sample was varied by varying the time during which the network was in contact with the MeONa reagent. Zero time was taken as the moment when the last drop of the degrading reagent had been added. At the end of the specified degradation period, the reaction was terminated by the addition of regenerated strongly acidic ion exchange resin Dowex 50W-X8. Prior to isolating the sol, the mixture was stirred for 10-15 minutes in order to ensure full exchange of the basic species. A pH meter was actually found to be useful for monitoring the ion exchange process.

Isolation of Degradation Sols

The sol isolation procedure was applied immediately after the degradation procedure. The sols were never allowed to remain in contact with the ion exchange resin for more than 10-15 minutes. The mixture of ion exchange resin, undegraded network and swelling medium was filtered through a fine porous filter funnel (preferably without vacuum application) into a round bottom flask. The residue was then washed with 3 × 20 mL predistilled THF and the extracts were evaporated to dryness as soon as possible. The network residue was then quantitatively transferred from the porous funnel into a beaker, and was mixed with 50 mL predistilled THF. Any residual sol species were further removed by stirring the mixture overnight. After filtration into the original sol sample, the process was repeated. This ensured quantitative removal of sol from the network. The weight of sol is a critical quantity in this kinetic experiment, as it is further involved in calculations. For this reason it was further clarified. The thus isolated dry sol was dissolved in predistilled THF so as to give ≈1% w/v solution. The solution was then quantitatively filtered through a 0.5 μm Millipore type FG filter (Waters Associates) into a predried, preweighed round bottomed flask. After removal of the solvent, the sol sample was dried in a vacuum dessicator over KOH at 10^{-3} mm Hg to constant weight. Each experiment was repeated with fresh network so as to arrive at the next degree of solubilization reported in Figure 1.

REFERENCES

1. Yan, J.F. and Johnson, D.C.: *J. Appl. Pol. Sci.* 26, 1623 (1981).
2. Yan, J.F.: *Tappi*, 63, (11), 154 (1980).
3. Szabo, A. and Goring, D.A.I.: *Tappi*, 51 (10), 440 (1968).
4. Bolker, H.I. and Brenner, H.S.: *Science*, 170, 173 (1970).
5. Bolker, H.I., Rhodes, H.E.W. and Lee, K.S.: *J. Agric. Food Chem.*, 25 (4), 708 (1977).
6. Dolk, M., Pla, F., Yan, J.F., McCarthy, J.L.: *Macromolecules* 19 (5), 1464, 1471 (1986).
7. Yan, J.F. and Johnson, D.C.: *J. Agric. Food Chem.* 28, 850 (1980).
8. Yan, J.F.: *Macromolecules* 12, 260 (1979).
9. Yan, J.F.: *Polym. Plast. Technol. Eng.* 14 (1), 47 (1980).
10. Argyropoulos, D.S. and Bolker, H.I.: Paper submitted for publication to *Makromolecular Chem.*, Jan. (1987).
11. Argyropoulos, D.S. and Bolker, H.I.: *Makromol. Chem.* 187, 1887-1894 (1986).
12. Argyropoulos, D.S. and Bolker, H.I.: Paper submitted for publication to *Macromolecules*, Dec. (1986).
13. Flory, P.J.: *"Principles of Polymer Chemistry"*, Cornell University Press, Ithaca, N.Y., 1953, Ch. IX.

14. Stockmayer, W.H.: *J. Chem. Phys.* 11, 45 (1943).

15. Stockmayer, W.H.: *J. Chem. Phys.* 12, 125 (1944).

16. Whittle, P.: *Proc. Cambridge Philos. Soc.* 61, 475 (1965).

17. Favis, B.D., Choi, P.M.K., Adler, P.M. and Goring, D.A.I.: *Trans. Tech. Sect. CPPA*, 7:TR35 (1981).

18. Favis, B.D.: *Ph.D. Thesis*, McGill University, Montreal, Canada (1981).

19. Margenau, H. and Murphy, G.M.: *"The Mathematics of Physics and Chemistry"*, Van Nostrand, Princeton (1956), p. 40, 2nd edition.

20. Hägglund, E. and Hedlund, R.: *Papier Fabrik*, 30 (6), 61 (1932).

21. Hägglund, E.: *Tappi*, 32 (6), 241 (1949).