

Table III. Essential Amino Acids in Duckweed Protein Concentrate Compared to FAO Reference Pattern, Corn, and Rice (g/100 g of Protein)

amino acid	duckweed ^a	FAO	corn	rice
Lys	4.0	4.2	2.3	3.2
Ile	3.6	4.2	6.2	5.2
Leu	6.7	4.8	15.0	8.2
Met	0.9	2.2	3.1	3.4
Phe	4.2	2.8	5.1	5.0
Thr	3.13	2.8	3.7	3.8
Val	4.4	4.2	5.3	6.2
Trp		1.4	0.6	1.3

^a Mean of four species.

source of lysine, which is present in low amounts in grains. In many of the underdeveloped countries, corn and rice are the main foods consumed by the population. These foods are deficient in lysine, containing only 0.2-0.3% of the amino acid on a dry matter basis (FAO, 1954; NAS-NRC, 1958), whereas duckweed protein concentrate contains 1.6-2.0% on a dry matter basis. It is evident that duckweed protein concentrate has potential as an effective supplement to grains for animal and human consumption.

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LITERATURE CITED

- AOAC, "Official Methods of Analysis", 12th ed., Washington, DC, 1975.
- Bhanthumnavin, K., McGarry, M. G., *Nature (London)* **232**, 495 (1971).
- Boyd, C. E., *Econ. Bot.* **22**, 359 (1968).
- Chang, S.-M., Yang, C.-C., Sung, S.-C., *Bull. Inst. Chem., Acad. Sin.* **24**, 19 (1977).
- Culley, D. D., Jr., personal communication, School of Forestry and Wildlife Management, Louisiana State University, Baton Rouge, LA, 1978.

- Culley, D. D., Jr., Epps, E. A., *J. Water Pollut. Control Fed.* **45**, 337 (1973).
- FAO, "Nutrition Studies. Rice and Rice Diets", Rome, 1954.
- FAO, "Lives in Peril: Protein and the Child", FAO, Rome, 1970.
- FAO, "Assessment of World Food Situation—Present and Future", UN World Food Conference Documents, Rome, Nov 1974.
- FAO, "Population, Food Supply, and Agriculture Development", FAO, Rome, 1975.
- FAO/Who, "Energy Requirements and Protein Requirements", FAO Nutrition Meeting Report Series 52, Rome, 1973, p 63.
- Hillman, W. S., *Bot. Rev.* **27**, 221 (1961).
- Hillman, W. S., Culley, D. D., Jr., *Am. Sci.* **66**, 442 (1978).
- Maciejewska-Potapczk, W., Konopska, L., Narzumska, E., *Acta Soc. Bot. Pol.* **39**(2), 251 (1970); *Chem. Abstr.* **74**, 97 (1971).
- Maciejewska-Potapczk, W., Konopska, L., Olechnowicz, K., *Biochem. Physiol. Pflanz.* **167**, 105 (1975); *Chem. Abstr.* **82**, 279 (1975).
- Monroe, H. N., Heck, A., *Analyst (London)* **91**, 78 (1966).
- Muztar, A. J., Slinger, S. J., Burton, J. H., *Can. J. Plant Sci.* **58**, 843 (1978).
- NAS, "Making Aquatic Plants Useful: Some Perspectives for Developing Countries", Washington, DC, 1976.
- NAS-NRC, "Composition of Cereal Grains and Forages", Publ. 585, Washington, DC, June 1958.
- Rusoff, L. L., Gantt, D. T., Williams, D. M., Gholson, J. H., *J. Dairy Sci.* **60**, Suppl. 1, 161 (1977).
- Rusoff, L. L., Zeringue, S. P., Achacoso, A. S., Culley, D. D., Jr., *J. Dairy Sci.* **61**, Suppl. 1, 186 (1978).
- Said, Z. M., Culley, D. D., Jr., Standifer, L. C., Epps, E. A., Myers, R. W., Boney, S. A., *Proc. Annu. Meet.—World Maric. Soc.*, in press (1979).
- Tan, Y. T., *J. Fish Biol.* **2**, 253 (1970).
- Tulaganov, A., *Dokl. Akad. Nauk Uzb. SSR* **29**(7), 56 (1972); *Chem. Abstr.* **78**, 240 (26440p) (1973).
- USDA, "The World Food Situation and Prospects to 1985", Foreign Agr., Econ. Rpts. No. 98, E.R.S., USDA, Washington, DC, 1974.

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Molecular Weight Distribution in the Lignin Sol

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The mechanism of delignification proposed by Szabo and Goring and that by Bolker and Brenner are compared and discussed on the basis of the Flory-Stockmayer distribution. A recently derived univariate Stockmayer distribution is used to illustrate the change of lignin molecular weight with delignification. A continuous distribution is proposed for application to the gel permeation chromatography (GPC) characterization. It is demonstrated that the initial chain size distribution is important in determining the shape of GPC elution curves as well as the post gel properties.

Chemical pulping, or delignification, is an important industrial process by which the lignin in wood is dissolved and separated from the cellulose fibers. Although this process has been practiced for a long time, the detailed chemistry involved is still poorly understood. Nevertheless,

it appears that a fundamental principle in the physical chemistry of nonlinear polymers may emerge as a useful tool in elucidating the mechanism of delignification.

One of the proposed mechanisms of delignification involves the application of the Flory-Stockmayer (F-S) theory of condensation of polyfunctional polymers (Szabo and Goring, 1968; Goring, 1971; Bolker and Brenner, 1970; Bolker et al., 1977). In this application delignification is treated as a reverse process of the condensation beyond

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the gel point (Flory, 1953; Stockmayer, 1943, 1944), or simply stated, delignification is assumed to be a degelation process.

The prerequisite of applying this theory is to establish that lignin is indeed a gel, or infinite network. While this degelation mechanism is not yet widely accepted, experimental observations and data interpretation do tend to support the validity of a lignin gel. This evidence has been extensively discussed by Goring (1971) and Bolker et al. (1977). Among the gel properties are the insolubility of lignin in good solvents and the broad molecular weight distribution of its degraded products. Quite apart from the intention of the mechanistic interpretation is the growing interest in characterizing the soluble fraction of lignin (the sol) by GPC (gel permeation chromatography). Bolker and co-workers (1977) first attempted to bring a fundamental theory to a practical application in characterization. Their argument indicated that both delignification and the GPC elution curves of the lignin sol were explicable with the F-S theory. The main requirement in this argument was that a high molecular weight peak, on the position of exclusion limit, should be discounted from the molecular weight calculation. This peak was shown to be an artifact which could be eliminated by choosing a more porous gel in the chromatographic column. In the literature, it is surprising that this artifact of high molecular weight peak has not been discussed extensively, even for linear polymers. However, a low exclusion volume peak for a high molecular weight polystyrene has indeed been observed (Cooper, 1978).

COMPARISON OF THE THEORIES

Fundamentally speaking the theories of Goring and Bolker bear more similarities than differences, namely because both are based on the F-S theory of gelation. However, they differ in the interpretation of the important parameter α (the cross-linking density or the extent of reaction or the fraction of functional groups reacted). This difference is reflected in their treatments of the weight-average molecular weight vs. delignification curves. Also, for the basic building unit of lignin, Szabo and Goring (1968) assume it is a trifunctional unit, whereas Bolker and Brenner (1970) demonstrate by calculation that it has an average degree of polymerization (DP) of 18 for both dioxane and sulfite lignins. Therefore, it appears that these two theories differ in the assumption or the calculation of the size of initial chains which cross-link to form a branched polymer and eventually lead to the formation of a gel.

The effect of initial average size on the final DP distribution was considered by Flory (1953) and Stockmayer (1944). The F-S theory has recently been extended to include the cross-linking (or condensation) of chains with any initial size distribution (Yan, 1979). This allows one to differentiate whether the lignin building block is a trifunctional monomer or an 18-mer, by comparing their post gel properties and distribution curves. In this paper, such a comparison is made, and both the theories of delignification are discussed. In addition, a GPC curve is simulated by using this extended F-S theory.

UNIVARIATE STOCKMAYER DISTRIBUTION

The extended F-S theory is formulated with a modern statistical technique involving probability generating functions. The result is expressed in a molecular weight distribution function called the univariate Stockmayer distribution (Yan, 1979). This distribution has the following properties: (a) The curve shape of this distribution is dependent upon the initial chain size and chain size distribution. (b) Average post gel properties such as weight

average DP in the sol fraction (\bar{x}_w) and weight fraction of the sol (s) and the gel (g) are also strongly influenced by the initial chain size distribution.

Previously we presented a multimodal distribution curve for a narrow (Poisson) chain size distribution; also given were the changes of \bar{x}_w , g , and ρ (the post gel cross-linking density in the sol) with α (Yan, 1980). For an arbitrarily distributed chain length, the expression for the final distribution is given in the Appendix, together with its continuous equivalent, which is more convenient in application. The Appendix also lists the symbols used in this study.

THEORY OF SZABO AND GORING

In applying the F-S theory to delignification, Szabo and Goring (1968) make two assumptions: (i) that the basic unit in lignin is a monomer with equally reactive trifunctional groups and (ii) that there are two forms of gel (therefore two forms of sol) specified by two rate constants that defined ρ for the lignins in the middle lamella and secondary cell wall. The first assumption has been criticized by Bolker and Brenner (1970) on the ground that the three functional groups in the monomer, presumably a C_9 unit, are of vastly different reactivity. The second assumption was made to bring the weight average vs. delignification (\bar{x}_w vs. s) curve to an acceptable position in line with experimental data. This has an intuitive appeal in explaining the topochemical difference in the delignification of middle lamella and secondary wall lignins. Closely related to this assumption is the proposed delignification kinetics (Szabo and Goring, 1968):

$$d\rho_1/dt = -k_1\rho_1 \quad (1)$$

$$d\rho_2/dt = -(k_2\rho_2 + k'\rho_2^2) \quad (2)$$

Unfortunately this kinetic scheme is in direct contradiction with the F-S theory. The kinetics associated with the condensation of the F-S type is given by Stockmayer (1943), for the pregel stage:

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

This kinetics is uniquely equivalent with the Flory-Stockmayer distribution and has been reaffirmed and emphasized by various authors on a statistical basis (Stockmayer, 1943; Whittle, 1965; Casassa, 1974). In application to delignification, the rate in eq 3 should change sign, with α replaced by ρ or ρ_1 and ρ_2 .

Equation 3 means that the rate of change of the extent of reaction is proportional to the square of the unreacted fraction. This is obviously in line with the principle of chemical condensation; i.e., it takes two unreacted groups to form a linkage. This kinetic scheme is therefore a natural consequence of the F-S type of polycondensation. Since α is always smaller than 1, there is no way that eq 3 can be reduced to eq 1 or eq 2 by approximations. Thus we conclude that Szabo and Goring have used the F-S distribution function without using its equivalent kinetic scheme.

THEORY OF BOLKER AND BRENNER

Without attempting to interpret the topochemical difference in middle lamella and cell wall lignins, Bolker and Brenner relax the condition of a trifunctional monomer. Instead, they argue that among the three functional groups in the C_9 (phenylpropane) unit, the benzyl ether group is more reactive than either of the other two ether linkages. On degradation in acid, lignin behaves as if it were made up of ether-linked primary chains which are cross-linked through the benzyl ether bonds to form branched polymers and hence the gel. Bolker and Brenner calculated the

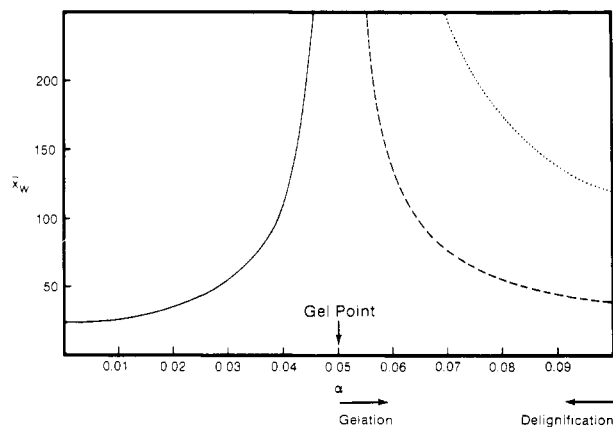


Figure 1. Change of \bar{x}_w with α before and after gelation for a branched polymer obtained by cross-linking initial chains with $\lambda = 20$: (—) pregel region, (---) postgel region with a primary Poisson distribution, (···) postgel region with a "most probable" distribution.

chain size as containing 18 C_9 units, using the post gel relations in the F-S theory. These authors then invoked Freudenberg's picture of this 18-mer to explain the delignification process.

The \bar{x}_w vs. s plot obtained from this theory does indeed fit the experimental data better than that from the one-gel theory of Szabo and Goring or even a two-gel one. However, to simplify the calculation, Bolker and Brenner assumed that the 18-mers are uniformly distributed. That this is not the case is reflected in the fact that the narrowest distributed polymer chains, natural or synthetic, have a Poisson distribution (Flory, 1953). This, together with the fact that the curve shape of an \bar{x}_w vs. s plot is highly dependent on the distribution of the primary chains (see below), casts doubts on this 18-mer theory.

In the next section, we further relax the conditions concerning the initial chains by allowing both the average chain length and chain length distribution to vary. As far as the sulfite and dioxane lignins are concerned, we can see that the average initial chain may not be an 18-mer, depending on the broadness of the distribution assumed.

AVERAGE POST GEL PROPERTIES

The F-S theory was formulated for the condensation polymerization in the pregelation stage and later extended to the post gel region. At the "gel point", specified by a critical cross-linking density α_c , the weight average DP becomes infinite (Flory, 1953; Stockmayer, 1943, 1944). For α values larger than α_c values, the F-S theory is again applicable, but only to the sol fraction. The conversion of α in the pregel stage to ρ in the postgel stage and hence the transformation of pregel properties to the post gel ones are discussed extensively by Flory (1953). Recently it has been shown that after gelation both the initial and cross-linked size distributions maintain the same forms as those in the pregel stage (Yan, 1980).

The properties concerning delignification are the average post gel properties in the context of the F-S theory. For the purpose of illustration, consider a primary chain with a weight average DP of 21 before gelation. The \bar{x}_w vs. α relationship is shown in Figure 1. It is clear that the pregel curve is independent of the initial chain size distribution, whereas the post gel curves are not. Since delignification proceeds in the post gel region (also see Figure 1), we can expect that the post gel curves behave differently if the initial chain has a Poisson distribution (dashed curve) or a "most probable" distribution (dotted curve). The Poisson distribution is the narrowest known for all poly-

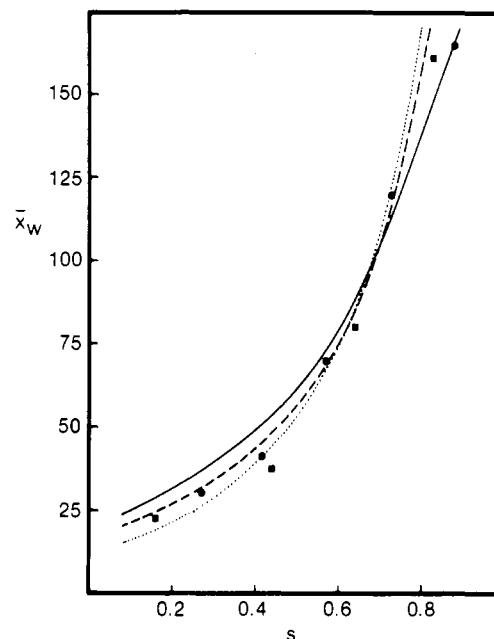


Figure 2. Change of \bar{x}_w with s and influence of initial distributions. Experimental points: ■ = dioxane lignin, ● = lignosulfonic acid. (—) Uniform primary 18-mer (Bolker and Brenner, 1970), (---) primary Poisson distribution with $\lambda = 11$, (···) primary "most probable" distribution with $2q/p = 27$.

mers, whereas Flory's "most probable" distribution is valid for a (bifunctional) condensation polymer which is considered broad for linear polymers.

Converting this relation to an \bar{x}_w vs. s plot, as shown in Figure 2, we can see that the experimental points on sulfite and dioxane lignins can be adequately fitted with a uniform chain with a length of 18. This is the result obtained by Bolker and Brenner. However, the experimental data (taken from the graph of Bolker and Brenner) may also fit the Poisson distribution of chains with a weight average length of 12, or a "most probable" distribution with a weight average length of 28.

In fitting these curves in Figure 2, we place more emphasis on the general curve shape instead of using the criterion of calculated deviations, as did Bolker and Brenner (1970). This is done because the F-S distribution has its own assumptions and limitations (Flory, 1953; Stockmayer, 1943; Yan, 1978, 1979) which are less appropriate in the vicinity of the gel point (or high values of s). Therefore, an indiscriminatory standard deviation calculation tends to bias the curve toward the high s values. This is the reason that the Bolker-Brenner curve shows larger deviations than our new curves in the low s (or high yield) region.

In addition to this curve, Bolker and Brenner also used a plot of s vs. ρ to support their 18-mer theory. Values of ρ were estimated for Braun's native lignin and dioxane and alcoholysis lignins. However, for yet another lignin (Cl_2O -treated cuoxam lignin) the universality of the 18-mer breaks down; the primary chain was found to be a 7-mer (Bolker et al., 1977).

Recently a more elaborate work was performed by Pla (1980). Dioxane lignin at the high yield region (low s values) was characterized with both number average and weight average molecular weights. These averages are of primary importance for branched polymers. In fact, expressions for these averages can be used to generate the entire distribution curve in terms of the parameter α (Yan, 1978).

Pla also obtained a curve similar to those shown in

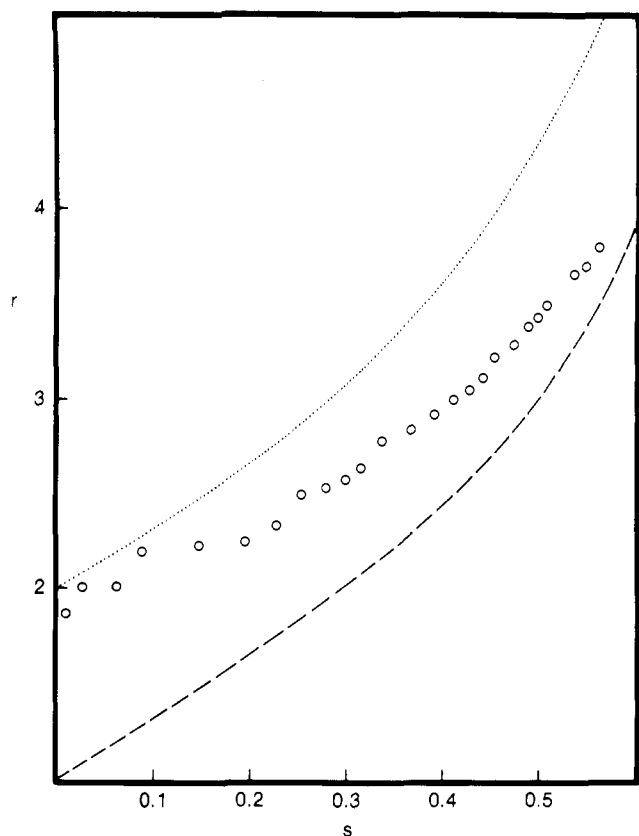


Figure 3. The dispersion ratio r plotted as a function of s . (O) Data obtained by Pla (1980). (---) Initial Poisson distribution with $\lambda = 11$; (···) most probable distribution with $\lambda = 27$.

Figure 2. At very low s (or low ρ), the weight average molecular weight was found to be 3600. Using a value of 200 for the molecular weight of monomeric repeating unit, we found the weight average DP of the initial chain to again be 18. Pla's data are not shown in Figure 2, but it is sufficient to point out that, as may be expected, the data points fall on the solid curve of Bolker and Brenner for s values in the range 0–0.2. In the s range 0.2–0.4, the points fall onto the dashed "Poisson" curve; at even higher s values, they approach the dotted curve. Since Pla measured both averages, he was able to calculate the dispersion ratio r (defined in the Appendix). At very low s , this ratio is 2, which is the value characterized by a "most probable" distribution. Therefore, the initial chains are broadly distributed.

Pla's data for r are shown in Figure 3, together with those calculated theoretically. At the beginning of delignification, the r values are close to those of a most probable distribution with $\lambda = 27$. A uniform chain size distribution gives a curve overlapping the Poisson one.

It is possible to choose an initial chain size distribution with broadness between the Poisson and the most probable, but this exercise would not have theoretical interest. The F-S theory suggests that the form of initial and final distributions in the sol phase remains unchanged during the course of condensation reaction (Yan, 1980). Pla's data appear to suggest that in the course of delignification, the initial chains have a broad distribution at the beginning and then change to a narrow distribution as s increases. This "change" of initial size distribution cannot be explained with the current theory. Possibly the data reflect two-gel behavior where the initial size distributions differ in the middle lamella and secondary wall. Pla's data deserve a more thorough analysis before reaching firm conclusions.

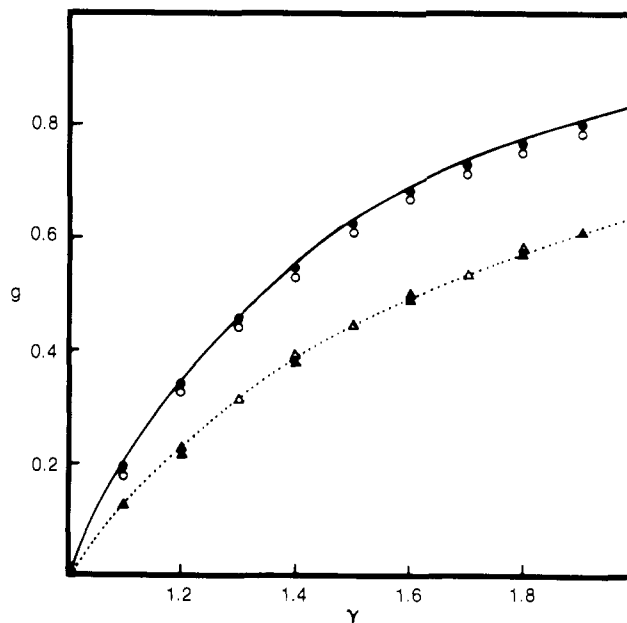


Figure 4. Change of g with γ . (—) Uniform chain with $\lambda = 20$. (●) Primary Poisson distribution with $\lambda = 11$; (○) primary Poisson distribution with $\lambda = 20$. (▲) Most probable distribution of chains with $2q/p = 27$; (△) most probable distribution of chains with $2q/p = 20$.

Detailed mathematical formulas for these calculations are given in previous publications (Yan, 1979). A common application of these formulas is the g vs. γ relation shown in Figure 4. This is a plot for characterizing branched polymers by the simple technique of partitioning the sol and the gel (Rijke and Madelkern, 1971). It can be seen, from plots of this kind, that a Poisson distribution is practically indistinguishable from a uniform distribution of the chains. However, a broad distribution such as "most probable" (shown as dotted line) can effectively lower this curve. Figure 4 also indicates that a change in the average initial size has very little effect on these curves. Thus, we conclude that the curves are mostly affected by the primary distributions rather than by the initial averages. The relation shown in Figure 4 is fairly common in characterizing a gel; however, it has not been used in delignification studies.

SIZE DISTRIBUTION IN THE SOL

The final, cross-linked polymer size distribution has been discussed previously (Yan, 1979). In the Appendix we also give the final distribution obtained by cross-linking polymer chains with an arbitrary distribution. When the initial chain length distribution is narrow, e.g., Poisson with a weight average $\lambda + 1$, the final distribution is multimodal, with modes (peaks) appearing at λ , 2λ , 3λ , ... in the distribution curve. This means that "monomeric" chains having an approximate average length of λ cross-link to form "dimers" with average 2λ , "trimers" with average 3λ , and so on. This mechanism is in perfect agreement with the condensation process proposed in the F-S theory.

In practice, molecular weight distribution of the lignin sol has been known for a long time to be very broad, even broader than a log-normal distribution (Felicetta et al., 1955). In more recent works using the GPC technique, which were reviewed extensively by Bolker et al. (1977), the GPC elution curves may be bimodal with a broadly distributed low molecular weight fraction. The high molecular weight "fraction", located at the exclusion limit, has been shown to be an artifact. Even if both GPC peaks are real, the pattern of the peaks does not agree with the

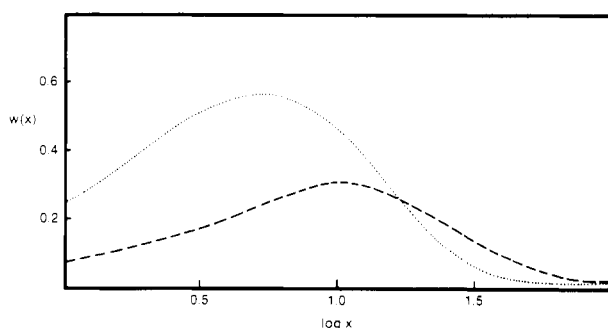


Figure 5. Plots of $w(x)$ vs. $\log x$ with $\gamma = 0.3$, $n = 2$. (---) $\mu = 0.1$, (···) $\mu = 0.2$. See Appendix for parameters used.

F-S mechanism for which the most visible peaks should be the ones at λ and 2λ (Yan, 1979).

The rejection of the high molecular weight peak is in agreement with the F-S theory. The theory requires that this peak be suppressed and spread out to the molecular weight range higher than the exclusion limit. A long, spread tail is a common feature of all the F-S distributions (Bolker et al., 1977; Yan, 1979). With these arguments, we can readily see that the molecular weight distribution of the lignin sol is indeed very broad. A broad distribution of this kind can only result from the cross-linking of broadly distributed initial chains (Yan, 1979).

As an exercise to examine the shape of GPC curves, we use the "most probable" distribution as an example for the initial chain size distribution. The final, continuous form of distribution of the cross-linked molecules is given by eq A5 (see Appendix). On the assumption that $\bar{y}_w = 10$ and 20, the plots of the weight fraction $w(x)$ vs. $\log x$ are shown in Figure 5. These curves show broad distributions, even when the DP is expressed in logarithmic scale.

Since the elution volume in GPC is commonly calibrated and shown to be a linear function of $\log x$, and the detection signal is assumed to be proportional to the weight fraction, Figure 5 contains simulated GPC curves, provided that the direction of $\log x$ is reversed in the abscissa.

It can be seen that the resemblance between the curves of Figure 5 and a unimodal, experimental GPC curve is striking. Examples of unimodal elution curves can be found in Cl_2O -treated periodate lignin (Bolker et al., 1977) as well as in sulfite (Herrick et al., 1979) and dioxane (Crozier et al., 1979) lignins. In practice, for a more refined fit, eq A4 can be used to match an experimental curve. This can be developed with a suitable computer program (Tung, 1966). The adjustable parameters in this program are the mode x_m , which can be detected from an elution curve, and the parameter n . The value of n gives the information on the broadness of the initial chain size distribution.

DISCUSSION AND CONCLUSIONS

The F-S distribution is known to be very important in polymer chemistry not only in its mathematical elegance (Flory, 1953; Stockmayer, 1943; Whittle, 1965) but also in its practical applications (Goring, 1971; Bolker and Brenner, 1970; Bolker et al., 1977). The applications to delignification discussed here result in better agreement with experimental data with regard to the average properties and the shape of the distribution curve. In addition, we have proposed an equation that can be used for characterizing the lignin sol by the GPC technique. However, we make no attempt to fit the GPC curves. This is left for future studies.

Both Goring's and Bolker's theories are discussed in terms of the F-S distribution. The application of the F-S theory to delignification appears justifiable from the ar-

guments given above, especially the elucidation of GPC curves. There are, however, other related phenomena to support a degelation concept. For example, on heat aging, a sulfite lignin was noted to increase in viscosity, whereas its molecular weight decreased with heating time (Herrick et al., 1979). Both phenomena suggest an increase in the fraction of linear chains, which have higher viscosities than branched polymers. In fact, a GPC separation with intrinsic viscosity detection offers a technique to detect branching (Ambler et al., 1974). Again, this technique has not been used for the lignin sol.

The F-S theory, though mathematically complicated, is a simple resource to characterize natural branched polymers. In addition to lignin, application of this theory can also be found in amylopectin and glycogen (Erlander and French, 1956). For this reason a better understanding of this theory is necessary. Extension, refinement, and modification of this theory have continued to be made even after more than three decades since its formulation (Yan, 1979; Donoghue and Gibbs, 1979). So far it appears well established that the theory is valid at low cross-linking densities both before and after the gel point.

In applying this theory to delignification studies, we have shown that any one of the average property curves (Figures 2-4) or the GPC curve (Figure 4) alone is not sufficient to characterize the lignin sol. The curve shape in Figure 2 can remain the same by proper combinations of the initial distribution and average size. On the other hand, curves in Figures 3 and 4 are affected most by the broadness of initial distribution. The change in average size has practically no effect for a given distribution. A GPC curve reflects both the characteristics of the initial and final distributions. However, as pointed out by Bolker et al. (1977), one must first ascertain that all peaks in the elution curve are real. A well-known difficulty in interpreting a GPC curve is the lack of proper calibration standards. This difficulty is even more pronounced in delignification studies.

APPENDIX

I. Abbreviations and Symbols

DP	degree of polymerization
GPC	gel permeation chromatography
chains	preformed linear polymers before cross-linking
$k, k', k_1,$ k_2	rate constants
t	time
y	DP of initial chains
x	DP of cross-linked molecules
α	overall cross-linking density = extent of reaction
α_c	critical values of α at the gel point
n	an integer
$p = 1 - q$	parameters in the "most probable" distribution and eq A1
μ	parameter in the γ distribution
\bar{y}_w	weight average DP of initial chains = $\lambda + 1$
\bar{x}_n	number average DP of cross-linked molecules
\bar{x}_w	weight average DP of cross-linked molecules
λ	$\bar{y}_w - 1$
γ	cross-linking index in the sol = $\lambda\rho$
ρ	cross-linking density in the sol
ρ_1	cross-linking density in the sol of middle lamella lignin

ρ_2	cross-linking density in the sol of secondary wall lignin
s	$1 - g$ = weight fraction of the sol
g	weight fraction of the gel
$f(y)$	weight distribution of initial chains = weight fraction of y -meric chains
$w(x)$	weight fraction of x -meric cross-linked molecules
$w(x) dx$	weight fraction of x -mers between x and $x + dx$

II. Final Distribution

To allow for a wide range of broadness and skewness, the initial distribution is assumed to be a negative binomial distribution (Yan, 1980):

$$f(y) = \binom{n+y-1}{y} p^n q^y \quad p + q = 1 \quad (\text{A1})$$

with

$$\bar{y}_w = nq/p \quad (\text{A2})$$

The Poisson distribution is a special case at the limit $n \rightarrow \infty$, $q \rightarrow 0$ with $nq \rightarrow \lambda$; the "most probable" distribution is obtained by setting $n = 2$. Thus this distribution does cover a wide range of polydispersity for linear polymers.

The final distribution $w(x)$, or the weight fraction of the x -mer, is obtained by compounding the above distribution with a Borel distribution (Yan, 1979); the latter has been used by Bolker et al. in discussing GPC curves (1977).

$$w(x) = \sum_{y=0}^{\infty} \frac{(\gamma\gamma)^{y-1}}{y!} e^{-\gamma y} \binom{ny+x-1}{x} p^{ny} q^x \quad (\text{A3})$$

In practice it is more convenient to use a continuous equivalent of eq A1, the γ distribution, known in polymer chemistry as the Schulz-Zimm distribution. For integer n , $p/q \rightarrow \mu$, the result is

$$w(x) dx = \frac{\beta e^{-\mu x}}{\gamma x} \left[\frac{1}{(n-1)!} + \frac{\beta}{(2n-1)!} + \frac{3}{2} \frac{\beta^2}{(3n-1)!} + \dots \right] dx \quad (\text{A4})$$

where $\beta = \gamma e^{-\gamma(\mu x)^n}$, $\gamma = n\rho/\mu$. The weight average of the initial chains is

$$\bar{y}_w = n/\mu$$

The final weight average DP is

$$\bar{x}_w = \frac{n}{\mu} (1 - \gamma)^{-1}$$

The dispersion ratio (the ratio of weight average to number average) can be shown to be

$$r = \bar{x}_w / \bar{x}_n = \frac{n}{1 - \gamma} \left(\frac{1}{n-1} - \frac{\gamma}{2n} \right)$$

As a special case for $n = 2$ (the "most probable")

$$w(x) dx = \frac{\beta e^{-\mu x}}{\gamma x} (1 + 0.1666\beta + 0.0125\beta^2 + 5.29 \times 10^{-4}\beta^3 + 1.435 \times 10^{-5}\beta^4 + 2.706 \times 10^{-7}\beta^5 + 3.7 \times 10^{-9}\beta^6 + 3.98 \times 10^{-11}\beta^7 + \dots) dx \quad (\text{A5})$$

In eq A4, the first term in the bracket is proportional to the weight fraction of the "monomeric" chains. Therefore, the maximum in $\beta e^{-\mu x}/\gamma x$ is the first mode

$$x_m = (n-1)/\mu$$

This first mode is close to the mode of the overall distribution. For a broad final distribution, this peak shifts toward higher molecular weight. The detection of this mode is made easier with a higher resolution. It is, therefore, still desirable to run a GPC experiment with high resolution at the low molecular weight range; even this creates an artificial peak at the end of high molecular weight. For example, in Figure 5, where $n = 2$ and $\gamma = 0.3$, we have modes located as follows: for $\mu = 0.1$, $x_m = 10$ or $\log x_m = 1$; for $\mu = 0.2$, $x_m = 5$ or $\log x_m = 0.7$. These modes are also the modes in the primary "most probable" distributions. The dispersion ratio in this example is $r = 2.64$.

LITERATURE CITED

- Ambler, M. R., Mate, R. D., Purdon, J. R., Jr., *J. Polym. Sci., Polym. Chem. Ed.* **12**, 1759 (1974).
- Bolker, H. I., Brenner, H. S., *Science* **170**, 173 (1970).
- Bolker, H. I., Rhodes, H. E. W., Lee, K. S., *J. Agric. Food Chem.* **25**(4), 708 (1977).
- Casassa, E. F., *J. Polym. Sci., Polym. Phys. Ed.* **12**, 809 (1974).
- Cooper, A. R., in "Chromatography of Synthetic and Biological Polymers", Vol. 1, Epton, R., Ed., Ellis Horwood Chichester, England, 1978, p 344.
- Crozier, T. E., Johnson, D. C., Thompson, N. S., *Tappi* **62**(9), 107 (1979).
- Donoghue, D., Gibbs, J. H., *J. Chem. Phys.* **70**, 2346 (1979).
- Erlander, E., French, D., *J. Polym. Sci.* **20**, 7 (1956).
- Felicetta, V. J., Ahola, A., McCarthy, J. L., *J. Am. Chem. Soc.* **78**, 1899 (1955).
- Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953, Chapter IX.
- Goring, D. A. I., in "Lignins", Sarkanen, K. V., Ludwig, C. H., Eds., Wiley-Interscience, New York, 1971, Chapter 17.
- Herrick, F. W., Engen, R. J., Goldschmid, O., *Tappi* **62**(2), 81 (1979).
- Pla, F., Ph.D. Thesis, "Etude de la Structure Macromoleculaire des Lignines", University of Grenoble, 1980.
- Rijke, A. M., Madelkern, L., *Macromolecules* **4**, 594 (1971).
- Stockmayer, W. H., *J. Chem. Phys.* **11**, 45 (1943).
- Stockmayer, W. H., *J. Chem. Phys.* **12**, 125 (1944).
- Szabo, A., Goring, D. A. I., *Tappi* **51**(10), 440 (1968).
- Tung, L. H., *J. Appl. Polym. Sci.* **10**, 375 (1966).
- Whittle, P., *Proc. Cambridge Philos. Soc.* **61**, 475 (1965).
- Yan, J. F., *Macromolecules* **11**, 648 (1978).
- Yan, J. F., *Macromolecules* **12**, 260 (1979).
- Yan, J. F., *Polym. Plast. Technol. Eng.*, **14**(1), 47 (1980).

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