Rationalization for the Molecular Weight Distributions of Coal Pyrolysis Liquids

A model for coal thermal depolymerization is described and used to predict molecular weight distributions (MWD) of primary coal pyrolysis liquids. The model assumes that rupture of kinetically similar bonds in the coal is the preferred pathway for release of oligomers which ultimately become tars or extractables. The analysis provides the liquids MWD as a probability function of finding different oligomers composed of whole integer numbers of monomers and it is in excellent qualitative agreement with measured MWDs of coal pyrolysis liquids. The predicted MWDs are of the form of the gamma distribution function (GDF), and its parameters are interpreted in terms of the postulated chemistry of coal thermal depolymerization. Consequently, successful empirical correlations of experimental data on coal pyrolysis liquids MWDs with the GDF are better understood. Thus a protocol is provided to predict MWDs of pyrolysis liquids from knowledge of coal molecular structure.

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Introduction

Pyrolytic decomposition to char and volatiles is an important step in all coal thermal utilization processes, including combustion, gasification, liquefaction, and coke manufacture. Tar is an important pyrolysis product for most coals and usually dominates the mass and heating value of bituminous coal volatiles.

Studies of tar yields and properties shed light on parent coal structure, give insights on improving product yields and quality in coal conversion processes, and provide new understanding of ignition and pollutant evolution in coal combustion. Mathematical modeling of the release rates and global properties of coal pyrolysis tars is thus desirable from both fundamental and process simulation perspectives. However, the task is formidable because the initial and postthermolysis chemistries are inherently complex and because the kinetics of key reactions are typically coupled to attendant rates of heat, mass, and occasionally even momentum transport within and/or adjacent to the coal particles.

Liquid products of pyrolysis consist of material that escapes the coal particle and condenses at ambient conditions (tar), and of liquids that remain within the coal matrix after pyrolysis. The latter are often referred to as extract or extractables since, depending on conditions and coal type, some or most of these liquids are recoverable from the partially devolatilized coal matrix by solvent extraction. Extractables yields vary significantly with coal rank and pyrolysis conditions—from ~6 wt. % for a lignite (Darivakis, 1989) to from ~20 to over 50 wt. % for high volatile bituminous coals (Fong et al., 1986; Griffin, 1989; Unger and Suuberg, 1984). Secondary reactions of tar and extract can lead to char and gases (Fong et al., 1986; Serio et al., 1987). When secondary reactions are unimportant, the combined make of extractables and tar—that is, the total yield of pyrolysis liquids—can be considered as a primary product of thermal decomposition of the parent coal.

Several studies have modeled the kinetics of tar generation or release during coal devolatilization. Suuberg et al. (1978, 1979) described global kinetics of tar release by assuming that tar is formed by two or more independent parallel reactions, whose detailed chemical nature was not specified. Tar yields from rapid devolatilization of bituminous coal were assumed to be determined by the net impact of tar generation by initial decomposition of the coal, tar destruction by secondary (cracking) reactions, and tar release by evaporation and diffusion away from the coal particle (Suuberg et al., 1979). An approximate molecular weight distribution (MWD) for tars was assumed in order to compute tar vapor pressure at the coal particle surface and corresponding rates of tar release by diffusion through the coal–ambient boundary layer. Suuberg and his coworkers have continued to investigate the applicability of tar evaporation models to coal devolatilization kinetics (Unger and Suuberg, 1981; 1984, Suuberg, 1985). Their work shows the value of *a* *priori* knowledge of molecular weight characteristics for pyrolysis tars.

Other efforts have related tar release and other features of coal devolatilization kinetics to details of the coal molecular structure. Gavalas et al. (1981 a,b) developed a detailed chemical model for coal devolatilization and tar formation. The coal was treated as a polymer and tar was assumed to be formed mainly by dissociation of methylene, ethylene, and ether bridges that interconnect the monomers. Only monomers were considered as tar precursors. The formation rates of all products were described in terms of elementary reactions involving a variety of chemical functional groups. Candidate chemical functionalities were inferred from ^1H and ^{13}C NMR spectra. The required reaction rate parameters were estimated from gas phase kinetics or treated as adjustable inputs to achieve agreement between model predictions and experimental data.

Niksa and Kerstein (1986, 1987) also assumed that coal structure can be modeled as a polymeric network. They described the devolatilization chemistry with four global chemical reactions:

Formation of monomers by bridge dissociation
Tar and char formation by monomer decomposition and recombination, respectively
Gas formation from peripheral groups

The model predicts very high conversion of the polymeric structure into monomers (up to 96%), requires a molecular weight for the monomer as high as 1,400 amu, and assigns a single molecular weight for the tar, equal to one-half the molecular weight of the monomer. The model uses chain statistics to describe tar and char formation and addresses the competition between these two processes.

In a more recent approach, Niksa (1988, 1989) described tar formation as a flash distillation process. Concentrations of tar in the vapor and the condensed phases were related using an extended form of Raoult's law, developed by Cotterman et al. (1985) and Cotterman and Prausnitz (1985), for flash calculations on multicomponent liquid mixtures. Niksa's model assumes that decomposition of the coal structure generates a set of primary fragment molecules which then instantaneously partition between two phases: metaplast (condensed tarlike liquid) and tar vapor (tar components sufficiently volatile to immediately evaporate). The model also assumes that these primary fragments have a distribution of molecular weights the probability density of which can be reliably represented by a known continuous mathematical function, often referred to as the gamma distribution, $F(I)$. This function has been found empirically to well correlate experimentally determined molecular weight distributions for coal liquids. Such data from Unger and Suuberg (1984) and Oh (1985) were best-fitted by Niksa to the gamma distribution function, known more formally as the probability density function of the Pearson type III distribution (Zalen and Severo, 1972). The resulting best-fit parameters were then used to input $F(I)$ for the primary fragments into the flash distillation model, allowing tar and gas yields as well as tar molecular weight distributions to be predicted for various pyrolysis conditions.

Solomon and coworkers (1987, 1988) developed a detailed model of coal devolatilization treating coal depolymerization, stabilization, crosslinking, and mass transport of the resulting fragment molecules. This model also assumes a polymeric structure for the coal. It uses stochastic calculations to first construct a representation of the structure and to describe subsequent bond-breaking and bond-forming steps during depolymerization of the structure. The kinetics have been assumed to be independent of coal rank. The molecular weight distribution of the monomers is described by a gaussian function parametrized so that the model predictions fit experimental MWDs of coal pyrolysis liquids under certain conditions (e.g., MWD of tar obtained under vacuum at a heating rate of 3°C/min to 500°C). The resulting gaussian parameters were then used for model predictions at other conditions.

In another chemical model of coal devolatilization Grant et al. (1989) use percolation theory to describe the formation of fragments of different sizes during depolymerization of a parent structure. The model assumes a tree-branchlike lattice structure for coal, utilizes NMR data (Solum et al., 1989) for estimation of some of the structural parameters, and correlates char, tar, and gas yields. Mass transport and secondary reactions were not included in the model.

The present paper deduces from first principles the molecular weight distribution for "primary" coal liquids, that is, liquids newly formed by coal pyrolysis and not modified by secondary reactions. As noted in the preceding literature review, several devolatilization models utilize information on the molecular weight distribution of primary tar fragments. Typically this information is obtained from experiments, or by fitting the model or assumed mathematical forms of the MWD to experimental data. The present analysis correctly predicts *a priori* the functional form of the molecular weight distribution, thereby providing a basis for quantitative predictions of MWDs once the prerequisite parameters are available. Thus the total number of adjustable parameters required to implement devolatilization models can be reduced, and parameters used in empirically selected molecular weight probability density functions such as the gamma distribution can be related to underlying physicochemical features of coal pyrolysis and tar fragment generation.

The approach followed here is to:

a. Utilize generally agreed upon features of coal molecular structure

b. Estimate preferred pathways for thermal depolymerization of that structure to monomers and oligomers

c. Apply probability theory to predict the likelihood of obtaining tar components (oligomers) with different degrees of polymerization

Model Formulation

Coal molecular structure

Knowledge of chemical structure is important to understanding coal pyrolysis behavior, including effects of coal rank. Although the complete molecular structure of coal is unknown, certain features accepted by many investigators are especially useful in explaining tar generation and molecular weight distributions. Coal is assumed to have a crosslinked polymeric structure in which different monomeric units are interconnected with chemical linkages. Each monomeric unit contains one or more aromatic rings and a nonaromatic part, which may contain hydroaromatic, heterocyclic, or aliphatic substituents (Larsen and Kovac, 1978; Lucht and Peppas, 1981; Green et al., 1982; Gerstein et al., 1982; Attar and Hedrickson, 1982). The linkages consist of one or more chemical functional groups and their identity can vary widely (Gavalas, 1982). This conceptualization of coal structure is shown in Figure 1.

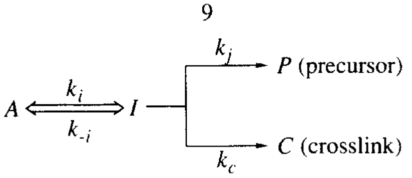
Initial thermolysis of coal

Liquids precursors are assumed to be formed by thermal scission of one or more linkages in the parent coal (Gavalas et al., 1981 a,b; Niksa et al., 1986; Niksa, 1988; Solomon et al., 1988; Grant et al., 1989). With reasonable assumptions about the allowed bond-breaking sequence, a mechanistic model for coal depolymerization can be formulated. Depending on the number of linkages that anchor a monomer in the structure, three types of monomers are distinguished as represented in Figure 1:

1. Monomers at the ends of polymeric chains (end monomers) bonded to the structure by one linkage
2. Regular monomers connected into the main structure by two linkages
3. Crosslinked monomers that are connected into the main structure by three or possibly more linkages

Liberation of a viable liquids precursor from the macromolecular condensed phase of the coal thus may require the rupture of one, two, or three (or more) bonds to set free end, regular, and crosslinked monomers, respectively. Since the concentration of the regular monomers is expected to be higher than the concentrations of end and crosslinked monomers, the average number of bonds that must be ruptured for the release of a liquids precursor is expected to be close to two. Deviations from this value can arise from release of end and crosslinked monomers. The magnitude of these deviations will obviously depend on the degrees of polymerization and crosslinking of the initial coal structure. For the present analysis it is useful to introduce a parameter r, which represents the number of linkages that must break in order to form a liquids precursor. The average value of r is expected to be close to two.

Consideration of the kinetics of sequential bond-breaking events provides important insights in formulating the desired model. To simplify this part of the discussion, it is for the moment assumed that rupture of exactly two linkages is required to liberate a liquids precursor, that is, $r = 2$. The most likely process for monomer/oligomer release is then sequential scission of two linkages, resulting in the detachment of a chain of n connected monomers, that is, an oligomer of degree of polymerization n. The pertinent steps can be modeled by the following simple network of chemical reactions:



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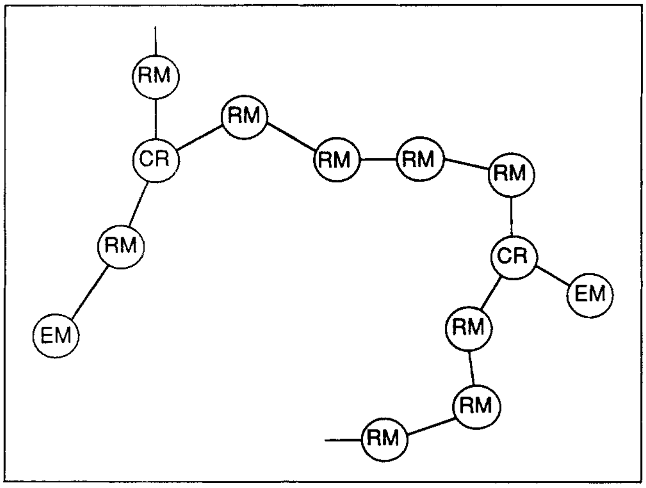

Figure 1. Conceptualization of the coal polymeric structure.

— linkages; RM, regular monomers; CR, crosslinked monomers; EM, end monomers

where A represents a portion of the parent coal (a stable structure that contains a specific linkage i), I is an immobile intermediate structure formed by the rupture of one linkage and thus still part of the parent coal, and P is a potential liquids precursor, formed by rupture of a second linkage on I. Note that in the above reaction network each of the four steps (i, $-i$, j, c) are considered primary reaction pathways. In the absence of further (i.e., secondary) reactions, other than stabilization of radicals, the primary product P could contribute to measured yields of pyrolysis liquids in two ways. If stabilized and retained within the coal particle, some or most of P would be recovered by solvent extraction and hence counted as extractables. If stabilized and then liberated from the condensed phase by evaporation or other means of mass transfer, P would contribute to the observed tar yield.

In this mechanism, k_i and k_j are the rate constants for rupture of two parent coal linkages denoted i and j, respectively, with i being more labile than j. Note that linkages i and j are not necessarily adjacent and thus the tar precursor P may contain one or more monomeric units. The rate constants k_{-i} and k_c represent a radical recombination and a crosslinking rate constant, respectively. These allow for the possibility that I, being immobile, may remain in the condensed phase for sufficient time to further react and form stable but immobile species (A or C). Evaporation affects P, but not I, which cannot escape the reactive environment since it is still partially bonded to the nonvolatile structure. Each rate constant is assumed to have the standard Arrhenius temperature dependence:

$$k_m = k_{mo} \exp(-E_m/RT) \quad (m{:}i, -i, j, c) \tag{2}$$

where k_{mo} is the frequency factor and E_m is the activation energy.

The effect of the relative magnitudes of k_i and k_j on the conversion of A to the desired product P is shown in Figure 2b for the simple case $k_{-1} = k_c = 0$ and the nonisothermal temperature–time profile displayed in Figure 2c. Figure 2 shows that small differences in the chemical kinetic behavior of the two linkages, here expressed by the difference in the activation energy for their (assumed single reaction) dissociation rate constants, can significantly delay the liberation of the liquid precursor P, Figure 2b, and thus provide more opportunity for *in situ* recombination and crosslinking reactions of the reactive intermediate I, Figure 2a. Figure 2b shows that simultaneous

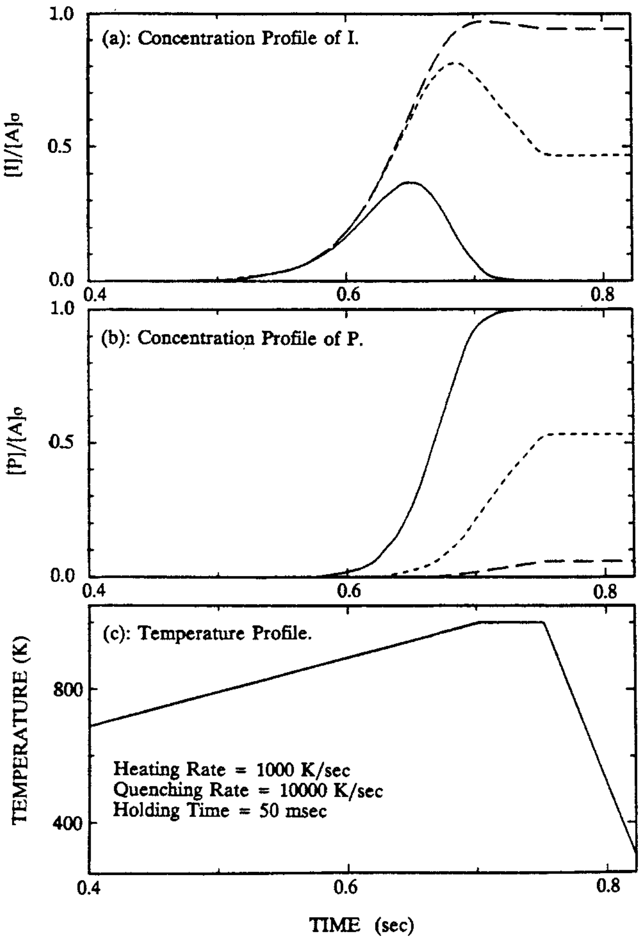

Figure 2. Products concentration and temperatures at various pyrolysis times for two consecutive reactions in series.

$A \xrightarrow{k_i} I \xrightarrow{k_j} P$

$k_i = 10^{13} \exp(-50)$ kcal/mol · RT; $k_j = 10^{13} \exp[-(50+\Delta E)]$ kcal/mol · RT

—— $\Delta E = 0$; -------- $\Delta E = 5$; - - - $\Delta E = 10$

dissociation of two linkages, which occurs with kinetically identical linkages, would then enhance liquids formation, and that consecutive linkage dissociation, which arises when the second linkage is of higher activation energy, would inhibit liquids generation. These observations imply that to the extent the present model is a good approximation of the initial coal decomposition chemistry, monomers or oligomers bonded by kinetically similar or ideally kinetically identical linkages—here represented by similar or identical activation energies—are preferred candidates to become liquids precursors. The issue of different activation energies for linkage cleavage has also been discussed by Gavalas et al. (1981 a,b), who used the ratio of methylene to ethylene linkages as a parameter in their model. The difference in activation energy between these two linkages is ~25 kcal/mol. Here it is seen that much smaller differences (5–10 kcal/mol) can have a very significant effect on liquids formation, as discussed previously.

The special case illustrated here ($k_{-1} = k_c = 0$) is the most conservative, since even without competition from recombination and crosslinking, an activation energy difference of 5 kcal/mol can inhibit generation of P, Figure 2. Recombination and crosslinking reactions, k_{-i} and k_c, respectively, would interfere with production of P, thus further lowering its yield. For example, since radical recombination rates are much faster than bond dissociation rates, the dissociation of the i linkage could become equilibrated. This would result in very low yields of P, since the equilibrium would favor the stable species A over the radical I at typical pyrolysis conditions.

The present model considers the effects of crosslinking and recombination reactions. When there is a delay between the breakage of linkages i and j, crosslinking rapidly depletes the intermediate I, which was generated by rupture of linkage i. This virtually eliminates the possibility of forming product P and hence of forming liquids. This is because I contains two free radicals, and free radical reactions would here be expected to be rapid compared to thermal scission of stable linkages such as j. Thus, before linkage j can break, I would be depleted by crosslinking and recombination reactions (c and $-i$, respectively, in Eq. 1). On the other hand, when linkages i and j break simultaneously, product P is formed. Then, according to this model, crosslinking and recombination are inhibited whenever P is sufficiently mobile to separate from candidate partners for crosslinking, by evaporation or other means of mass transfer, Figure 3. The thermal fragmentation of a polymeric network at kinetically identical linkages (denoted i) is depicted in Figure 3.

It is also possible that there is a propagation step in coal

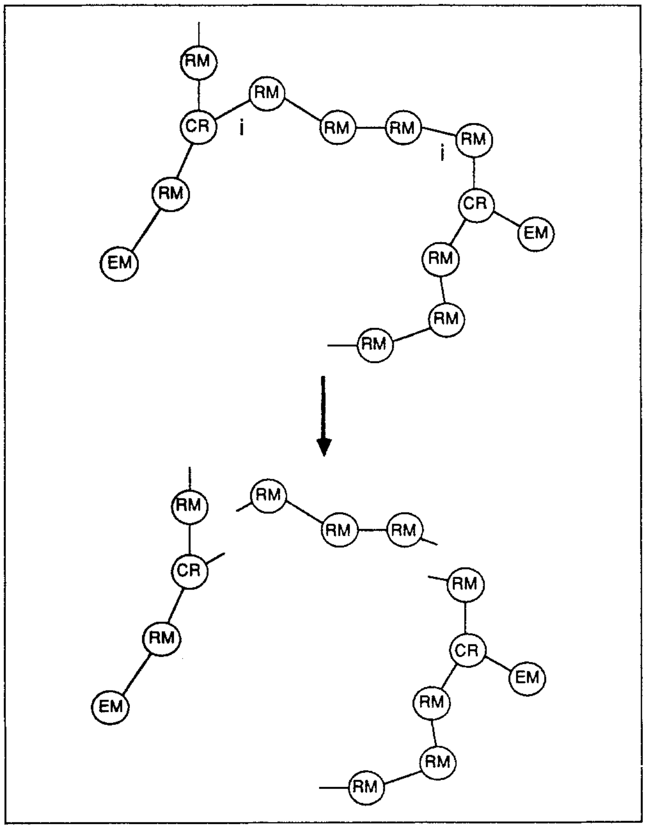

Figure 3. Formation of a liquids precursor by chain rupture at positions where linkages are kinetically similar or identical.

depolymerization. Then, formation of one radical in a chain (initiation step) initiates propagating mechanisms, which could be β-scission reactions (Stein, 1981, 1985) and/or hydrogen transfer from H donors (McMillen et al., 1987, 1988). In pyrolysis environments, contributions of β scissions and H-transfer reactions to propagation of depolymerization of the coal structure seem unlikely. The β-scission reactions require relatively long linkages ($\geq$3 carbon atoms). If these were present in the structure, they would be weak bonds, and would therefore be expected to break first, thus contributing primarily to the initial step in the decomposition of the structure. It is possible that β scissions are important in the generation of other pyrolysis products, such as light gases. Hydrogen transfer has been identified as a depolymerization propagation mechanism in coal liquefaction (McMillen et al., 1987, 1988), where the solvent, because of its mobility, can function as a radical carrier and often donates the hydrogen atoms for transfer. However these effects are not expected in pure pyrolysis, where there is no external solvent or external hydrogen. Further, in many cases tar is an early product, formed in the virtual absence of other mobile radical species. In nonsoftening coals, newly liberated tar molecules remain in the solid phase unless they evaporate and therefore their mobility may be very limited. In softening coals a more mobile liquid phase does form, but probably as a consequence of depolymerization rather than a promoter or catalyst for propagation.

Predicting MWD of tar precursors

The above kinetics analysis leads to the hypothesis that at given pyrolysis conditions monomers and oligomers connected to or within the coal structure by kinetically similar or, ideally, identical linkages are preferred precursors to liquid products. Designation of two linkages as kinetically similar means that for the heating conditions of interest the two linkages have similar dissociation rates, even though they may not have the same chemical structure. It proves instructive to estimate the probability of finding in the parent coal structure different size oligomeric building blocks that are bonded by kinetically identical linkages of a given type, say *i*. Here "size" refers to the number of monomeric units in the oligomers. There are two possibilities for each linkage: either it is of type *i* or it is not. The required probability can therefore be computed exactly from the theory of Bernoulli trials (Feller, 1968) if the fraction y_i of all the linkages in the parent structure that are of type *i* is known. For a parent polymeric structure of *n* linkages the requirement is to compute the probability that in a random inspection of *n* linkages at least *r* of the linkages are of type *i*, if the fraction of the total *n* linkages that are of type *i* is y_i. This is analogous to computing the probability that in *n* independent trials, an event will occur at least *r* times, when the probability of the event occurring in a single try is y_i. The probability that such an event will occur exactly *k* times in *n* independent tries is given by the binomial distribution (Feller, 1968):

$$p(k; n, y_i) = \frac{n!}{(n-k)!k!} y_i^k (1 - y_i)^{n-k} \qquad (3)$$

The required probability is that for finding at least *r* identical type *i* linkages among *n* choices, and is therefore obtained by summing Eq. 3 over all values of $k \geq r$, giving a cumulative binomial probability distribution function:

$$P(n, y_i) = \sum_{k=r}^{n} \frac{n!}{(n-k)!k!} y_i^k (1 - y_i)^{n-k} \quad r \leq n < \infty \qquad (4)$$

Figure 4 presents calculated values of $P(n, y_i)$ for three different values of y_i and $r = 2$.

When one can assume that pyrolysis conditions are such that scission of the type *i* linkages is thermodynamically and kinetically allowed, Eq. 4 also gives the probability of obtaining liquids precursors, that is, liberated oligomers, of degree of polymerization (DP) up to and including $n - (r - 1)$. For example, when $r = 2$ there are up to $n - 1$ monomers in a liberated fragment, Figure 5. For the less probable cases of $r = 1$ or 3, the fragment may contain up to *n* and $n - 2$ monomers, respectively, Figure 5. Generalizing, the difference $[P(n, y_i) - P((n - 1), y_i)]$ gives the probability of forming a fragment with DP $n - (r - 1)$. Equation 4 can thus also be used to compute the probability density function, that is, the MWD of liquids precursors in terms of DP. This has been done in Figure 6, which displays molecular weight distributions computed by graphical stepwise differentiation with respect to *n* of the cumulative probabilities displayed in Figure 4. The qualitative similarity of the results to measured MWDs for pyrolysis tars from North Dakota lignite (PSOC No. 1507) (Darivakis, 1989), shown in Figure 7, is very encouraging, especially given that the present qualitative predictions are obtained entirely from first principles, without fitting adjustable parameters to measured molecular weight distributions. Experimental MWD data for tars and extractables from other coals and for different pyrolysis conditions are qualitatively similar to the data in Figure 7, implying

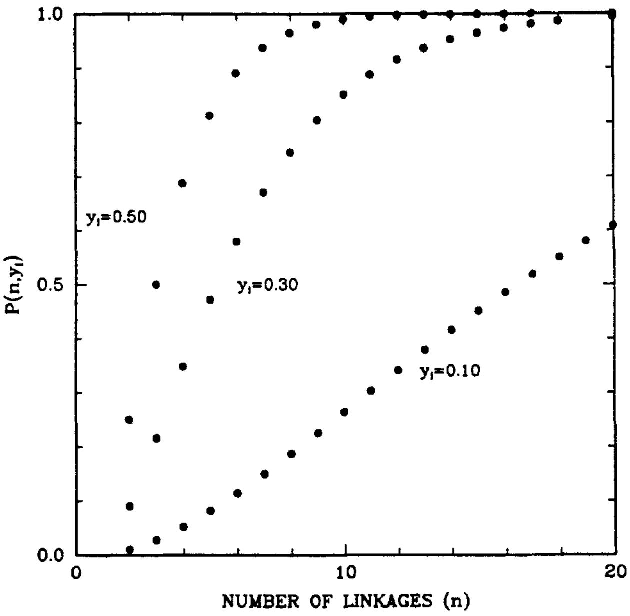

Figure 4. Probability of formation of liquids precursors with degree of polymerization from 1 up to and including $n - 1$.
Calculated from Eq. 4 for $r = 2$

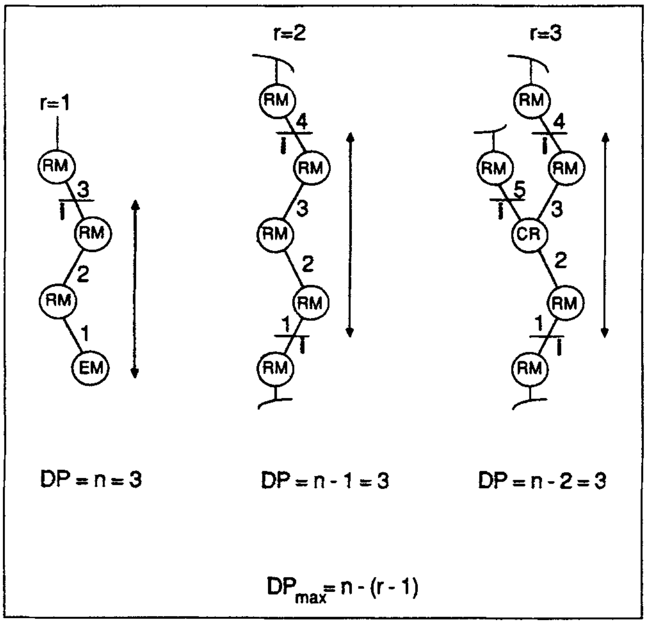

Figure 5. Example monomer configuration for each of three *r* values.

that the present analysis can be more generally applied in coal pyrolysis.

Equation 4 computes the probabilities that in the parent coal specific size oligomers exist in configurations from which they will be fully disengaged by scission of just r identical chemical bonds. In applying those probabilities to compute a molecular weight distribution for pyrolysis tars, it has been assumed that reaction conditions allow those bonds to break, and that heat and mass transport limitations and secondary reactions of the newly formed tars are all negligible. In practice, the validity of these assumptions depends on the details of the pyrolysis conditions—temperature, heating rate, total ambient pressure, coal particle size—and on coal type.

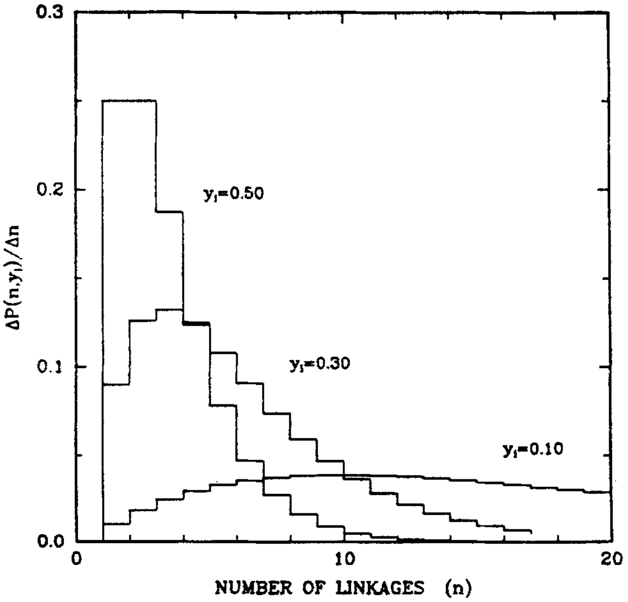

Figure 6. Predicted MWD of liquids precursors expressed in terms of degree of polymerization.

DP = n − 1, i.e., for r = 2

Curves calculated by stepwise graphical differentiation with respect to n of the cumulative probabilities in Figure 4

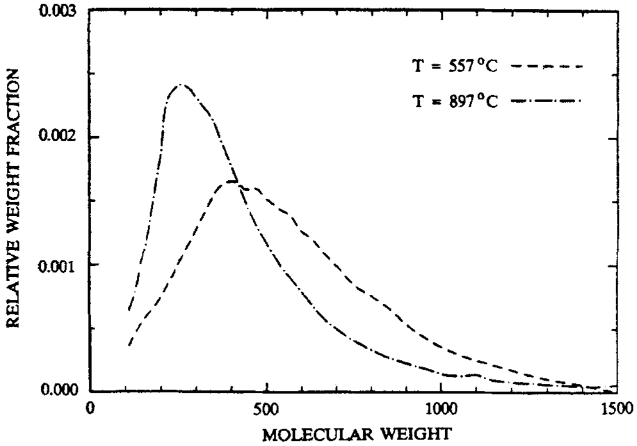

Figure 7. Experimental MWDs of tar from rapid pyrolysis of North Dakota lignite (PSOC No. 1507) at two peak temperatures.

Heating rate ~4,000°C/s; cooling rate ~7,500°C/s
Data from Darivakis (1989)

Figure 6 shows that more narrow molecular weight distributions are predicted as y_i increases. This parameter can be thought of as an approximate index of the chemical uniformity of the parent coal structure. High y_i values imply a high probability, even in a single try, of finding a chemical linkage of the prescribed type in the parent polymer and hence that a large fraction of the macromolecular network is held together by kinetically identical bonds. On the other hand, low y_i values represent significant chemical heterogeneity and hence the presence of many different types of bonds in the parent structure. Figure 6 shows that for high values of y_i the mean molecular weight decreases, and that for low values of y_i the predicted molecular weight distributions are very broad. Both observations would be expected. When y_i values approach unity, the distribution is increasingly dominated by monomers and low molecular weight oligomers. Decreasing y_i values open up nonzero probabilities for oligomers of larger degree of polymerization, but the probability for already included oligomers of lower DP decreases. Therefore the distribution broadens as y_i decreases.

Rationalization of the Gamma Distribution Function for Fitting Coal Liquids Molecular Weight Data

Experimental data on the molecular weight distribution of coal pyrolysis tars have been successfully correlated (Niksa, 1988, 1989) using the continuous function:

$$F(I) = \frac{(I-\gamma)^{\alpha-1}}{\Gamma(\alpha)\beta^{\alpha}} \exp\left[-\frac{(I-\gamma)}{\beta}\right] \tag{5}$$

where I represents the molecular weight and α, β, γ are parameters of the function that can be best fitted to the data.

This function is sometimes referred to as the gamma distribution function. Rigorously, $F(I)$ is the derivative of a continuous distribution function, and is formally denoted as a probability density function (PDF) or a frequency function. The form given in Eq. 5 is the PDF of the Pearson type III (PTT) continuous distribution function (Zalen and Severo, 1972).

Subject to certain conditions on y_i and n, a gamma PDF and the PTT PDF of Eq 5. can be derived analytically from Eq. 4 (Larsen and Marx, 1986). The derivation utilizes the fact that as $n \rightarrow \infty$ for values of y_i sufficiently small that $\lambda = ny_i$ is of moderate magnitude, the binomial distribution, Eq. 3, is well approximated by the Poisson distribution. For the stated conditions it can be proved that (Larsen and Marx, 1986):

$$\frac{n!}{(n-k)!k!} y_i^k (1-y_i)^{n-k} \approx \frac{\exp(-\lambda)\lambda^k}{k!} \tag{6}$$

where the symbols are as defined in Eq. 3. Thus, subject to the stated conditions Eq. 4 can be written as:

$$\begin{aligned} P(n, y_i) &= \sum_{k=r}^{n} \frac{n!}{(n-k)!k!} y_i^k (1-y_i)^{n-k} \\ &\approx \sum_{k=r}^{\infty} \frac{\exp(-\lambda)\lambda^k}{k!} \qquad r \le n < \infty \end{aligned} \tag{7}$$

The goodness of the approximation in Eq. 7 at small values of n was assessed by calculating the ratio of the cumulative binomial probability to the cumulative Poisson probability (i.e., in Eq. 7 the ratio of the second to the third entry) for a range of n values from 2 to 100. The result showed that even for n values as low as 5 the approximation was within 20% of the exact probability for values of y_i throughout the range of interest ($0 \le y_i \le 1$), and that the error of the approximation decreased rapidly with increasing values of n. For lower values of n the error increases but is still within 40% for $0.1 < y_i < 0.8$ and $n = 2$. For most practical applications of the model to coal, these values of y_i and n represent the most severe test of the approximation.

Substituting explicitly for λ and recognizing that the Poisson distribution is normalized, that is,

$$\sum_{k=0}^{\infty} \frac{\exp(-\lambda)\lambda^k}{k!} = 1 \tag{8}$$

Eq. 7 can be rewritten as (Larsen and Marx, 1986):

$$\begin{aligned} P(n, y_i) &= \sum_{k=r}^{\infty} \frac{\exp(-y_i n)(y_i n)^k}{k!} \\ &= 1 - \sum_{k=0}^{r-1} \frac{\exp(-y_i n)(y_i n)^k}{k!} \qquad r \le n < \infty \end{aligned} \tag{9}$$

Assuming that differentiation of Eq. 9 with respect to n is allowed, one can obtain a molecular weight distribution of the liquids precursors in terms of the number of monomers in each oligomer $[n - (r - 1)]$, as:

$$\begin{aligned} g(n, y_i) &= \frac{dP(\mathrm{n}, y_i)}{dn} = \frac{d}{dn}\left[1 - \sum_{k=0}^{r-1} \frac{\exp(-y_i n)(y_i n)^k}{k!}\right] \\ &= -\frac{d}{dn}\left[\sum_{k=0}^{r-1} \frac{\exp(-y_i n)(y_i n)^k}{k!}\right] \\ &= -\frac{d}{dn}\left[\exp(-y_i n) + \sum_{k=1}^{r-1} \frac{\exp(-y_i n)(y_i n)^k}{k!}\right] \\ &= -\left[-y_i \exp(-y_i n) + \sum_{k=1}^{r-1} \frac{(-y_i)\exp(-y_i n)(y_i n)^k}{k!}\right. \\ &\qquad \left. + \sum_{k=1}^{r-1} \frac{\exp(-y_i n) k y_i (y_i n)^{k-1}}{k!}\right] \\ &= \sum_{k=0}^{r-1} \frac{y_i \exp(-y_i n)(y_i n)^k}{k!} - \sum_{k=1}^{r-1} \frac{y_i \exp(-y_i n)(y_i n)^{k-1}}{(k-1)!} \end{aligned} \tag{10}$$

or, changing the index in the second summation from k to $k - 1$,

$$\begin{aligned} &= \sum_{k=0}^{r-1} \frac{y_i \exp(-y_i n)(y_i n)^k}{k!} - \sum_{k=0}^{r-2} \frac{y_i \exp(-y_i n)(y_i n)^k}{k!} \\ &= \frac{y_i \exp(-y_i n)(y_i n)^{r-1}}{(r-1)!} \end{aligned} \tag{11}$$

$$= \frac{y_i^r}{\Gamma(r)} n^{r-1} \exp(-y_i n) \qquad r \le n < \infty \tag{12}$$

since $\Gamma(r) = (r - 1)!$. The variable n in Eq. 12 indexes the number of tries at breaking linkages in the parent coal structure to generate liquids precursor fragments; n is not the degree of polymerization (i.e., the number of monomers) in those fragments. The model requires that the number of tries at breaking linkages be at least equal to the minimum number of linkages that must break to disengage a fragment r; that is, mathematically, $r \le n < \infty$. As written, Eq. 12 is of the correct form but violates the constraint on n by allowing for nonzero probabilities for n values $<r$. This can be corrected by shifting the origin of $g(n, y_i)$ so that $g(r, y_i) = 0$, that is, by translating n to $n - r$, giving:

$$g(n) \equiv \frac{y_i^r}{\Gamma(r)} (n-r)^{r-1} \exp[-y_i(n - \mathrm{r})] \qquad n \ge r \tag{13}$$

The parameter r has so far been treated as an integer. However, best fits of Eq. 13 to experimental data give r values that are noninteger, real numbers. This is expectable because a best-fitted r value represents an average of all r's in the coal structure—those expected to dominate most structures ($r = 2$), and those reflecting contributions from end monomers ($r = 1$) and crosslinked monomers ($r \ge 3$), Figure 1.

To the extent that the present model is an appropriate representation of the primary coal decomposition, the probability densities from Eq. 4 and Eq. 13 are, respectively, discrete and continuous probability densities functions that can be used to compute coal pyrolysis tars MWDs in terms of the likelihood of occurrence of oligomers containing 1, 2, 3, etc. (i.e., whole integer numbers of) monomers. Both functions are thus useful mathematical tools for analyzing and correlating experimental data on molecular weight of tars and extracts (Darivakis, 1989).

It is also useful to mathematically describe the MWD in terms of a probability density function of the molecular weight itself, rather than the degree of polymerization [DP $= n - (r - 1)$]. For instance, Cotterman et al. (1985) and Cotterman and Prausnitz (1985) use continuous functions of a suitable macroscopic property of multicomponent mixtures, for example, the normal boiling point or molecular weight, to quantitatively describe phase equilibria of such mixtures by the methods of continuous thermodynamics. Here the desired function is derived by transforming the function $g(n, y_i)$ from Eq. 13 to a continuous function of molecular weight. We begin by noting that since $g(n)$ is also a continuous probability density function, it can, by definition (Zalen and Severo, 1972) be written as the derivative with respect to n of a cumulative continuous distribution function $G(n)$:

$$\text{Eq. 13} = g(n) = \frac{dG(n)}{dn} \tag{14}$$

The molecular weight M of the liberated tar precursors is given by:

$$M = [n - (r - 1)]\overline{M} \quad \text{with } n \geq r \tag{15}$$

where $\overline{M}$ is the average molecular weight of a monomer. Equation 15 implies that:

$$(n - r) = \frac{M}{\overline{M}} - 1 \tag{16}$$

and that since $n \geq r$, $M \geq \overline{M}$.

Eq. 16 shows that

$$dn = \frac{dM}{\overline{M}} \tag{17}$$

Also by definition (Zalen and Severo, 1972), the sought-after probability density function of the continuous variable M, here denoted $f(M)$, must be accurately represented by the form:

$$f(M) = \frac{dF(M)}{dM} \tag{18}$$

where $F(M)$ is a continuous cumulative distribution function. Comparing Eqs. 14 and 18 using Eq. 17 shows that:

$$f(M) = \frac{g(M)}{\overline{M}} \quad M \geq \overline{M} \tag{19}$$

Substituting for $(n - r)$ in Eq. 13 using Eq. 16 gives:

$$g(M) = \frac{y_i^r}{\Gamma(r)} \left[\frac{M}{\overline{M}} - 1\right]^{r-1} \exp\left[-y_i \left(\frac{M}{\overline{M}} - 1\right)\right] \tag{20}$$

Substituting in Eq. 19 and rearranging gives:

$$f(M) = \frac{1}{(\overline{M}/y_i)\Gamma(r)} \left[\frac{(M - \overline{M})}{(\overline{M}/y_i)}\right]^{r-1} \exp\left[-\frac{(M - \overline{M})}{(\overline{M}/y_i)}\right] \tag{21}$$

Table 1 shows that the functions $F(I)$ in Eq. 5, and $f(M)$ in Eq. 21 are equivalent forms of the probability density function of the Pearson type III (PTT) probability distribution (Zalen and Severo, 1972). Providing simplicity of nomenclature and clarity of presentation, $F(I)$ has been referred to in some literature as the gamma distribution function (Niksa, 1988, 1989: Cotterman et al., 1985; Cotterman and Prausnitz, 1985). Comparison of Eq. 21 with Eq. 5 shows how the parameters for the two functions are related, Table 1, when the two functions correspond exactly. The present model allows the three parameters of $f(M)$, r, $\overline{M}$, and y_i, and hence the corresponding parameters α, β, γ of $F(I)$, Table 1, to be interpreted in terms of the underlying chemistry of the thermal depolymerization of coal.

The parameter r in $f(M)$, which equals α in $F(I)$, denotes the number of bonds required to break to liberate an oligomer that becomes a liquids precursor. According to the present model, the average value of r is expected to be close to 2, although some deviations from this value are possible due to contributions from

Table 1. Three Equivalent Forms of a Continuous Probability Density Function for Correlating Molecular Weight Data on Coal Pyrolysis Liquids

	Pearson Type III (PTT)	Eq. 21	Eq. 5
Prob. dens. func. (PDF)	$f(x)$	$f(M)$	$F(I)$
Cont. variable	x	M	I
Parameter	α	$\overline{M}$	γ
Parameter	β	$\overline{M}/y_i$	β
Parameter	p	r	α
Domain*	$\alpha \leq x < \infty$	$\overline{M} \leq M < \infty$	$\gamma \leq I < \infty$
Function	$\dfrac{[(x-\alpha)/\beta]^{p-1}}{\beta\Gamma(p)} e^{-(x-\alpha)/\beta}$	$\dfrac{[(M-\overline{M})/(\overline{M}/y_i)]^{r-1}}{(\overline{M}/y_i)\Gamma(r)} e^{-[(M-\overline{M})/(\overline{M}/y_i)]}$	$\dfrac{[(I-\gamma)/\beta]^{\alpha-1}}{\beta\Gamma(\alpha)} e^{-(I-\gamma)/\beta}$
Source and nomenclature**	a	b	c

*Mathematically, the domain is defined as the values of the continuous variable for which the PDF is > 0 (Zalen and Severo, 1972)

**a. The PDF of the PTT one-dimensional continuous distribution function (Zalen and Severo, 1972)

b. Derived from the present model, beginning with Eq. 3 in the text

c. Previous users in fuels related applications include: Cotterman et al. (1985), Cotterman and Prausnitz (1985), and Niksa (1988), who have referred to *F(I)* as the gamma distribution (function). Cotterman et al. (1985) point out that *F(I)* dates back at least several decades, where it was also known as the Shultz (1940) distribution.

end monomers ($r = 1$), and crosslinked monomers ($r \geq 3$), Figure 1.

Table 1 shows that the parameter β in $F(I)$ is identical to $\overline{M}/y_i$ in $f(M)$. According to the present model, the parameter y_i is a measure of the degree of chemical homogeneity of the polymeric coal structure. Larger y_i values denote a higher probability of finding kinetically identical bonds throughout the parent coal structure, and further imply that pyrolysis of that structure will produce liquids with a more narrow molecular weight distribution skewed toward lower average molecular weights, Figure 6. The proportionality factor $\overline{M}$ arises because y_i provides probabilistic accounting of discrete partitions of molecular weight, namely monomers and oligomers composed of whole integer multiples of monomers, Eqs. 3 and 4, whereas $F(I)$ and $f(M)$ treat molecular weight as a fully continuous variable. The quantity β is thus an index of the degree of chemical heterogeneity in the polymeric structure of the parent coal. Larger β values (smaller y_i values) denote a higher probability of finding kinetically dissimilar bonds throughout the parent coal structure. These interpretations are consistent with two other important properties of the Pearson type III PDF, namely that the mean and variance of this function are equal to (using $F(I)$ nomenclature) $\gamma + \alpha\beta$ and $\alpha\beta^2$, respectively (Zalen and Severo, 1972). Thus for fixed α and γ, larger βs denote a larger mean and a broader molecular weight distribution function, as would be expected for primary liquids with decreasing y_i values.

Equations 5 and 21 show that γ and $\overline{M}$, respectively, are the smallest molecular weight values in the MWDs. When only one distinct monomer contributes to the MWD, $\overline{M}$ (and γ) is the molecular weight of that monomer. In practice, however, a given structure may produce monomer fragments with a range of molecular weights, all in the volatility range normally associated with liquids. Then $\overline{M}$ is still defined as the average molecular weight of a monomer. However, the origin of the molecular weight distribution must change to a value (M_o) lower than $\overline{M}$ representing the lowest molecular weight (or smallest monomer) that contributes to the distribution. Further, now M_o corresponds exactly to γ and the term $M - \overline{M}$ appearing twice in Eq. 21 is replaced by $M - M_o$. These and related refinements could be captured quantitatively by utilizing a distribution of $\overline{M}$ values in the present model, but the complexity of adding the necessary additional parameters did not seem justified in the present analysis.

In some applications of $F(I)$ to measured molecular weight distributions, the origin (the γ value) has been defined as the minimum molecular weight, which separates condensibles from noncondensibles (Unger et al., 1984; Niksa, 1988). It can also be the minimum molecular weight that is detectable by the analytical tecniques used in the experiments. Thus γ values may also reflect the effects of experimental constraints and/or empirical definitions.

The above physicochemical interpretations provide a basis for *a priori* estimates of the parameters $\overline{M}$, y_i, and r, Table 1, from knowledge of coal molecular structure, and thus for predicting MWDs of coal pyrolysis liquids without measuring them. The model assumes that r is generally close to 2, although detailed inspection of the molecular structure for a given coal could give guidance on the extent to which r should be adjusted to account for contributions from end monomers ($r = 1$) and crosslinked monomers ($r \geq 3$). The parameter $\overline{M}$ can be estimated from postulated structures for coal "molecules," for example, as the molecular weight of the smallest structural subunit connected by a bond known to be labile for the pyrolysis conditions of interest. The parameter y_i can also be estimated from data on the molecular structure of the parent coal by evaluating the relative occurrence of bonds of similar chemical strength or, more accurately, similar or identical kinetic response; recall Eqs. 1 and 2 and Figure 2.

Comparison with Experimental Results

The present model was tested against experimental data for coal pyrolysis liquids. To do this an experimentally derived molecular weight distribution for primary liquids was needed. In response, it was assumed that a weighted combination of the MWDs of tars and extractables would be a better representation of the MWD of primary liquids than would either MWD separately. The desired distribution was synthesized as a linear combination of the separately measured MWDs for tar and extractables, obtained at the same pyrolysis conditions. The weighing coefficients were the relative weight fraction of each component, as shown by the equation:

$$f_{PL}(M) = [Y_{TAR}/(Y_{TAR} + Y_{EXT})] f_{TAR}(M) + [Y_{EXT}/(Y_{TAR} + Y_{EXT})] f_{EXT}(M) \quad (22)$$

where $f_i(M)$ is the value of $f(M)$ at M for the i component (i = primary liquids, PL; tar, TAR; and extractable material, EXT) and Y_j is the yield of the j component (j = tar, TAR; extractable material, EXT).

Then all three distributions were fitted with $F(I)$, or equivalently $f(M)$, to obtain values for the parameters α ($\equiv r$), β ($\equiv \overline{M}/y_i$). In the fitting γ was fixed at 100. This value has been used elsewhere (Niksa, 1988, 1989) and is reasonable in light of experimental observations. Figure 8 compares the model calculations with experimental data obtained for Pittsburgh No. 8 bituminous coal by Unger et al. (1984) at a pressure of 1 atm He and a peak pyrolysis temperature of 547°C. The data from

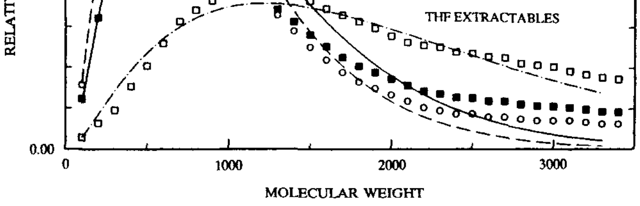

Figure 8. Model predictions (lines) and experimental (symbols) MWDs of coal pyrolysis liquids.

■ Primary liquids, synthesized from MWDs of tar and extractables (Eq. 22); ○ tar; □ THF extractables
Tar and extractables data from Unger et al. (1984)
Model: Eq. 5 with γ fixed at 100 and α and β values fitted to experimental data

Unger et al. were partially integrated within ±100 amu at each molecular weight, and this feature was taken into account in the curve fitting by partially integrating Eq. 5 as well. Very good agreement is achieved with parameter values of $\alpha = 1.3$ and $\beta = 471, 390, 920$ for the primary liquids, the tar, and the tetrahydrofuran (THF) extractables, respectively. Niksa assumed that tar obtained under vacuum closely represents the primary fragments for his flash distillation model, and empirically fitted molecular weight distribution data for tars from vacuum pyrolysis of Pittsburgh No. 8 coal at this same peak temperature (547°C). He reported α and β values of 1.5 and 500, respectively, while the value of γ was set to 100. These parameter values are very close to those obtained in the present work by fitting Eq. 5 to the primary liquids MWDs synthesized from tar and extractables MWDs ($\alpha = 1.3, \beta = 471, \gamma = 100$).

A set of experimental molecular weight distribution data for tar and pyridine extractables was obtained by Oh (1985) for Pittsburgh No. 8 bituminous coal at vacuum for a peak pyrolysis temperature of 600°C. Parameter values obtained here by fitting Eq. 5 to Oh's data were: $\alpha = 3$ and $\beta = 154$, 122 and 185 for the primary fragments, the tar, and the extractables, respectively. The value of γ was set to 100. As shown in Figure 9, the agreement between the model calculations and Oh's experimental results is very good.

The parameter values obtained by curve-fitting the above two sets of measured molecular weight distributions are quite different, despite the similarities between them regarding the coal type and the pyrolysis temperature. These differences are not attributed to limitations in the present model. They may arise from differences in experimental methods and could possibly be explained by further study of experimental procedures.

In general, the predictions of the present model are in excellent qualitative agreement with experimental observations. The model mechanistically rationalizes the shape of the experimental MWDs of coal pyrolysis liquids. Quantitative comparisons require use of appropriate experimental data, that is, MWDs closely representing primary liquids, since the model does not consider mass transport and secondary reactions. Here it was assumed that such data can be synthesized from molecular weight distributions for tar and extractables (Unger et al., 1984; Oh, 1985) from coal pyrolysis at moderate temperatures (550–600°C) and pressures ($P \leq 1$ atm), where secondary reactions and mass transport limitations are expected to have relatively small effects.

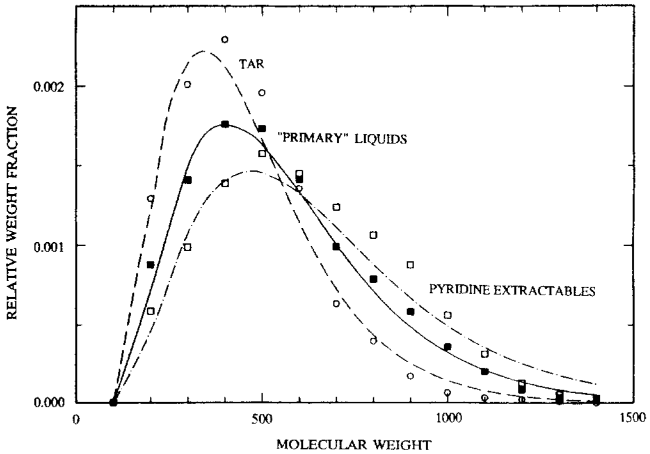

Figure 9. Model predictions (lines) and experimental (symbols) MWDs of coal pyrolysis liquids.

■ Primary liquids, synthesized from the molecular weight distributions of tar and extractables (Eq. 22); ○ tar; □ pyridine extractables
Tar and extractables data from Oh (1985)
Model: Eq. 5 with γ fixed at 100 and α and β values fitted to experimental data

The range of α ($= r$) values obtained by fitting the experimental data (1.3–3.0) is in very good agreement with expectations from the model—that is, a most likely r value of 2 with values of 1 and 3 also possible due to contributions from end monomers and crosslinked monomers respectively. A priori predictions of β require knowledge of the MW of the monomer, $\overline{M}$, and of the fraction of the parent coal linkages likely to contribute to liquids precursor formation, y_l. Assuming that the molecular weight of the monomer is 100 and a y_l of 0.5, a β value of 200 is obtained. This estimate is in quite satisfactory agreement with the range of β values obtained here by fitting experimental data (154–471).

More rigorously, y_l is expected to depend upon pyrolysis conditions, including temperature and heating rate. Assuming that the temperature is high enough so that rupture of the linkages is feasible, then at low heating rates linkages must be chemically similar to exhibit similar fragmentation rates. However, at higher heating rates more chemically different linkages become potential contributors to liquids formation. This is because more rapid heating brings the coal to temperatures sufficiently high for additional reaction channels to contribute, before the more labile linkages are completely consumed (Darivakis, 1989; Niksa and Kerstein, 1986). Therefore, at higher heating rates higher y_l are expected and according to the present analysis they should result in lower mean molecular weights and more narrow molecular weight distributions for the coal liquids, Figure 6. These predictions are in qualitative agreement with experimental observations of heating rate effects on tar molecular weights from pyrolysis of a lignite (Darivakis, 1989) and a bituminous coal (Griffin, 1989).

Conclusions

Subject to certain caveats, various approximations for the chemistry of tar generation in coal pyrolysis are useful in engineering calculations. Here it has proved instructive to model liquids production as the release of monomeric and oligomeric precursors by rupture of, on average, two kinetically similar bonds in the coal.

The kinetic similarity between the linkages is required so that they essentially break simultaneously. This dissociation mode is considered to favor formation of liquid products. Kinetically dissimilar linkages dissociate at different rates, with the more labile bonds breaking first. The result is the formation of reactive sites in a condensed and immobile phase, where strong steric limitations are expected. In consequence, radical recombination and char-forming crosslinking reactions are likely to dominate and inhibit the generation of liquids precursors, that is, fragments with sufficient chemical stability and mobility to (potentially) survive pyrolysis of the coal and be counted as extractables or tars.

Formal statistical accounting for the probability of obtaining different size precursors then predicts, without fitted or adjustable parameters, molecular weight distributions of primary coal liquids in good qualitative agreement with experimental data.

It is shown analytically that the predicted molecular weight distributions for coal pyrolysis liquids, when expressed as a continuous function of molecular weight, correspond exactly to the Pearson type III probability density function, referred to in some literature as the gamma distribution function. The present analysis interprets the parameters α, β, and γ of the gamma distribution function in terms of the underlying chemistry of coal thermal depolymerization. Consequently, the successful utilization of the gamma distribution function to empirically fit experimental data on MWDs of coal pyrolysis tars can be better understood in terms of coal pyrolysis chemistry. Furthermore, this analysis correctly predicts *a priori* the functional form of the MWD, thereby providing a basis for quantitative predictions of molecular weight distributions once the prerequisite parameters are available.

Molecular weight distributions calculated with the present model are in good qualitative and quantitative agreement with experimental observations. The model could be used as a component of a more general devolatilization model that addresses effects of evaporation, mass transfer, and secondary reactions. Relatively little complexity would be added, since the present model is straightforward and requires little computational effort. Alternatively, fitting the present model to measured molecular weight distributions for primary coal liquids can be used to directly estimate features of the coal molecular structure, for example, the molecular weight of smallest structural units contributing to liquids ($\overline{M}$), the degree of chemical similarity in the coal structure (y_i), and the relative importance of isolated, doubly linked, and crosslinked structures in primary liquids formation ($r = 1, 2, 3$, etc.).

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