QUANTITATIVE DESCRIPTION OF OXIDATIVE DEGRADATION OF BROWN COAL IN AQUEOUS PHASE BASED ON LATTICE STATISTICS

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INTRODUCTION

Some recently developed pyrolysis models[1-3] reasonably combine the kinetics of bridge breaking/formation with the Bethe lattiee statistics[4,5] that reeognizes aromatic clusters and bridges as *sites and bonds*, respectively. The assumption of coal as a lattice can be examined by analyzing the characteristics of its degradation, which provides the measurable structural changes of coal, namely, the decrease in the bridge concentration and corresponding increase in the fraction of low-molecular-mass components released from the network. The relationship between these changes may be quantitatively described by assuming coal as a lattice having a particular chain configuration. The authors[6,7] found that an O_2 oxidation in weakly alkaline aqueous phase solubilizes low rank coals to considerable extent. The oxidation increased the mass fraction of solvent-extractable material in a brown coal from 0.15 to 0.97. Analyses of the products revealed that aromatic carbon was selectively oxidized into carboxyls in the residual solid as oxidized coal, water-soluble non-aromatic acids and carbon dioxide, while aliphatic carbon was minimally involved in the reaction. Considering that the coal consists of aromatic clusters and inter-cluster bridges, they proposed a reaction mechanism that the oxidation converted aromatic carbons bonded to bridges into peripheral carboxyl groups on the neighboring clusters, and did the other aromatic carbons into non-aromatic acids or carbon dioxide. According to this mechanism as illustrated in Figure 1, the oxidation decomposes the macromolecular network of the coal by eliminating clusters as *sites* and converting bridges as *bonds* into peripherals. If the mechanism is valid, the extent of the degradation can be quantified by determining the amounts of lost bridges and clusters from those of formed carboxyls and oxidized aromatic carbon, respectively. In addition, the number of carboxyls formed as peripherals is expected to be equal to that of bridges which were bonded to eliminated clusters. The present paper examines the validity of the above-described mechanism of the oxidation and the applicability of general lattice statistics to the analysis of the degradation characteristics.

EXPERIMENTAL

Acid washed Morwell brown coal was oxidized at 85 °C for 1 – 12 h in an aqueous solution of Na_2CO_3, into which atmospheric oxygen gas was continuously bubbled. Details of the experimental procedure were described elsewhere[7]. The oxidized coal obtained through the oxidation for X h is hereafter referred to as SX. The oxidized coals were analyzed by a CP/MAS ^{13}C-NMR, and the carbon type distributions of the individual samples were determined. Details of the measurements, peak assignment and curve resolution of spectra were reported previously[7]. The concentrations of carbonylic, carboxylic and phenolic groups were measured by means of oximation, ion exchange and acetylation, respectively. The samples were also subjected to exhaustive extraction with various single and mixed solvents at ambient temperature under ultrasonic irradiation. For the all samples, the mass fraction of solvent-extractable material was defined as that of material extracted with DMF that gave the greatest fractions among the solvents employed[7]. Molecular mass distribution of the extracts was measured by a laser desorption-ionization spectrometry (LD/MS) on a spectrometer (Japan Perseptive, model Voyager™ RP-DE). The spectra were observed in a linear mode under the following conditions: accelerating voltage; 25 kV, mass range; 50 – 100000, pressure; $1 - 2\cdot10^{-7}$ torr. Pulses of a nitrogen laser operating at 337 nm was used for the laser desorption.

RESULTS AND DISCUSSION

The structural analyses determined the fractions of different types of carbon found in the oxidized coals: f_{CO} (carbonylic carbon), f_{COOH} (carboxylic carbon), f_{OH} (phenolic carbon), $f_{a\text{-}e}$ (aromatic C bonded to ether), $f_{a\text{-}C}$ (aromatic C bonded to carbon), $f_{a\text{-}H}$ (protonated aromatic C), $f_{a\text{-}O}$ (aliphatic C bonded to O other than methoxy carbon), $f_{al\text{-}OCH3}$ (methoxy), $f_{al\text{-}\alpha CH2}$ (methylene or methin at α position to aromatic C), $f_{al\text{-}CH2}$ (methylene at β position), $f_{al\text{-}\alpha CH3}$ (methyl at α position) and $f_{al\text{-}rCH3}$ (methyl at remote position). These fractions are indicated in the unit of mol-C per 100-mol C in S0. The fractions of total aromatic and aliphatic carbons, referred to as f_a and f_{al}, respectively, are defined as

$$f_a = f_{a-e} + f_{a-OH} + f_{a-C} + f_{a-H}$$

$$f_{al} = f_{al-O} + f_{al-OCH3} + f_{al-\alpha CH2} + f_{al-CH2} + f_{al-\alpha CH3} + f_{al-rCH3} + f_{al-acids}$$

$f_{al\text{-}acids}$ is the fraction of aliphatic carbon contained in non-aromatic acids. $f_{a\text{-}e}$ was calculated by the difference between the fraction of oxygen-bonded aromatic carbon that was determined by the NMR and $f_{a\text{-}OH}$. Figure 2 shows f_a, f_{al} and f_{COOH} as a function of oxidation time. f_a decreases monotonously with time while f_{al} remains unchanged. It is also seen that f_{COOH} increases as the oxidation progresses. Here, the differences of f_a and f_{COOH} from those of S0 are defined as Δf_a and Δf_{COOH}, respectively. The figure also shows the change in the fraction of aromatic carbon bonded to bridges, $f_{a\text{-}b}$, which was calculated according to Solum et al.[8].

$$f_{a-b} = f_{a-C} + f_{a-e} - \left(f_{COOH} + f_{al-OCH3} + f_{al-rCH3} + f_{al-\alpha CH3}\right)$$

The decrease in f_{a-b} with time indicates the loss of bridges by the oxidation. The total amount of bridges is calculated from a simple stoichiometry.

$$N_b = f_{a-b}/2$$

The loss of bridges, ΔN_b, is here defined as

$$\Delta N_b = N_b \text{ (for S0)} - N_b \text{ (for SX)}$$

When aromatic clusters are eliminated by the oxidation of aromatic carbon involved in them, the amount of eliminated clusters (ΔN_c) is expected to have a linear relationship with the loss of aromatic carbon *leading to the elimination*, defined as Δf_a*. ΔN_c and Δf_a* are expressed in the units of mol-cluster/100 mol-C in S0 and mol-C/100 mol-C in S0, respectively. They are related as

$$\Delta N_c = \Delta f_a{}^* / n_a$$

where Δf_a* is the loss of aromatic carbon accompanied with the loss of an aromatic ring, and is a little smaller than the observed loss, Δf_a, due to the formation of a small amount of quinones that never contributes to the elimination of clusters. The calculation of Δf_a* was described in our previous report[7]. n_a is the average number of aromatic carbon atoms per cluster. The number can be estimated from the abundance of bridgehead carbon relative to total aromatic carbon[8]. As reported previously, for S0 – S12, f_{b-ah} was found to account for at most 4 % of f_a. Such appreciably small values of f_{a-bh} indicate that the assumption of monoaromatic rings, in other words, n_a is 6 mol-C/mol-cluster, is reasonable for the all samples.

Figure 3 shows ΔN_b and Δf_{COOH} as a function of ΔN_c. ΔN_b is seen to be in good agreement with Δf_{COOH} as expected by the proposed mechanism of the oxidation, although some deviations are seen. Also, ΔN_b and Δf_{COOH} can be related linearly with ΔN_c at a slope of about 2.2. This means that 2.2 bridges are lost when an aromatic cluster is eliminated by the oxidation, and hence that each of the lost clusters was bonded to the same number of bridges in average. Moreover, the linear relationship itself should be noted when the mechanism of the oxidation is considered. As illustrated in Figure 1, the elimination of a cluster accompanies the formation of carboxyl groups at the chain ends of the neighboring clusters. As we described in the previous paper[7], aromatic rings carrying carboxyls generally have oxidation reactivities orders-of-magnitude smaller than do those without carboxyls. Therefore the neighboring clusters may behave as inert ones after carboxyls are formed, while they also lose bridges initially connected to them. Thus, the elimination of clusters would occur non-randomly, producing deactivated clusters that accumulate as the oxidation progresses. Here, let us consider the degradation of a macromolecular network or lattice consisting of clusters and bridges, of which initial concentration of inter-cluster bridges is $n_{b,0}$ (= $2 \cdot N_{b,0}/N_{c,0}$). The degradation is supposed to be caused by the elimination of clusters (or sites). In the case of a degradation involving deactivation processes as described above, the average number of bridges bonded to a remaining 'reactive' cluster is independent of $N_c/N_{c,0}$, and equals to the initial bridge concentration, namely $n_{b,0}$. Then, when a cluster is eliminated, $n_{b,0}$ bridges are always lost, and the following relationship holds.

$$n_b = 2N_b/N_c = 2\left\{N_{b,0} - n_{b,0}\left(N_{c,0} - N_c\right)\right\}/N_c = n_{b,0}\left\{2\left(N_c/N_{c,0}\right) - 1\right\}/\left(N_c/N_{c,0}\right) \qquad (1)$$

where $N_c/N_{c,0}$ is the fraction of remaining clusters to that before degradation and is a measure of the extant of cluster elimination. Figure 4 shows the observed n_b as a function of $N_c/N_{c,0}$ together with lines drawn on the basis of Eq.(1) assuming $n_{b,0}$ = 2.23. The observed change of n_b is seen to be well explained by the equation, i.e., the non-random degradation. Eq.(1) can apply to any lattices having different dimensions, coordination numbers and bridge densities. Thus, the results shown in Figures 2-4 reveal that the changes in f_{COOH}, N_c and N_b are reasonably explained on the basis of the proposed oxidation mechanism, and are also quantitatively described by the assumption that the coal is a lattice with $n_{b,0}$ of 2.2, while other parameters such as the coordination number are so far unknown.

The above explanation of the change in n_b by Eq.(1) not only provides the initial bridge concentration but also allows us to analyze other characteristics of the degradation assuming that the coal is a lattice. Bethe pseudo lattices are statistical lattices, each of which has infinite number of sites and is defined by the coordination number (Z) and site occupation probability (p, $0 \le p \le 1$) that is the number fraction of occupied sites to the total number of sites. When two sites neighboring to each other are both occupied, they are recognized to be linked by a bridge. Another characteristic of Bethe lattices is that no loops are allowed in them. The absence of loops provides analytical solutions of states of the lattices by only giving the parameters, Z and p, and this is the reason why the coal is assumed to be a Bethe lattice in the models described below. For a Bethe lattice with Z and p, n_b is expressed as

$$n_b = Z \times p$$

When the degradation of the lattice occurs with a random site-elimination mechanism, a given probability p^* and corresponding bridge concentration n_b* are related as follows.

$$n_b^*/n_{b,0} = p^*/p_0 \qquad (2)$$

where p_0 is the site-occupation probability of the initial lattice with $n_{b,0} = Z \times p_0$. The lattice statistics can also provide the distribution of degree of polymerization. The possibility of that an occupied site belongs to m-mers, each of which consists of m sites and $(m-1)$ bridges, is given as

$$F_m\left(p^*\right) = mb_m p^{(m-1)}\left(1-p^*\right)^{\{m(Z-2)+2\}}$$

where mb_m is the total number of configurations possible for m-mers. $F_m(p^*)$ is essentially the same as the fraction of m-mer with regard to the occupied-sites. Figure 5 shows the fractions of finite-sized m-mers as a function of p^* for the Bethe lattice with $Z = 3$. $F_{i-j}(p^*)$ seen in the figure is defined as

$$F_{i-j}(p^*) = \sum_{m=i}^{m=j} F_m(p^*)$$

Further details of the Bethe lattice statistics are well described in literature[4-5], and are therefore not done here. Eq.(2) that gives the relationship between the changes in n_b^* and p^* is applicable to the description of Bethe lattice degradation only when the elimination of sites occurs randomly (Case-I). In another case (Case-II) that the elimination of a site accompanies the deactivation of the neighboring sites as seen in the present oxidation, the elimination of a site results in the loss of $n_{b,0}$ bridges. Then, n_b at a site occupation probability, p, is expressed as

$$n_b / n_{b,0} = \{1 - 2(p_0 - p)/p_0\} / (p/p_0) \qquad (3)$$

Eq.(3) is directly derived from Eq.(2), since $p/p_0 = N_c/N_{c,0}$. As shown in Figure 6, n_b in Case-II is smaller than n_b^* in Case-I when $p = p^*$. Essentially, degradation of lattice/network is brought about by the elimination of bridges, and in this sense, the extent of degradation could be evaluated on the basis of the decrease in the bridge concentration, *i.e.*, n_b. Considering the above, p can be converted into another probability, p^{**}, that gives n_b equivalent to n_b^*. p^{**} is then calculated as

$$p^{**} = p_0\{1 - 2(p_0 - p)/p_0\} / (p/p_0)$$

Thus, if the chemical network of the coal can be assumed to be a Bethe lattice, its degradation caused by the oxidation would be approximately described by a random degradation using p^{**}.

Here, a structural model of the coal are proposed and examined on the applicability to quantitative explanation of changes in the fraction of extractable material caused by the oxidation and molecular mass distribution of the material. The first model assumes the followings:

1. S0 consists of solvent extractable material and a fully developed network. The extractable material comprises of m-mers with m ranging from 1 – 40, while the network is described as a Bethe lattice with $p_0 = 1$ and thus $n_{b,0} = Z$.
2. The fractions of the network and extractable material in S0 are 0.85 and 0.15, respectively, which is based on the observed Y_{DMF} for S0, 0.15.
3. The concentration of bridges for the extractable material (referred to as $n^e_{b,0}$) is 1.8, which was determined by analyzing a CP/MAS ^{13}C-NMRspectrum of DMF extract from S0.
4. When a site is eliminated, the probability of that the site belongs to the network is 0.85. This is based on the assumption that the network and extractable material have equivalent reactivity to the oxidation.
5. The solvent extractable material, given as DMF extract, consists of molecules whose degree of polymerization ranges from 1 to 40. The basis of this assumption is mentioned below.

In addition to the above, the second assumption for the model A is also considered in the model B. Figure 7 compares calculated $F_{1\text{-}40}(p)$ as a function of p^{**}/p_0 with Y_{DMF}. It should be noted that $F_{1\text{-}40}(p)$ strongly depends on Z and also agrees well with Y_{DMF} at Z = 2.18. In the model B, the bridge concentration of S0, namely $n_{b,0}$ is given as

$$n_{b,0} = 0.85Z + 0.15n^e_{b,0}$$

and then $n_{b,0}$ is calculated as 2.1 using $Z = 2.2$. This value of $n_{b,0}$ is in good agreement with that determined from the results shown in Figure 5, i.e., 2.2. This is, however, not enough to demonstrate the validity of the model B. The predicted distribution of molecular mass or degree of polymerization of the solvent extractable material should also be in agreement with that observed. Figure 8 illustrates LD/MS spectra of DMF extracts from S0, S3, S6, S9 and S12. The spectra reveal that the features common among the extracts from different oxidized coals; that the molecular mass distributes widely over the range from 100 up to 8,000 and that compounds with molecular mass of around 300 are the most abundant. Moreover, the distribution seems not to vary significantly with the extent of the oxidation. The distribution of molecular mass could be converted into that of degree of polymerization, by giving the average molecular mass of the monomeric unit. The average molecular mass, M_m, was calculated as about 200 by considering the carbon content, n_a and f_a. The value of M_m means that the degree of polymerization of the extracts ranges from 1 to approximately 40. This is the basis of that $F_{1\text{-}40}(p)$ is considered in the above-described models. Figure 9 shows the molecular mass distribution predicted by the model B assuming $M_m = 200$. The calculated distribution is little sensitive to the probability p^{**} as seen for the mass spectra of DMF extracts. It should also be noted that the distribution agrees well with that observed, although the quantitative comparison of them is difficult at present, due to that the molecular mass per monomeric unit itself should more or less distribute due to variety of chemical structure of peripherals and bridges.

CONCLUSIONS

The oxidation depolymerizes the coal by eliminating aromatic clusters. When a cluster is eliminated, the bridges that have been connected to the cluster are converted into peripheral chains of the neighboring clusters, and carboxyl groups are formed at the ends of the peripherals. The elimination of the cluster also accompanies the deactivation of the neighboring clusters due to the formed carboxyls. The mechanism of the oxidation allows us to describe the following relationships;

$\Delta f_{COOH} \approx \Delta N_b$ and $\Delta f_{COOH} / \Delta N_c \approx \Delta N_b / \Delta N_c = n_{b,0} \approx 2.2$

The model B, which assumes that coal is a mixture of a fully developed Bethe lattice with $Z = 2.2$ and $p_0 = 1$, and solvent extractable material with $n^{e}_{b,0} = 1.8$, reasonably predicts the observed increase in the fraction of DMF extractable material. The model can also predict the extract's molecular mass distribution semi-quantitatively as a function of p^{**}, the corrected.

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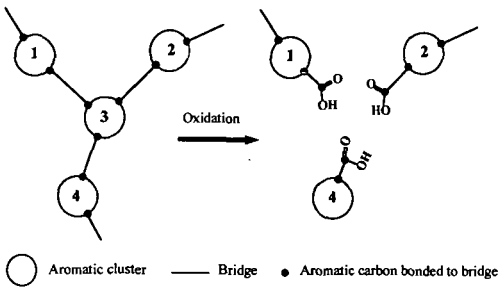

Figure 1. Elimination of aromatic cluster and conversion of inter-cluster bridge into carboxyl group by oxidation.

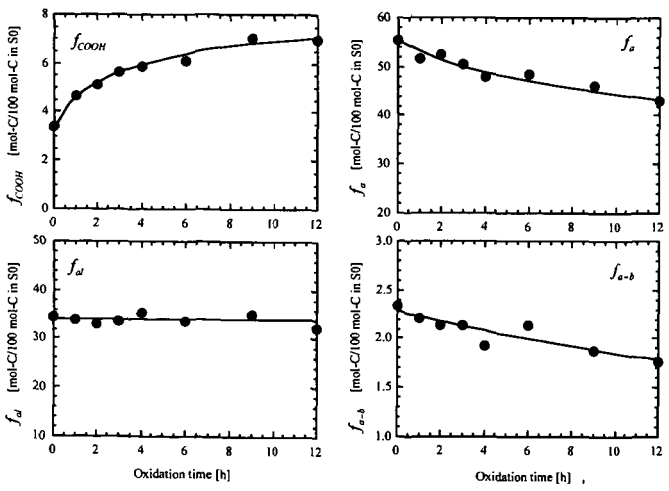

Figure 2. Fraction of different types of carbon, f_a, f_{al}, f_{COOH} and f_{a-b}, as a function of oxidation time.

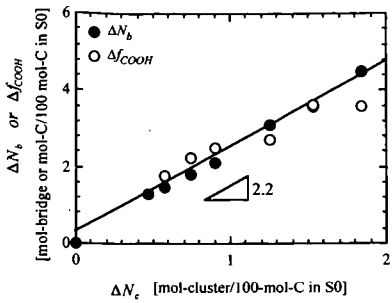

Figure 3. Δf_{COOH} and ΔN_b as a function of loss of aromatic clusters, ΔN_c.

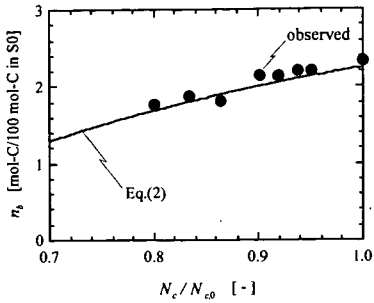

Figure 4. Observed and calculated n_b as a function of $N_c/N_{c,0}$.

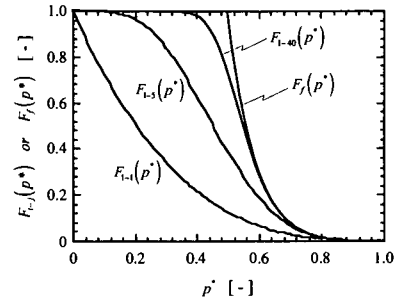

Figure 5. Fraction of site belonging to m-mers as a function of site-occupation probability, p^*.

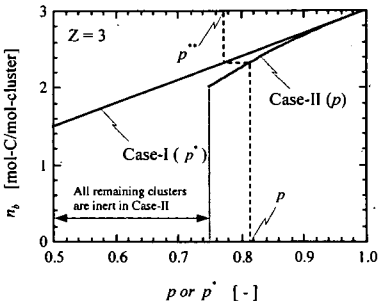

Figure 6. n_b^* as a function of p^* in random degradation (Case I), n_b as a function of p in non-random degradation (Case II) and p^{**} calculated from relationship between n_b^* and n_b.

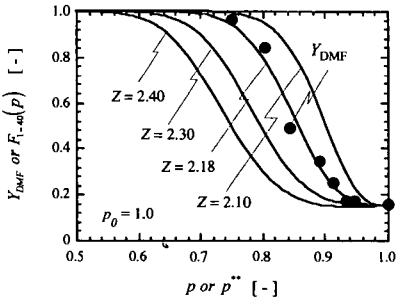

Figure 7. Fraction of DMF-extractable material, Y_{DMF}, as a function of normalized probability p^{**}/p_0 and its comparison with $F_{1\text{-}40}(p)$ predicted by model-B assuming different values of Z.

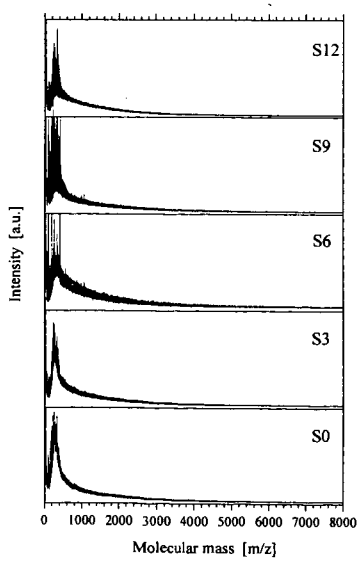

Figure 8. MALDI spectra of DMF extracts.

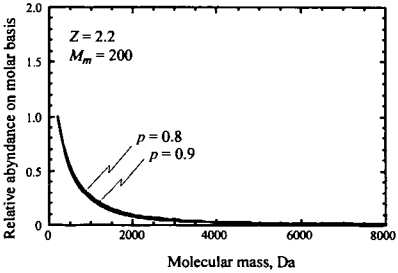

Figure 9. Molecular mass distribution predicted by model assuming $M_m = 200$.