

CHEMICAL STRUCTURE CHANGES OF COAL, CHAR, AND TAR DURING DEVOLATILIZATION

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Introduction

Enormous progress has been made in coal pyrolysis research during the last decade. Models of coal devolatilization have progressed from simple rate expressions based on total mass release^{1, 2} to empirical relationships based on the elemental composition of the parent coal³ to models that attempt to describe the macromolecular network of the coal.⁴⁻⁶ Measurements of particle temperature during devolatilization have eliminated much of the controversy regarding overall rates of devolatilization.⁷⁻¹⁰ In the last several years, advancements in chemical analysis techniques have allowed quantitative investigations of the chemical structure of both coal and its pyrolysis products, including the nature of the resulting char. A prominent research goal is to accurately predict the rates, yields, and products of devolatilization from measurements of the parent coal structure. This goal necessitates modeling the reaction processes on the molecular scale, with activation energies that relate to chemical bond breaking rather than release of products from the coal. ¹³C and ¹H NMR spectroscopy have proven particularly useful in obtaining average values of chemical structure features of coal, char, and tar.¹¹⁻¹⁴ This paper reviews experimental data regarding chemical structure features of coal, char, and tar during rapid devolatilization, and how these data have impacted the development and input parameters for devolatilization models. In particular, the relationship between pyridine extract yields and extract yields predicted purely from NMR chemical structure data is discussed.

Parent Coal Structure

Coal consists of a macromolecular structure of fused aromatic rings connected by non-aromatic bridges and loops. Although measurement of carbon aromaticity in coals has been possible for a number of years, more detailed quantification of chemical features of coal structure has become possible in the last five years. Advanced solid state ¹³C NMR techniques (CP/MAS and dipolar dephasing), combined with carbon counting, have been used to determine the chemical structure features of the Argonne Premium Coals.^{11, 15} In addition to carbon aromaticity (f_a), the distinction between aromatic carbons with and without attachments (such as hydrogen, carbon, or oxygen) is measured. A correlation was made to determine the average number of aromatic carbons per fused aromatic cluster assuming circular rather than linear catenation.¹¹ The specification of the number of aromatic carbons per cluster (C_c) provides the basis for the determination of many interesting chemical structure features. Probably one of the most useful quantities is the number of attachments per aromatic cluster, referred to as the coordination number ($\sigma+1$), which is determined from the number of alkylated (f_a^P) and phenolic (f_a^S) attachments to aromatic carbons, as follows:

$$\sigma + 1 = \frac{(f_a^P + f_a^S) C_c}{f_a} \quad (1)$$

In addition to the total number of attachments per cluster, it is possible to determine the fraction of total carbons in methyl and methoxy groups. This quantity identifies methyl groups, which, to a first approximation, are considered to be the only chain terminators. This allows quantification of the total attachments per cluster into chains that terminate (i.e., attachments with methyl groups, referred to as side chains) and chains that connect to other aromatic clusters (referred to as bridges and loops). Since this is a carbon counting method, there may be some discrepancy in that oxygen bridges are not counted. The fraction of attachments that are bridges between clusters (p) is determined as follows:

$$p = \frac{f_a^P + f_a^S - f_{al}^*}{f_a^P + f_a^S} \quad (2)$$

and $(1-p)$ is the fraction of attachments that are side chains. Orendt, et al.¹⁵ showed that the coordination number varies from 3.9 to 5.6 for the Argonne premium coals, while the fraction of attachments existing as bridges and loops (p_0) ranged from 0.49 to 0.74. This means that on average, each aromatic cluster is connected to other aromatic clusters at $p(\sigma+1)$ or 2.5 to 3.6 points. In contrast, a long chain-like polymer with no crosslinks contains 2.0 connecting bridges

per aromatic cluster. In general, the more crosslinks per aromatic cluster (i.e., as the coordination number increases beyond 2.0), the harder it is for a material to thermally decompose.

Once the number of aromatic carbons per cluster and the number of total attachments per cluster are determined, the average cluster molecular weight (M_{cl} , including side chains and one-half the bridges and loops) can be determined using the elemental carbon composition (x_C) and the molecular weight of carbon (M_C).^{4, 11}

$$M_{cl} = \frac{C_{cl} M_C}{f_a' x_C} \quad (3)$$

This corresponds to the size of the average monomer unit in the coal macromolecule. The average molecular weight of a side chain (M_δ) can also be determined:

$$M_\delta = \frac{M_{cl} - C_{cl} M_C}{\sigma + 1} \quad (4)$$

Values of cluster molecular weights (M_{cl}) in parent coals determined using this method range from 270 to 410 amu, with no clear trend with coal rank. Side chain molecular weight (M_δ) show a clear trend with coal rank, ranging from 12 amu for the high rank coals to 52 for the low rank coals (see Fig. 1). These average values of M_δ roughly correspond to methyl groups (15 amu) and carboxylic acid groups (45 amu), respectively. It must be remembered, however, that these values represent weighted average of many types of attachments.

Structure of Pyrolysis Products (Chars and Tars)

Char and tar samples were obtained as a function of residence time in a devolatilization experiment (1250 K, 2×10^4 K/s in nitrogen) and just subsequent to devolatilization in a laminar flame-fired experiment (1500 K, 5×10^4 K/s).¹⁴ Quantitative measurements of chemical structure were performed on the coals and chars using the ¹³C NMR techniques described above. Results show that the chemical structures of fully-devolatilized chars are very similar, even though a wide diversity is seen in the parent coal structures. For example, the average cluster molecular weights of the fully-pyrolyzed chars span a range of only 50 amu, in contrast to the span of 150 amu observed in the parent coals. Side chain molecular weights of the fully-pyrolyzed chars span a narrow range from 11 to 18 amu, which contrasts even more with the parent coal data (see Fig. 1). The change in side chain molecular weight is most dramatic for the low rank coals, corresponding to the release of large amounts of aliphatic material as light gases. The similarity in chemical structure of fully-devolatilized coal chars suggests that differences in measured heterogeneous char reactivities may be influenced primarily by physical structure.¹⁴

Use of Chemical Structure Features in Devolatilization Models

The use of statistics applied to polymer chains was applied to coal devolatilization by Niksa and Kerstein.¹⁶ Devolatilization models have evolved to use network structures that represent coal as aromatic clusters connected by labile bridge material.⁴⁻⁶ A summary of these three models was recently published.¹⁷ A non-linear relationship exists between the number of intact labile bridges and the amount of clusters disconnected from the "infinite" lattice structure.¹⁸ Closed-form solutions have been formulated to relate the breakup of the lattice structure to the bridge population and the initial characteristics of the lattice. Both straight chain lattices⁵ and Bethe lattices^{6, 18} have been used to represent the coal macromolecular structure.

The three coal devolatilization models utilize the chemical structure features available from solid-state NMR analyses in different ways. All of the models use or reference the number of aromatic carbons per cluster (i.e., $MW_{cluster}$). The number of attachments per cluster ($\sigma+1$) are used directly in the CPD and FG-DVC models, but straight chains are used in FLASHCHAIN. The molecular weight per side chain (MW_δ) is used directly in the CPD model, and directly impacts the light gas yield. In the FG-DVC model, the light gas species evolution is specified based on empirical fits of light gas yields in TG-FTIR experiments, and therefore does not link the light gas evolution directly to the lattice structure of the parent coal. In FLASHCHAIN, the molecular weights of the bridge material are much larger than the NMR data, and a correction factor is used to specify the final molecular weight of the light gas.

The direct use of NMR data to specify the coal-dependent parameters is illustrated in Fig. 2, which compares predicted tar and total volatiles yields for sixteen coals during devolatilization at heating rates from 1 to 10,000 K/s agree with measured values.¹⁴ For most coals, no adjustable parameters were used to tune the predictions to match the yields. However, one adjustable parameter was used for lignite to represent early crosslinking, while this same parameter was adjusted to represent stable bi-aryl bridges in high rank coals (i.e., Iv bituminous). In these predictions, the total gas yield was calculated without the use of yield factors from previous pyrolysis experiments.

The initial fraction of the labile bridges that are intact specifies the connectivity of the lattice. The initial lattice is generally not fully connected, and a certain amount of free or

disconnected material is predicted by the lattice statistics. This material is generally thought to correspond to the solvent extracts from unreacted coals. However, there seems to be a discrepancy between the amount of "extracts" predicted by using the solid state NMR data and measured pyridine extract yields. Figure 3 shows pyridine extract yields from the Argonne Premium coals measured by Fletcher, et al.¹⁹ Also shown are the predicted amounts of unattached material (i.e., extract) based on a Bethe lattice with coordination number and fraction of intact bridges taken directly from NMR measurements using the CPD model. The measured pyridine extract yields are as high as 26% for the Pittsburgh #8 coal, while the predicted yields for this coal are significantly lower.

Possible reasons for the lack of agreement between measured pyridine extracts and predictions based on NMR structural data are:

- (i) errors in the NMR measurements and their interpretation
- (ii) the use of average NMR structural data rather than distributions
- (iii) the use of Bethe lattices as approximations of coal molecular structure
- (iv) the representation of the extract and the residue by the same lattice structure, even though they are chemically different

Of these hypotheses, (iv) seems to be the most rationale explanation for the disagreement shown in Fig. 3. For example, the total number of attachments per cluster ($\sigma+1$) determined by ¹³C NMR in the pyridine extracts is an average of 15% lower than in the corresponding residue, as shown in Fig. 4 for the Argonne Premium coals.¹⁹ The number of aromatic carbons per cluster in the pyridine extracts is also consistently lower than in the corresponding residues, and the result is lower molecular weights per cluster in the extracts (Fig. 5). The number of bridges and loops per cluster is also lower in the extracts than in the residues, although the molecular weight per side chain in the extracts is similar to that in the corresponding residues. The differences in average chemical structure features between the extracts and residues seems to confirm hypothesis (iv) above; the extract is chemically different from the residue and should not be treated with the same lattice structure. These results obviously have the most impact for those coals with high pyridine extract yields.

Conclusion

Coal pyrolysis research has progressed to the point that measurements of the chemical structure features of parent coals is useful in current devolatilization models. Chemical structure features of particular importance to modeling efforts seem to be the number of aromatic carbons per cluster, the number of attachments per cluster, and the total molecular weight per cluster (including attachments). Most current models are able to describe tar and gas yields as a function of time, temperature, heating rate, coal type, and pressure, although the network models of devolatilization appear to have the closest ties with coal structure. However, the models selectively use chemical structure information in order to attain agreement with measured tar and gas yields, while other pertinent data are ignored. One such example is that the models use as input parameters either measured pyridine extract yields *or* the fraction of intact connecting bridges. Chemical structure features of pyridine extracts do not match those of the corresponding residue, suggesting that models should treat extracts as a different chemical than the coal. The challenge for the models is to reduce the number of empirical parameters by using chemical structure information.

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References

1. Anthony, D. B., J. B. Howard, H. C. Hottel and H. P. Meissner *15th Symposium (International) on Combustion*; The Combustion Institute, Pittsburgh, PA: 1974; pp 1303-1317.
2. Kobayashi, H., J. B. Howard and A. F. Sarofim *16th Symposium (International) on Combustion*; The Combustion Institute, Pittsburgh, PA: 1976; pp 411-425.
3. Ko, G. H., D. M. Sanchez, W. A. Peters and J. B. Howard *22nd Symposium (International) on Combustion*; The Combustion Institute, Pittsburgh, PA: 1988; pp 115-124.
4. Fletcher, T. H., A. R. Kerstein, R. J. Pugmire and D. M. Grant *Energy and Fuels* 1992, 6, 414.
5. Niksa, S. *Energy and Fuels* 1991, 5, 673-683.

6. Solomon, P. R., D. G. Hamblen, R. M. Carangelo, M. A. Serio and G. V. Deshpande *Energy and Fuels* **1988**, 2, 405-422.
7. Solomon, P. R., M. R. Serio, R. M. Carangelo and J. R. Markham *Fuel* **1986**, 65, 182-193.
8. Fletcher, T. H. *Combustion Science and Technology* **1989**, 63, 89.
9. Fletcher, T. H. *Combustion and Flame* **1989**, 78, 223.
10. Solomon, P. R., T. H. Fletcher and R. J. Pugmire *Fuel* **1993**, 72, 587-597.
11. Solum, M. S., R. J. Pugmire and D. M. Grant *Energy and Fuels* **1989**, 3, 187.
12. Fletcher, T. H., M. S. Solum, D. M. Grant, S. Critchfield and R. J. Pugmire *23rd Symposium (International) on Combustion*; The Combustion Institute, Pittsburgh, PA: **1990**; pp 1231.
13. Pugmire, R. J., M. S. Solum, D. M. Grant, S. Critchfield and T. H. Fletcher *Fuel* **1991**, 70, 414.
14. Fletcher, T. H., M. S. Solum, D. M. Grant and R. J. Pugmire *Energy and Fuels* **1992**, 6, 643-650.
15. Orendt, A. M., M. S. Solum, N. K. Sethi, R. J. Pugmire and D. M. Grant In *Advances in Coal Spectroscopy*; H. L. C. Meuzelaar, Ed.; Plenum Press: New York, **1992**; pp 215-254.
16. Niksa, S. and A. R. Kerstein *Combustion and Flame* **1986**, 66, 95-109.
17. Smith, K. L., L. D. Smoot and T. H. Fletcher In *Fundamentals of Coal Combustion for Clean and Efficient Use*; L. D. Smoot, Ed.; Elsevier: New York, **1993**; pp 131-298.
18. Grant, D. M., R. J. Pugmire, T. H. Fletcher and A. R. Kerstein *Energy and Fuels* **1989**, 3, 175-186.
19. Fletcher, T. H., S. Bai, R. J. Pugmire, M. S. Solum, S. Wood and D. M. Grant *Energy and Fuels* **1993**, 7, 734-742.

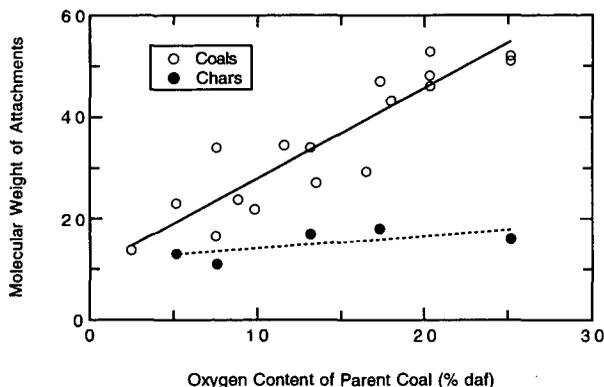


Figure 1. Average molecular weight of side chains attached to aromatic clusters in unreacted coals and fully-devolatilized chars. Oxygen content of the parent coal is used as a rank indicator. Lines represent linear correlations of the data (see Fletcher et al.¹⁴)

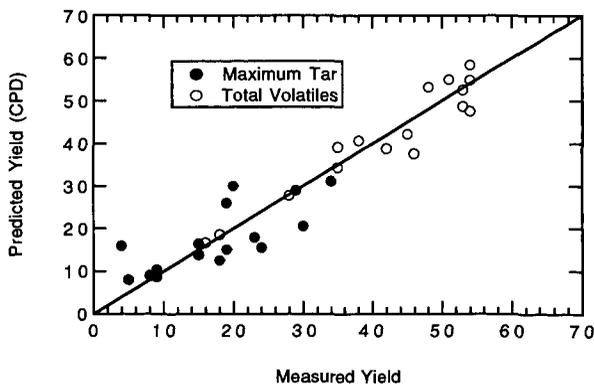


Figure 2. Comparison of predicted tar and total volatiles yields from NMR structural data versus measurements. Data are from sixteen coals during pyrolysis over a range of heating rates (see Fletcher et al.⁴)

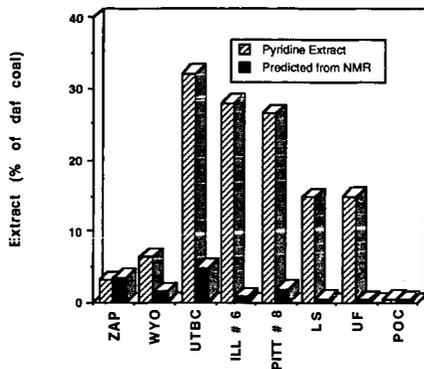


Figure 3. Measured pyridine extract yields compared with predictions of unconnected fragments in a Bethe lattice using ^{13}C NMR characterizations of average chemical structure (see Fletcher, et al.¹⁹).

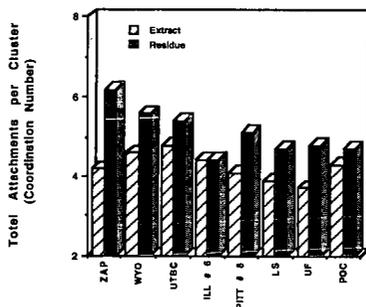


Figure 4. Coordination numbers ($\sigma+1$) determined from ^{13}C NMR analyses of pyridine extractions of the Argonne premium coals (see Fletcher, et al.¹⁹).

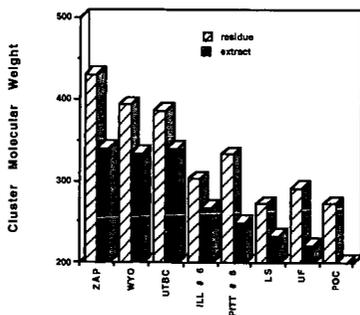


Figure 5. Average molecular weight per cluster determined from ^{13}C NMR analyses of pyridine extractions of the Argonne premium coals (data from Fletcher, et al.¹⁹).