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Full Length Article

Examination of structural models and bonding characteristics of coals

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HIGHLIGHTS

- Graphical coal models in literatures are evaluated using C%-f_a data of coals.
- A method is proposed to calculate concentrations of 9 covalent bonds in coals.
- Bonds concentrations in models are compared with that calculated from coals.
- The problems in many models are discussed.
- A matrix computation is established to quantify bond distribution in coals.

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ABSTRACT

More than 100 graphical coal structural models have proposed in the literature but their suitability has not been studied. All the coal models are in essence conceptual images, which are not very useful in quantitative analyses. This article analyzes the validity of 25 models selected from 134 models reported in the literature using the carbon content (C%) and aromaticity (f_a) data of coals reported in the literatures. Eighteen of the models are found to be reasonably good because they meet the C%-f_a relation within ±10% in f_a. The concentrations of 9 covalent bonds in the 18 models are compared with those calculated by a method established in the paper based on ultimate analysis and ^{13}C NMR data of coals. The pros and cons of the models are discussed and a matrix computation is proposed to represent the bonding structure of coals in a C% range of 59–91%.

1. Introduction

Coal is very complex in structure. To understand its core organic structure more than 134 graphical structural models have been proposed at least since 1942 [1]. The reason of so many models been proposed may be attributed to the fact that some of the models at best are able to represent the main structural characteristics of a single coal and none of them is valid for different coals of similar rank. In fact some of the models were considered to be incorrect even for a single coal or a coal constituent [2].

This problem is understandable because of the following factors. Firstly, in principle there should be no single structural model to accurately represent a coal because coal is a mixture of macerals including vitrinite, inertinite and liptinite, and their proportion vary in coal bed, even from one sample to another sample. The structure of vitrinite varies with coal rank while that of inertinite or liptinite changes little. Secondly, even if there is a representative organic structure of coal, a graphical coal structure model has to be simple to show only the core information because it is not possible to include a huge number of atoms in a model. Assumptions made to eliminate the "unimportant" structures result also from the limited capability of analytical methods available. The assumptions would inevitably reduce the effectiveness of the models. Thirdly, because of the presence of a large number of isomers, many models of different structures may be constructed from the same set of experimental characterization results, such as element contents, aromaticity (f_a) and chain length. This certainly would lead to uncertainty in validity of a graphical model.

It should be noted that, however, in spite of so many unfortunate difficulties in constructing graphical coal models it is certain that some of the models are better than others if they are limited to only a specific coal rank or a narrow carbon content (C%) range. Furthermore, it is well recognized that the main bonding structure of coals varies systematically with their C%. This is because that vitrinite is the dominant constituent of most coals with mass fraction of usually 75–80% [3]. The effects of inertinite and liptinite on coal structure are relatively small, especially their structures change insignificantly in the course of coalification.

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Above discussion suggests that it is possible and necessary to examine the graphical coal structure models reported in the literature to identify those that better fit the structure parameters derived from experimental characterization. However, very few such works have been reported in the literature. Nakamura et al. applied CAMD software to calculate density of coal models composed of polyaromatic hydrocarbons and polymethylene bridges. They found that the densities of the models varied from 0.63 to 1.09 g/cm^3, which were much lower than those of coals (1.25–1.6 g/cm^3) [4]. Toshimasa et al. compared the ^{13}C NMR spectra simulated from a graphical coal model with that from the ^{13}C NMR experiments used in developing the model. They observed that the simulated spectra were quite different from that of the actual spectra, and the difference could only be reduced by many rounds of model modifications [5]. These works demonstrate the necessity of validating graphical coal models. It was believed by many that the computer built coal models reported in recent decade were better than those of "hand-constructed" models because that energy minimization of structure could be performed by computer to ensure the model to be stable. However, the resulting models were generally not as good as expected because their reactivity was usually much lower than that of the actual coals [5–7]. It is sure that the chemical structure of coal is not stable in principle, otherwise it will not evolve from lignite to anthracite during coalification.

Since the coal structure underwent systematic change during coalification resulting in increases in both C% and f_a, and decreases in hydrogen (H) and oxygen (O) contents, C% and f_a of coals have been used as the main parameters to characterize their chemical structure. It is therefore logical to examine the coal models proposed so far using the experimental determined C%-f_a relation of coals.

Furthermore, it is worth to note that all the graphical coal structural models are conceptual images in nature and it is difficult to use these models to quantify coal structures and to correlate them with reactivity and thermodynamic calculations, no matter how closely the models are in representing the actual coal structures. To overcome these difficulties Liu suggested to represent coals by concentrations of main covalent bonds, such as $C_{ar}—C_{ar}$, $C_{ar}—C_{al}$, $C_{al}—C_{al}$ and C—X, where C is a carbon atom, subscripts ar and al denote aromatic and aliphatic, respectively, and X is a heteroatom including O, sulfur (S) and nitrogen (N) [8]. If two types of carbon hydrogen bonds ($C_{ar}—H$ and $C_{al}—H$) are included, concentrations of the 11 bonds are needed to define the structure of any coal. This representation of coals allows thermodynamic calculation of coals' properties, determination of bonds that undergo cleavage at different temperatures, and reaction of radical fragments generated from the bonds cleavage, as evidenced partly by Guo et al. recently on kraft lignin [9]. Since the nature of a chemical reaction is restructuring of bonds, expressing the coal structures by the concentrations of bonds is meaningful, which also avoids the problems of selecting representative isomers in construction of graphical models.

Interpretation of coal pyrolysis behaviors according to the bonds population in coals has been attempted in the literature. Shi et al. recently fitted differential thermogravimetric curves (DTG) of 34 coals during pyrolysis into cleavage of 5 types of covalent bonds and assigned these bonds to specific bonding forms [10]. Kong et al. simulated bond cleavage of coals in pyrolysis using model compounds and concluded that the O atoms in coals reduced dissociation energy of some bonds and consequently promoted coal pyrolysis rate [11]. These efforts extended the understanding on relations between pyrolysis behaviors and bonds in coals, but yielded little information on concentration of various bonds in coals. Obviously, representing coals by concentrations of covalent bonds is important in future studies.

Following the above discussion, this article firstly examines the graphical coal structure models reported in the literature based on experimental C%-f_a data of coals to identify the models that are more correct than others. Secondly, the distribution of main covalent bonds of the identified models is compared with that determined from experimental data using a method developed from the formula reported by Gyul'maliev et al. [12]. The validity of the models is analyzed further with respect to covalent bonds, and then a bonding structure model and a typical bonding diagram of coals are proposed.

2. Methods

2.1. Selection and examination of graphical coal structural models

As indicated earlier more than 100 graphical coal structural models can be found in the literature and some of them are incorrect due to various reasons. To make this study more efficient a few criteria are set to screen out the poor models first. The models remained in the subsequent study are those: (1) 2D models proposed since 1942; (2) covering the full rank of coal, from lignite to anthracite; (3) comprising more than 50 carbon atoms. The validity of the selected models was then examined by the experimental C%-f_a data of 28 coals, derived from the ultimate analysis and ^{13}C NMR, reported in the literatures [13–20].

2.2. Calculation of bond concentration of models

As mentioned earlier, coal mainly contains 11 types of covalent bonds. Since the S and N contents of coals are usually low and vary little with C%, the bonds containing S and N are ignored and only 9 types of bonds are studied. These bonds include $C_{ar}—C_{ar}$, $C_{ar}—C_{al}$, $C_{al}—C_{al}$, $C_{ar}—H$, $C_{al}—H$, $C_{ar}—O$, $C_{al}—O$, $C_{al}{=}O$ and O—H, and their concentrations are determined by Eq. (1), where $con_{i—j}$ is the concentration of bond i—j in mol/g, $n_{i—j}$ is the number of bond i—j in a molecule; i represents C_{ar}, C_{al} or O while j represents C_{ar}, C_{al} or H; the denominator is the molecular weight of the models, which contain the atomic mass of C, H, O, N, S represented by n_C, n_H, n_O, n_S and n_N in g/mol, respectively.

$$con_{i—j} = \frac{n_{i—j}}{12n_C + n_H + 16n_O + 32n_S + 14n_N}\ (\text{mol/g}) \tag{1}$$

2.3. Calculation of bond concentration of coals

A simple method estimating the total number of single bonds in complex hydrocarbon matters was reported by Gyul'maliev et al. based solely on the ultimate analysis. The quantity of the bonds determined therefore is half of the unpaired electrons calculated from elemental composition [12]. Since all coals contain a large fraction of double bonds, such as $C_{ar}—C_{ar}$ (quasi double bond) and C=O bonds, Gyul'maliev's method has to be modified. This may be done by introducing a concept of 'half-bond', which is half of all covalent bonds, single and double. The quantities of the single and double bonds can be determined using ^{13}C NMR data as well as the ultimate analysis data. The bonding information contained in ^{13}C NMR data is shown in Table 1, which includes parameters for 7 carbon structures. The ultimate analysis data can be converted into elemental concentration in mol/g by dividing the mass fraction of each element by its atomic mass, such as C%/12, for example.

From the above, the concentrations of 9 bonds can be determined using Eqs. (2)–(10), where C%, H% and O% are in decimal form, 0.8 for 80%, for example. Specifically, Eqs. (2), (4), (6) and (10) are based on the balance of atom, half-bond and covalent bond, while other equations are based on only the ^{13}C NMR data.