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Fuel Processing Technology 77–78 (2002) 25–32

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# Towards an understanding of the coal structure: a review

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Received 31 January 2002; accepted 20 March 2002

In memoriam Professor Dr. Peter H. Given in gratitude and admiration for his scientific activity.

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## Abstract

This review is limited to studies that directly refer to the following concepts: (i) macromolecular structure of coal; (ii) the contribution of relatively low molecular substances in the structure; (iii) factors effecting capabilities of solvents in coal extraction and the extraction mechanism; as well as (iv) intermolecular forces occurring in coal organic matter. Although concept (i) was introduced in the 1970s, no great progress has been achieved. Available data for a few coals indicate that mass distribution of the macromolecular part are in the 1300–3500 amu range. There are no experimental data available that could describe the structure of the macromolecular part of coal. Referring to item (ii), the presence of significant amount of various substances in the  $\sim 100$ –500 amu range in coals was evidenced by mass spectrometry methods (field ionization mass spectrometry (FIMS) and matrix-assisted laser desorption/ionization–time-of-flight (MALDI–TOF)). As for item (iii), major contributors that influence solvent extraction capability is the electron-donicity of the solvent as well as the shape and size of its molecules. One major step of the mechanism of coal extraction is the substitution phenomenon. Presumably (in reference to item (iv)), all known intermolecular forces hold together coal organic matter. However, only hydrogen bonds can be directly detected, as yet. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Coal; Macromolecules; Molecules; Extraction mechanism; Intermolecular forces; FIMS; MALDI

## 1. Introduction

An extensive research on coal structure started in the 1970s, shortly after the World Oil Crisis. One of the alternatives was to get knowledge that could contribute to developing

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new economic technologies for the production of petroleum substitutes from coal. Another factor was the availability of new instrumental and analytical techniques. The present knowledge of coal structure has been a result of investigation carried out by hundreds of researchers. Therefore, it is impossible to describe their efforts and results in a short review. This paper is rather aimed at supplementing the already published reviews [1–6].

## **2. Average molecule concept of coal structure**

Since 1960s, coal chemists attempted to create models of coal structure which would represent a synthetic view of principle characteristics of coal organic matter. One of the strategies consisted of constructing “average structural unit” of coal organic matter. Structural units were, in fact, molecules described in a classically chemical way using atoms, chemical bonds and some functional groups. Probably, Fuchs and Sandhoff worked out the first such model in 1942. Later, other average structural units were published by: A. Gillet in 1950; L. Cartz and P.B. Hirsch in 1960; P.H. Given in 1960; W.R. Ladner in 1963; W.H. Wisner in 1975; G.J. Pitt in 1979; L.A. Heredy and I. Wender in 1980; C. Spiro in 1982; and J.H. Shinn in 1984 (for drawings of the models, see Refs. [1,3–5]). The structures had been built on the basis that they were characterized by the same values of parameters (such as elemental composition; carbon and hydrogen aromaticities; number of rings; size of aromatic clusters, etc.) as were determined for the total organic matter of some coals or for its major petrographic component i.e., vitrinite. However, in 1984, P.H. Given questioned the view that one or even several molecules can be a representative of a coal organic matter [6a]. Hence, average structural models are not very useful and they rather represented some sort of professional divergence among chemists when they were involved in coal research.

In the late 1970s, coal scientists began to apply a number of physical methods suitable for solid-state characterization. One of the methods was transmission electron microscopy (TEM) in its dark field (DF) mode. A. Oberlin and her collaborator J.N. Rouzaud developed it [7,8]. The technique enabled researchers to directly observe, in coal organic matter, the diameters of polyaromatic units (BSU) as well as their space orientation. It was shown [7,8] that the sizes of BSU are around 1 nm (which may correspond to the range of 4–12 condensed aromatic rings). For bituminous coals, the sizes remain nearly constant up to the anthracite range. In lower-rank coals, the BSUs are randomly oriented and are held so by the presence of various, mostly heteroatomic, chemical bonds. For higher-rank coals, increasing parallel orientation of BSUs is observed. The TEM-DF technique is not able to observe objects smaller than 0.7 nm.

## **3. Macromolecular concept of coal structure**

In the meantime, a new idea began to penetrate coal science due to the influence of polymer science. Most man-made polymers were known to be soluble in common organic solvents in spite of their extremely high molecular weights. The insoluble exceptions were the cross-linked polymers that formed three-dimensional network. Since coals were known to be rather insoluble, a view appeared that coal organic matter might show such cross-linked

polymer nature. Having in mind this view, Larsen and Kovac [9] used the statistical theory of polymer network to calculate the average molecular weight ( $M_c$ ) of a chain (composed of aromatic and hydroaromatic units linked together) between two cross-links in various coals, from experimental data on solvent swelling and mechanical properties of coal. They concluded that  $M_c$  for bituminous coals was in the 1500–1800 amu range. Later, a great deal of attention was paid to the concept of cross-linked polymer character of coals. Measurements of  $M_c$  were continued by Larsen and Kovac as well as by Lucht and Peppas [10] and a number of others. The problem was extensively reviewed by Peter Given [6b]. He concluded: “we must accept that coals are cross-linked macromolecular solids. But. . .they are sui generis, of a class by themselves, of unrivalled complexity.” Recently, the macromolecular character of at least, part of coal organic matter, was also experimentally confirmed by Krzesinska [11] who applied molecular acoustics methods. The methods, however, cannot discriminate between cross-linked and entanglement structures.

The problem of occurrence and chemical character of cross-links has been not clarified as yet. An analogy between insoluble polymers and insoluble part of coal implied that coal cross-links are formed by covalently linked atoms or groupings (ether, methylene chain, sulfide, etc). However, coal extraction experiments (carried out in mild conditions that most likely exclude a rupture of covalent bonds) clearly show that the content of coal insoluble part depends on the solvent used for extraction. For example, studies on extraction with the use of binary and ternary solvent systems—pioneered by Iino et al. [12] and recently developed by Dyrkacz and co-worker [13,14]—indicated that the coal insoluble part assumed to be covalently cross-linked matter, might constitute less than 30 wt.% (data for 87% Cdaf coal: 70 wt.% of the coal was solubilized by CS<sub>2</sub>/NMP mixture). The same coal contains approximately 65 wt.% of insolubles when neat NMP solvent is used. The question is whether there are any cross-links in the part of coal matter that is not soluble in NMP but can be dissolved when CS<sub>2</sub>/NMP is used. And what is the content of the covalent three-dimensional network that cannot be dissolved in any organic solvent? There is also a lack of analytical data referring to the composition of high yield extracts resulting from the application of binary or ternary solvent mixtures although there are available analytical techniques (LD or MALDI–TOF mass spectrometry; for explanation of the acronyms, see Section 4.2) that could be used for tracing low molecular as well as very high molecular weights. Such available data for a few raw coals indicate that mass distribution of macromolecules are in the 1300–3500 amu range.

Recently, the concept of network structure of coals and nature of forces that bind the network together had been discussed by Iino [15]. The conclusion is “there is no clear evidence for covalent network model, though it is sure that (such) network exists in coal from swelling and elasticity measurements of coals.”

## 4. Molecular components of coal structure

### 4.1. Coal extraction studies

For long time, not much attention had been paid to the soluble part of coals and its role as the component of coal structure. The data on coal extraction referred to the application

of organic solvents at their boiling points or at higher temperatures when extractions were carried out in autoclaves [6c]. Well before the 1980s, it was already known that low molecular substances are components of coal organic material. However, the following questions remained unclear: what is the content of the low molecular substances in coal; what is their chemical nature and molecular weight distribution; why extraction capabilities of various organic solvents are so different; and what forces hold together the low molecular and macromolecular substances.

In 1977, systematic studies of coal extraction had been undertaken. First of all, with the aim to avoid cleavage of covalent bonds, extractions were carried out at room temperature and the extracts were freed from solvents in rotary evaporators under reduced pressure [16–18]. Numerous organic solvents used for coal extraction had been characterized by quantitative measures [16] of their electron-donor (DN) and electron-acceptor (AN) properties (Gutmann's [19] donor and acceptor numbers) as well as by Hildebrand's solubility parameter and Snyder's polarity index. Correlations were found between the extract yields on one hand and donor numbers of the solvents as well as the differences (DN – AN), on the other. Later studies revealed much stronger correlations in question when a logarithmic coordinate was used [20]. Thus, there is no question that nucleophilic solvent properties and, to a lesser extent, electrophilic properties, are determinant factors of solvent extraction capabilities. In general terms, the mechanism of coal extraction seems to consist in substitution: electron-donating solvent molecules replace the coal electron-donor participants in the forces [16]. The higher the electron-donor capability of the solvents, the more coal electron-donor centers are replaced by solvent molecules and therefore, the higher the extract yields [16]. Additional but significant information on the extraction mechanism arose from the detailed studies of various binary/ternary solvents [14]. The authors concluded: "the basicity of the solvent is a major contributor to the extraction of a coal" however, "two other factors may also be acting." One is a steric requirement of the flat molecular shape (characteristic for aromatic rings compared with saturated rings). Flat molecules likely have better access to coal matter interior. The second one is unsaturation of a fragment of solvent molecule that may lead to Pi–Pi interactions with coal. The interactions presumably disturb original Pi–Pi forces in coal.

#### 4.2. Mass spectrometry (FIMS, MALDI) of coal extracts and of raw coals (MALDI)

Molecular masses of the extracts components were determined [17,18,21] with the use of FIMS (field ionization mass spectrometry), the technique that does not produce fragmentation ions. Moreover, successive heating of the extract samples inside the mass spectrometer (and the successive mass spectra recording) enabled investigators to get information on the extract composition without any interference with the sample thermal decomposition in the mass spectrometer. The detailed description of the applied FIMS technique can be found elsewhere [21,22]. The chemical nature of the components was determined by means of high-resolution MS [17,18,21] and low-voltage electron impact MS [23]. It is worth pointing out that FIMS spectra of the coal extracts (as well as of the extraction residues) showed extremely complex composition of coal organic matter. The estimated number of the detected extract components was approximately 2000 individual substances [21]. The number might be much higher if isomers could be detected by FIMS.

Summing up, the results for 81% Cdaf bituminous coal were as follows. The molecular mass distributions were similar, no matter what solvent was used nor what was the extract yield: the extracts were composed of substances in the 70–800 amu range, but substances in the 200–500 amu definitely predominated [17,18,21]. These substances constituted approximately 30 wt.% of the bituminous coal. The identified coal molecules represented the following classes:  $C_nH_{2n-z}$  ( $z=6-28$ ); CHN, CHN<sub>2</sub>, CHN<sub>3</sub>; CHO, CHO<sub>2</sub>, CHO<sub>3</sub>; CHON, CHON<sub>2</sub>, CHNO<sub>2</sub>, CHN<sub>2</sub>O<sub>2</sub>, CHN<sub>3</sub>O<sub>2</sub>; CHS, CHNS, CHOS [17,18,21,23].

In 1995, laser desorption (LDMS) and matrix-assisted laser desorption/ionization (MALDI) coupled with time-of-flight (TOF) mass spectrometry had been applied to the analysis of pyridine coal extracts [24] and of raw coals and some other extracts [25]. The results for bituminous coal extracts are essentially the same as the results derived from FIMS. The extracts displayed molecular mass distribution between roughly 200 and 500 amu with low intensity tailing to higher masses. The MALDI–TOF spectra of the raw coals showed bimodal molecular mass distribution, which covered the regions 130–600 and 1300–3500 amu. Thus, the latter provides information on the mass distribution of the macromolecular part of coal.

All the same, the question still remains whether the applied solvents that produced 30–40 wt.% extract yields were able to remove all molecular substances occurring in coal matter. The question is still open since no data has been found on molecular mass distribution of the high-yield extracts, obtained with the use of binary or ternary solvents.

#### 4.3. Application of <sup>1</sup>H NMR-free induction decay measurements

In 1978, solid-state <sup>1</sup>H NMR had been applied to observe protons in the coal by recording their free induction decay (FID) during pulsed exposure to a high-frequency field [26,27]. The technique was then used for observing the decay in a coal swollen with the use of fully deuterated solvents [28,29]. The FID signal in the swollen coals had been clearly deconvoluted into Gaussian and Lorentzian parts, corresponding to immobile protons of the rigid macromolecules and mobile protons of rotating molecules, respectively. Thus, the technique showed that coal organic matter, in the presence of solvents, indeed consists of two entirely different parts with regard of their rotational freedom. The calculations indicated approximately 40 wt.% content of mobile molecules in the coal swollen by pyridine-d<sub>5</sub> [28]; the value that was close to the extract yield obtained with the use of ethylenediamine/pyridine mixture [17]. In general, the experiments showed the following: when the same solvent was used for extraction and in <sup>1</sup>H NMR experiments, the content of mobile molecules indicated by the latter was always higher compared with the extract yield [28]. The discrepancy was ascribed to the occurrence of some molecules in pores having narrow orifices. The solvents could pass the orifices and make “mobile” the inside coal molecules; however, the molecules could not be extracted due to their large size and too narrow passages [30].

The described interpretation of the NMR spectra was the subject of the debate in print organized by Peter Given [31]. One of the conclusions was that the hydrogen atoms of some alkyl substituents of the network might also show high “mobility” comparable with the mobile protons of the relatively small molecules.

The results of extraction experiments, FI mass spectrometry and  $^1\text{H}$  NMR studies were then used by Marzec and co-worker [30,32] for working out the mechanism of coal extraction and swelling as well as the model of macromolecular/molecular structure of coal [32]. The model was tested and confirmed by others [33–36] and likewise contradicted [37]. With regard to swelling, it should be pointed out that Suuberg et al. [38] had presented in 1994 an advanced thermodynamic concept of coal swelling.

## 5. Nature of attractive forces in coal organic matter

The conclusion from the extraction studies [16,20] was that the molecular substances are attached to the macromolecular network by means of forces between electron-donor and electron-acceptor centers occurring in molecular as well as macromolecular parts of coal organic matter.

In late 1990s, Larsen and Gurewich [39] as well as Sakurovs [40] pointed out that whole coal organic matter is most likely held together by all of the attractive forces experienced by organic compounds. In his statement, Sakurovs included electrostatic interactions (ionic and hydrogen bonds) and electrodynamic interactions [40]. The latter occur when there are instantaneous variations in the distribution of electric charge on the species. The variations generate net attractive forces such as the van der Waals and  $\text{Pi-Pi}$  interactions. The presence in coal of various oxygen groups that may form hydrogen bonds, which in general have rather high energy ( $\sim 20 \text{ kJ mol}^{-1}$ ), support the view that the H bonds may be major attractive forces in coal organic matter [39]. On the other hand, aromatic rings are most abundant structures in bituminous coals and their  $\text{Pi-Pi}$  interactions may commonly occur. It is hard to assess the energy of  $\text{Pi-Pi}$  interactions in coal since it strongly depends on mutual position of the aromatic rings (face-to-face, displaced, etc.) and on the size of aromatic units—the conclusion was derived from molecular and quantum mechanics calculations for model aromatic hydrocarbons [41].

Later studies were aimed at experimental discriminations of the nature of attractive forces occurring in coal organic matter. Larsen [39] proposed a method of counting the hydrogen bonds in coals on the basis of swelling measurements. For swelling, he used series of mixtures of increasing content of pyridine in a nonpolar solvent; pyridine was assumed to destroy all hydrogen bonds occurring in coal. In 1998, an improved IR method of observation of the type of hydrogen bonds in coal by FTIR was proposed [42]. The method includes the removal of water from coal in a high vacuum chamber with  $\text{CaF}_2$  windows followed by in situ scanning of the IR spectra. Five types of hydrogen bonds were found in coal and its extracts. The thermal stability of the bonds was investigated by means of in situ pyrolysis FTIR. The stability follows the order:  $\text{OH-ether O} > \text{self-associated OH}$  and cyclic  $\text{OH} > \text{OH-N} > \text{OH-Pi}$  electrons.

With the aim to investigate the electrodynamic forces in coal, Sakurovs [40] applied proton NMR technique. He observed an increase of coal mobility in the presence of a number of aromatic hydrocarbon additives. The results were interpreted in terms of reduced interactions in coal that are electrodynamic in nature.

Molecular dynamics calculations had been used for simulating interactions between coal and solvents [43]. The results of the simulation indicated that “cooperative

interactions through hydrogen bonds and aromatic–aromatic interactions at several sites of coal molecules lead to a strong association structure i.e., even if one interaction is dissociated, many others can still hold the association structure.”

## 6. Conclusions

Available data (MALDI–TOF) for a few coals indicate that the mass distribution of the macromolecular part of coal is in the 1300–3500 amu range. However, the structure of the macromolecular part still poses an enigma.

The question whether at least some macromolecules form three-dimensional covalently linked network, the sort that cannot be dissolved in any organic solvent, is still open. Some binary or ternary solvent systems recently applied can dissolve as high as 70 wt.% of bituminous coal organic matter. How can we know that even more efficient solvent mixtures would not be found? On the other hand, can we be sure that strong basicity of highly efficient solvents does not decompose some covalent bonds? Moreover, solubility of coal organic matter does not exclude the possibility of the occurrence of other types of three-dimensional polymeric structures in the material. For example, some hyperbranched polymers, which form indeed, three-dimensional structures, are easily soluble in common organic solvents [44]. The same refers to some entangled structures.

There is no question that significant amount of various compounds of the  $\sim 100$ –500 amu range occur in bituminous coal matter. However, their total content is not known in any coal.

Nucleophilic property is a major factor that determines solvent effectiveness in coal extraction. A major contributor to the mechanism of coal extraction is a substitution phenomenon in which electron-donating solvent replaces the coal electron-donor participant in the intermolecular forces occurring in coal. Other factors that influence the solvent effectiveness is shape and size of solvent molecules, parameters which determine the solvent ability to penetrate the most inner spots of coal organic matter.

Most likely, all the types of intermolecular forces hold together coal organic matter. As yet, however, only hydrogen bonds can be directly detected.

## Acknowledgements

The title of the paper “Towards an Understanding of the Coal Structure” has been taken from “An Essay on the Organic Geochemistry of Coal” by P.H. Given [6]. The title accurately describes the past as well as the present situation in coal structure studies.

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