CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 3, No. 4, 2009 Chemical Technology

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COMPOSITION AND STRUCTURE OF COAL ORGANIC MASS. ANALYTICAL REVIEW

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Received: May 05, 2009

Abstract. The research works dedicated to the formation regularities of solid fuels chemical structure were analyzed. Modern conceptions of coals chemical structure, which are becoming deeper owing to tooling growth and facts accumulation, were examined by means of critical comparison of different hypothetical models of solid fuels "molecular" structure. The most general points of the respective theories were formulated, according to which "soft" influence on coal structure primary elements bonds system allows bringing its chemical potential to the maximum.

Keywords: metamorphism, coal, chemical structure.

1. Formation Regularities of Solid Fuel Chemical Structure

The quality of fossil fuels is determined by their chemical composition and structure, which are the results of continuous transformation of phytogenic initial material through the peat to the coal formations with different "chemical age", *i.e.* different metamorphism degree.

N. Panov [1] and E. Rogozina *et al.* [2] investigated metamorphism regularities by determining gas emission during the solid fuel coalification. V. Uspenskiy [3] made up a material balance of the processes taking place at coal bed metamorphism, considered carbonic acid, methane, and water among the main "volatile" metamorphism products and calculated the content of the mentioned compounds in the "volatile" products at different stages of the process. Although those results are in agreement with the data from G. Potonie paper [4], V. Uspenskiy justly notices: "The balance of the compounds total sum and characteristics of removed gaseous and liquid products may be obtained only by indirect ways with higher or lower degree of certainty".

However other authors also try to describe the metamorphism peculiarities using the calculation of "volatile" products composition. The greatest success was achieved by O. Radchenko with E. Rogozina [5] and by I. Eremina with C. Gagarin [6].

In [5] "the amount of coalification volatile products which emerge at different stages…" was calculated using V. Uspenskiy's method. The period from brown coals to graphite was divided into intervals of "humus smooth change" and "gassing splashes". It should be noted that the oscillation process described in [5] completely disagrees with the smooth pattern of the connection between organic substances sum (OS) and carbon content in the coals of different metamorphism stages.

In [6], similarly to other works, the decomposition ways of coal substance with gassing are determined irrespective of coal chemical structure and its transformation during metamorphism. They use the artificial coalification data, only without correlation with natural metamorphism.

At the same time the coal metamorphism as a process of "natural coalification of initial material" [7] becomes apparent in the change of coal elementary composition and shifts towards the formation of simple substances under the influence of natural factors [8].

In numerous publications [9-14] the effects of time and temperature are considered as alternatives and the majority of the authors directly or indirectly reduce metamorphism to the action of the only one factor, which is the temperature [15-17]. In [18] the works by J. Karweil [19], M. Levenshtein [20] and others are discussed, especially concerning the quantitative evaluation of time factor in metamorphism processes. They assert the incompleteness of the suggested methods, because deposit conditions and time cannot be considered separately.

M. Levenshtein [20] proved the increase of metamorphism degree with the increase of occurrence depth using coals of Donetsk coal basin as an example. This dependence is confirmed for other coal basins as well [21].

The research results concerning the formation of low-molecular compounds show that coalifaction of solid residue proceeds mainly due to the loss of oxygen-containing compounds. These data correlate with the data about elements content in the metamorphism solid residues. Hence, the coalification of the initial material takes place due to the decrease of oxygen weight [22, p. 14; 23, p. 331; 24].

There are attempts to implement and analyze coalification of the fuel organic mass [25]. The data of 6-year experiments are presented in this work. Brown coal was placed into soldered ampoules in nitrogen medium. The experiment started from 373 K. Such temperature practically excluded the presence of moisture and occluded gases in the samples. The temperature was gradually increased to 673 K by 1 K weekly. The obtained data were repeatedly used by various researchers for the analyses, *i.e.* for gassing analysis in metamorphism process [6].

2. Modern Conceptions of Coals Chemical Structure

Summarizing the experimental results of coal structure allows to consider the "molecule" of this substance as a set of various individual structures mainly of aromatic and aliphatic nature. They are connected with each other by the forces of different nature, value, and kind of the bond (covalent, donor-acceptor or hydrogen bonds, polyconjugatings owing to electrons delocalization, Van der Waals forces, *etc.*) [26-29].

The complexity of the coal chemical structure sets the direct relationship between the development of knowledge in this area and theoretical bases of chemistry and physics, and to even greater extent is dependent on the development of instrumental base for the implementation of physical and chemical investigation methods.

2.1. Investigation Methods

Today the fullest characteristics of the coal structure are obtained using X-ray analysis, electron microscopy, IR-spectroscopy, electron paramagnetic resonance, porometry, nuclear magnetic resonance, and wide spectrum of classical chemical and physico-chemical methods [30-32]. The combination of IR-spectroscopy and elemental analysis is used most often.

In a series of Oelert works (quoted from [33]) the parts of aromatic and aliphatic hydrogen and aromatic carbon were calculated on the basis of the mentioned methods. The nature of hydrogen and carbon distribution in various structures was determined for the coals with different metamorphism degree, as well as for the coal during its thermal decomposition. The formula for the calculation of aromatic hydrogen substitution degree was given. Further the Oelert formulae were applied and improved [33].

The increase of tooling and experimental facts extended the understanding of chemical structure of solid combustible fossils.

2.2. Hypothetic Models of Coal Structure

D. Van-Krewelen and Z. Shuer [31] together with V. Kasatochkin and N. Larina [34] show that organic coal substance is a totality of packs of condensed aromatic nuclei with side non-aromatic groups including oxygen, nitrogen, sulphur, and other hetero-atoms, which chemically bond the adjoined packs into three-dimensional polymer. Such approach suggests that during coalification the carbon-oxygen bonds are changed for the carbon-carbon ones in the side radicals [35].

In [36] the authors consider that it is necessary to divide "coal main components to: i) the components of aromatic nature, capable of melting; ii) high-molecular components of aromatic nature; iii) aliphatic and other volatile components…". This approach correlates with the "guest–host" theory of coal structure [37].

K. Medvedev [38] mentions a formula of coal "molecule" and assumes that micelles are formed from such molecules, so the change of coal physico-chemical properties with the increase of coalification degree results in the increase of degree of micelles consolidation. It should be noted that in [7] the same author has used the "molecule" formulae with the ratio between numbers of element atoms differing from elemental composition of the coal which is typical for many other papers.

It is suggested in [8] that the following processes compete in the course of metamorphism in the molecular structures of fossil fuels: alkyl radicals detachment from aromatics, interaction between two molecules with methane (alkane) formation and new chemical bond between their residues as well as cyclization of alkyl radicals with the formation of cycloalkyls, which are chemically bound with aromatic part of the molecules with further aromatic compounds formation.

The importance of the mentioned results is the creation and development of "non-regular polymer" conception which allows to present the coals structure by their average base units of different values and configurations, *i.e.* by aromatic, aliphatic, heterocyclic fragments, and typical bonds between them. Later on the conception was developed in [39, 40] as a "generalized structure model" of the coals.

Today the conception of two-component molecular structure, known as "guest-host" [37, 41], net structure [29, 42, 43], percolation lattice [44, 45], or two-phase model [26, 46, 47] is widely used. This conception originates from the studying of swelling and dilution of coal microcomponents in pyridine [48] and polar or non-polar solvents [49]. The obtained data were the basis for the development of structure model of coal organic mass

(COM) according to which it consists of molecular and macromolecular components. The considerable amount of cross-linkages forms the macromolecular component as the spatial net (matrix) in dimensional cells of which molecular "mobile" component of COM is located. Relatively small compounds of molecular component are connected with macromolecular net by electron-donor and electron-acceptor interactions (EDA).

The solvent replaces the COM molecular compound by solvent molecules which have higher donor or acceptor affinity with the centers of high or low π-electron density in the structure of macromolecular net. The presence of such centers is conditioned by the presence of heteroatoms (oxygen, nitrogen, sulfur), heteroatomic rings and condensed aromatic systems.

The "guest-host" model explains the relatively low values of activation energy of COM thermal destruction. It means that inside this model the mechanism of coal pyrolysis consists in overcoming of weak EDA-interactions between molecular and permolecular phases with the help of low energy consumption, in melting and evaporation of molecular phase as vapor gases (VG). The solid residue should be identified as COM macromolecular phase.

F. Derbyshire *et al.* [37] show that coal heating and high vacuum in the ionic source of mass-spectrometer considerably decrease the secondary reactions. Volatile products consist of molecular phase ions mainly and practically do not contain ions of macromolecular matrix. The following has been established:

- mobile protons content is 32 %, so 32 mas % of COM should be attributed to its molecular compound; it is agreed with V^{daf} value
- VG molecular mass is within the range from 80 to 800 atomic mass units (amu), however the main part of VG has molecular mass in the range from 230 to 430 amu
- volatile components are all homologous series of hydrocarbons from C_nH_{2n} to C_nH_{2n-28} (except C_nH_{2n-8}), compounds with one oxygen atom from $C_nH_{2n-2}O$ to $C_nH_{2n-28}O$ and compounds with two oxygen atoms from $C_nH_{2n-6}O_2$ to $C_nH_{2n-26}O_2$;
- compounds contain up to 5 aromatic rings and to 8 carbon atoms in alkyl substitutes of aromatic rings.

In [43, 44] authors try to present additional confirmation of the the COM two-phase structure. Using fluorescence microscopy for the coals with different metamorphism degrees F. Derbyshire *et al.* [37] show that the coals with $R_0 = 0.9$ have the maximum fluorescence intensity, which agrees with maximum fluidity by Giezeler and maximum yield of extract at coal dilution in chloroform.

N. Rus'yanova *et al.* [27, 50] consider that the basis of coal structure is a labile polyconjugate system mainly of non-aromatic character and stabilized by intermolecular interaction, whose strength and type is changed during metamorphism. Hydrogen bonds are typical of the coals with low metamorphism and EDA-interactions – for the coals with high metamorphism. Such structural model explains coal paramagnetism by electrons delocalization by polyconjugate system, EDA-interaction and the presence of "superunsaturated" fragments, *i.e.* carbon chains with alternate single and double bonds. The latter ones determine the coals high reactivity.

According to [51, 52], during metamorphism and pyrolysis, which differ by the rates but not by the character, the reconstruction of coal matter takes place resulting in the decrease of hydrogen bonds role and the increase of EDA-interaction role.

Within this theory there is an attempt to explain the minimum values of coal porosity and hardness at the middle stage of metamorphism, to connect the caking capacity with the changes in coal structures within the range from gas to lean coal and to answer the question, why supply of younger and older coals exceed supply of bituminous coals.

The conception of self-associated multimer formulated by A. Krichko [53] appeared practically along with the origin of "guest-host" and "self-conjugate structure" theories. Due to this conception COM consists of macromolecules of different chemical structure connected with multiplex bonds of non-valence character. EDA-interactions and hydrogen bonds which are considered as a particular case for EDA-interactions play the main role.

It is assumed that fragments of COM structure form the three-dimensional structure of self-associated multimer characterized by certain distribution of fragment sizes, as well as spatial and energy distribution of donor and acceptor centers. The presence of relatively unstable bonds is possible in the form of etheric and methylene bridges inside several base units [54].

The conception of self-associated multimer was further developed in [55-59]. According to [55] the loss of oxygen by the fuel during metamorphism and aromatization of solid residue decrease the role of heteroatoms and increase the role of the aromatic compounds. Their total contribution is described by the following equation:

$$\chi = \alpha \cdot f_0 + (1 - \alpha) \cdot f_a$$

where $f_0 = \frac{O}{C}$; $f_a = \frac{C_{arom}}{C}$

Dependences f_0 and f_a were found experimentally and value α was assumed as 0.5, *i.e.* specific contributions of heteroatoms and aromatics in the "self-associated factor" χ were equal.

S. Gagarin *et al.* [55] concluded from the above-mentioned equation that the conception of self-associated multimer satisfactorily explain the extremum of various physico-chemical properties of coals at C^{daf} equal to 85–86 mas %. However, it should be noted that "assumption" of another value α results in another estimation of C^{daf} value.

To our mind the conception formulated by G. Skripchenko [54, 60] coordinates with the mentioned theory. The original position of Skripchenko's conception is that aromatic nuclei in COM structure are spatially screened by cyclic non-aromatic fragments and end-groups. Therefore, during metamorphism the coal crosslinking proceeds as a process at which structures with small aromatic nuclei lose their three-dimensional peripheral hydrocarbon and oxygen-containing groups and become uniform and flat. Convergence and uniformity of aromatic structures increase EDA-interaction and form Van der Waals bonds. This process is accompanied by the destruction of macromolecules valence bonds. The expected variety of the formed products coordinates with the experimental results concerning coals extraction and coking under conditions excluding secondary pyrolysis [61-63].

Moreover, to our mind, the variety of individual products of high-temperature coking [64] is mainly the result of the initial structure destruction, but not the result of the following synthesis of new compounds from the reactive fragments [65, 66].

3. General Theses of Modern Theories about Coal Structure

In conclusion the general theses of the most essential conceptions concerning coal chemical structure should be stated:

1. During natural metamorphism, carbonization, forced coalification (pyrolysis), and dilution (extraction) COM changes from maximum variety of elemental composition toward minimum value.
2. Specific physico-chemical properties of coal at the middle stage of metamorphism are consequences of extremum change of coal composition and structure during such period.
3. During natural metamorphism (artificial carbonization) and pyrolysis the similar reactions proceed, but the process rates are different (the only objection is in [7]).
4. The "soft" influence on the system of coal structure primary elements bonds allows bringing chemical potential of coal to the maximum.

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ПРО СКЛАД І БУДОВУ ОРГАНІЧНОЇ МАСИ ВУГІЛЛЯ. АНАЛІТИЧНИЙ ОГЛЯД

Анотація. *Проаналізовано роботи, присвячені дослідженню закономірностей формування хімічної структури твердих палив. Сучасні уявлення про хімічну будову вугілля, що заглиблюються із зростанням інструментальної оснащеності та накопиченням фактичного матеріалу, розглянуто внаслідок критичного зіставлення різних гіпотетичних моделей "молекулярної" будови твердих палив. На цій основі сформульовано найбільш загальні положення відповідних теорій, згідно яким за допомогою "м'якої" дії на систему зв'язків первинних елементів структури вугілля можна максимально реалізувати його хімічний потенціал.*

Ключові слова: *метаморфізм, вугілля, хімічна будова.*