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THERMOCHEMICAL CONVERSION OF COAL UNDER MICROWAVE RADIATION

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Abstract. The paper presents diagrams of the organic mass structure of coal macromolecules. Investigations were carried out on the microwave treatment of Z grade coal. A mathematical model of microwave radiation effect on the structure of the macromolecule of low-metamorphosed coal was constructed. The effect of microwave treatment on thermochemical transformations of the coal organic mass using a scanning electron microscope was studied.

Keywords: coal macromolecule, chemical bonds, organic mass, high-frequency radiation, coal grains, thermo-chemical transformations.

1. Introduction

In the works [1, 2], an organic coal substance is represented as a collection of packets of condensed aromatic nucleus with side non-aromatic groups including oxygen, nitrogen, sulfur and other heteroatoms that chemically bind the neighboring packets to the spatial polymer. This view suggested that in the course of carbonization in lateral radicals, the carbon-oxygen bonds are replaced by carbon-carbon bonds [3].

F. Derbyshirc *et al.* [4] assumed that in the coals molecular structures in the course of metamorphism, the processes of alkyl radicals detachment from aromatics are competing. In this case, two molecules interact to form methane (alkane) and a new chemical bond between their residues. Further, the alkyl radicals are cyclized to form cycloalkyls and chemically bound to the aromatic part of the molecules, which are then converted to aromatic compounds.

The significance of the above mentioned works is the creation and development of the concept of an “irregular polymer”, which made it possible to represent the structure of coals by their average structural units of different size and configuration – aromatic, aliphatic, heterocyclic fragments and also characteristic bonds between them.

Modern ideas about the scheme of the structure of the organic mass of coal macromolecules are of a contradictory nature and are still very relevant topics for further research in this direction.

For example, Barsky and Vlasov [5] constructed model structures using hypothetical equations that characterize the thermochemical transformations of coals with regard to their metamorphism:

– at the initial moment:

$$[C_{27}H_{26}O_8 + C_{0.170}H_{0.340}O_{0.180}N_{0.690}S_{0.130}] \quad (1)$$

– during the formation of the equilibrium between oxygen and hydrogen:

$$[C_{22}H_{16}O + C_{0.026}H_{0.006}O_{0.002}N_{0.355}S_{0.125}] \quad (2)$$

Conditionally, the authors of [5] assume that transformation of (1) into (2) takes place when dehydration, decarboxylation, demethylation and dehydrogenation reactions occur. Thus it can be assumed that the relationship between the initial structure of the coal organic mass and the products of its thermochemical decomposition for the period before the onset of destruction can be described as a ratio in the form of a total reaction for the formation of hypothetically new substances:

$$[C_{27}H_{26}O_8+ C_{0.170}H_{0.340}O_{0.180}N_{0.690}S_{0.130}] = \\ = [C_{22}H_{16}O + C_{0.026}H_{0.006}O_{0.002}N_{0.355}S_{0.125}] + H_2O + \\ + 3CO_2 + 2CH_4 + [C_{0.144}H_{0.346}O_{0.182}N_{0.335}S_{0.005}] \quad (3)$$

If in integers of atoms, then the model substance of the organic mass of coal has the form:

$$C_{27}H_{26}O_8 = C_{22}H_{16}O + H_2O + 3CO_2 + 2CH_4 \quad (4)$$

The authors of the work, by hypothetical averaging of the “molecular” structures, established that the molecular weight of coal in accordance with the metamorphism varies from 498.89 to 247.00 a.u and the gross formulas will have the form (5-9):

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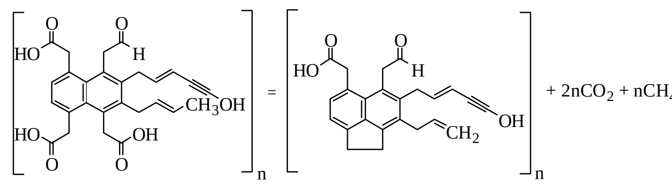
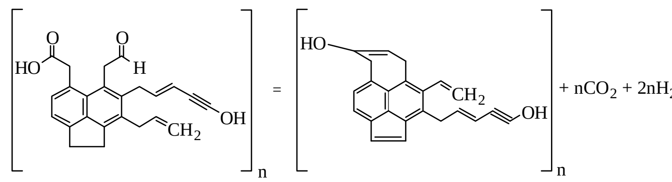


(5)



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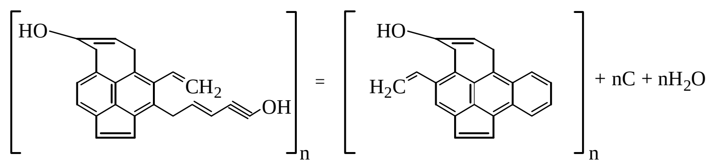

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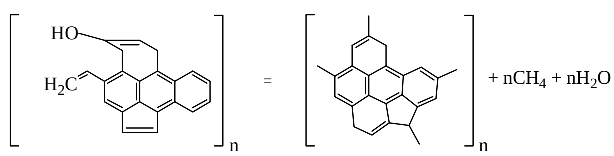

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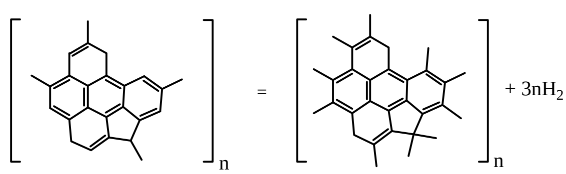


(9)

Table 1

Characteristics of the initial coal

Indicators of technical analysis, %			Plastometric indicators, mm		Petrographic composition, %					The average reflectance of vitrinite, %	Stage of vitrinite metamorphism, %				
Ash A^d, %	Sulfur S^d_t, %	Volatile matter V^{daf}, %	Contraction *x*	The thickness of the plastic layer *y*	*Vt*	*Sv*	*I*	*L*	∑OK	R^0	0.0.50–0.64	0.0.65–0.89	0.90–1.19	1.20–1.39	1.40–1.69
											The grade of coal, conditionally corresponds to the stages of vitrinite metamorphism				
											DG	G	Z	C	OC
7.5	0.85	31.3	29	15	86	–	11	3	11	1.02	–	15	77	8	–

This fact confirms: the difference of chemical structures that determines the coal organic mass and the processes of its natural and artificial metamorphism is the result of complex chemical-technological systems transformation.

Therefore the aim of this work was to study the effect of microwave irradiation on the coal thermo-chemical transformations.

2. Experimental

Investigations were carried out jointly with the employees of State Enterprise "Ukrainian State Research Institute of Coal Chemistry (UHIN)" using G grade coal withdrawn at central concentrator "Kalinina" (Ukraine). Its characteristics are given in Table 1. The dilatometric method of analysis and the scanning electron microscope (SEM) were used for the analysis.

The dilatation characteristics were studied at 743 K on the dilatometer apparatus.

Coal grain surface images were obtained using a scanning electron microscopy (SEM) on a Jeol JSM 840 scanning electron microscope. The image of the object under investigation was formed by scanning its surface focused to 5–10 nm in an electron beam.

Simulation of possible thermal decomposition products of coal was carried out using the Chem3D simulation program ChemOffice 2002.

At computational modeling we used the model with the smoothed thermophysical characteristics. The nonlinear equation of the heat balance of a single grain, taking into account the above assumptions, for the case of an axially symmetric temperature distribution, has the form:

$$c r(T)\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(l(T) r \frac{\partial T}{\partial r} \right) + W,$$

$$0 < r < r_0, \qquad 0 < t < \tau \qquad (10)$$

In Eq. (10), the left side of equation determines the change in the microwave radiation per unit volume of grain due to the temperature variation with time [6]. The right side of Eq. (10) reflects the diffusion transfer of internal thermal energy and the power function of the heat source. Also in the right side, the heating of the grain is taken into account due to the external irradiation of grain conductive heat exchange with ambient air and loss of thermal energy due to irradiation of the blackbody.

The coefficient of thermal conductivity depends on temperature and time, therefore we denote it by the variable $f(t, Tz)$. So,

$$l(T) = \frac{dTz}{dt} = f(t, Th), \; Tz(0) = z_0 \qquad (11)$$

After constructing the time grid, we write the time derivative as follows:

$$\left.\frac{dTz}{dt}\right|_{t=l+1} \approx \frac{Tz^{l+1} - Tz^{l}}{dt} \qquad (12)$$

In the simulation we use the following values of the parameters and physical constants: the grain diameter of the coal $6\cdot10^{-3}$ m; coefficient of thermal conductivity of air $7.5\cdot10^{-3}$ W/(m·K); specific heat capacity 1.09 kJ/(K·kg); density 1400 kg/m^3; initial temperature of coal grains 293 K; power 750 W; wave length 12.25 m; frequency 2450 MHz; coefficient of thermal conductivity of coal 0.2 W/m·K [7].

3. Results and Discussion

Based on the developed theory of Barsky and Vlasov [5] and using the simulation program, we modeled possible products of coal thermal decomposition and substances formed as a result of their decomposition (Table 2).

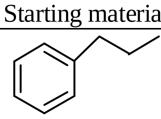
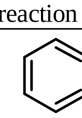
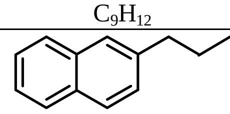
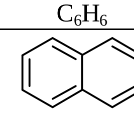
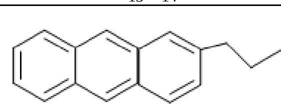
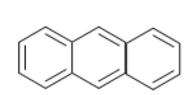
The simulation results show that under microwave radiation of coal the overwhelming content of complex aromatic compounds is possible in the vapor-gas phase (Fig. 1).

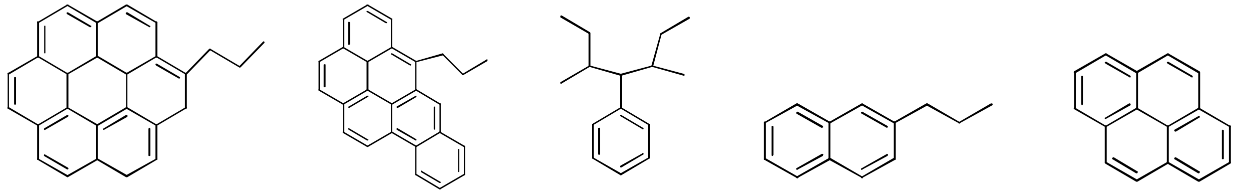
A. Starovoit *et al.* [8], when studying the formation of the structure of coke from coal, established that aromatic hydrocarbons play an important role in the process of association during the formation of carbides, carbenes, asphaltenes and maltens. Similar phenomena occur in coal-bearing peaks, which are a model substance, which illustrates the thermal transformations of such compounds [9].

As a result of such a process, pyrogenetic transformation of the coal organic mass occurs in each grain of coal and through the process of primary pyrolysis the solid, liquid and gaseous phases are formed. The latter is volatile aromatic hydrocarbons, which are the main constituents of the primary coal tar and create pressure on the inner surface of the coal grains.

Table 2

The variants of benzene, naphthalene and anthracene formation

Starting material	The reaction product
 C_9H_{12}	 C_6H_6
 $C_{13}H_{14}$	 $C_{10}H_8$
 $C_{17}H_{16}$	 $C_{14}H_{10}$



$C_{27}H_{24}$ $C_{26}H_{20}$ $C_{15}H_{24}$ $C_{13}H_{14}$ $C_{16}H_{10}$

Fig. 1. Model products of thermochemical transformations of the initial coal structure in the temperature range of 533–683 K

To confirm the expressed concept, a mathematical model of microwave radiation effect on coal grains was created. Transfer of the obtained knowledge from the model to the original and experimental verification will make it possible to clearly determine the conditions for conducting and influencing the microwave radiation. It is assumed that the coal grain has the shape of a sphere with radius *r*, which at the initial moment of time is in the microwave field with the intensity of the wave *I*. The kinetics of the grain behavior in the microwave beam depends on the initial temperature, the aggregate state, the thermophysical properties of the coal and parameters of microwave radiation.

The energy absorption by the coal grains occurs in such a way that it is spent on heating and melting, minus heat losses for thermal conductivity and thermal radiation. The internal pressure of heat generation source is proportional to the absorption of microwave radiation, which can be characterized by Bouguer's law [10].

To solve the mathematical description of the model, we used the Runge-Kutta method of the second order and determined the temperature of coal grains. The change in the coal grain temperature during microwave irradiation under given initial conditions is shown in Fig. 2.

Simulations have shown that the coal grains are capable to be heated to the maximum temperature close to 773 K.

For experimental verification of this phenomenon, we studied the effect of microwave irradiation on grains of G grade coal in the temperature range of 723–823 K. Fig. 3 depicts the initial coal from the central concentrator "Kalinina". At high temperatures of 723–773 K (Fig. 4) the grain of the investigated coal forms a plastic mass. Due to the complex of reactions proceeding with the breakdown of carbon bonds and under partial pressure, this mass causes the formation of a foam-like structure. When studying dilatation, we observed a straight line with a zero result of all indices, which characterizes the process of formation of char.

Thus, the presence of the side radicals weakly bound with the condensed aromatic nucleus in the coal macromolecule affects the polarization and, accordingly, the release of heat. Under the influence of the electromagnetic field, heat energy is released, due to which such aromatic complexes overcome the conventional distance and oscillations with certain amplitude. In this connection, the components of the coal organic mass are rearranged with the release of volatile products of coal tar and partial organic synthesis or "low" hydrogenation. Heating coal over 823 K leads to a decrease in thermochemical properties, and the structure becomes similar to a semi-coke with a large number of pores of 30–100 μm.

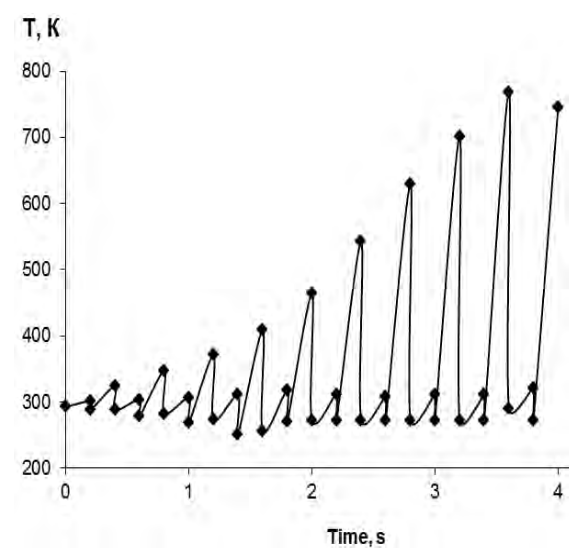


Fig. 2. Temperature of coal grain at microwave radiation

4. Conclusions

On the basis of the data obtained, it can be concluded that the destruction of coal grains allows to achieve deeper intramolecular changes in the coal organic mass due to the polarization process, which contributes to the generation of vibrational, pulsating and rotational motion in electric dipoles, charges and electrons, which in turn causes the release of thermal energy. Under microwave radiation with the passage of the polarization process, the grain is heated to 773 K, which causes the formation of a plastic mass inside the coal grain. Such a technological approach can be used in the thermal preparation of coal and coal charge before the coking process.

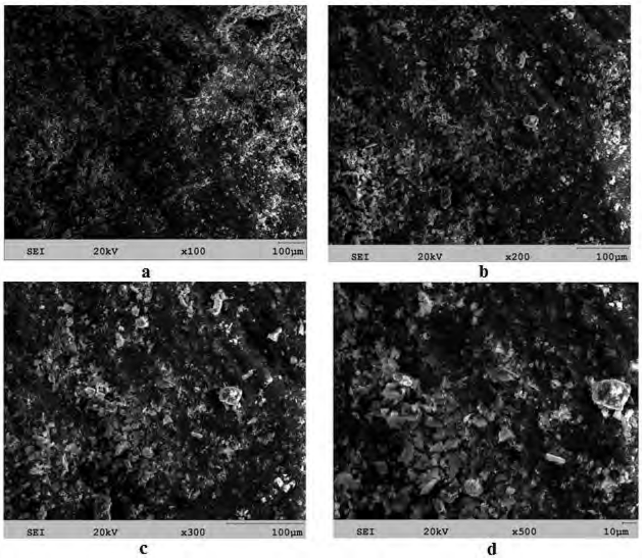


Fig. 3. Images of the surface of the initial Z grade coal. Magnification of: 100× (a); 200× (b); 300× (c) and 400× (d)

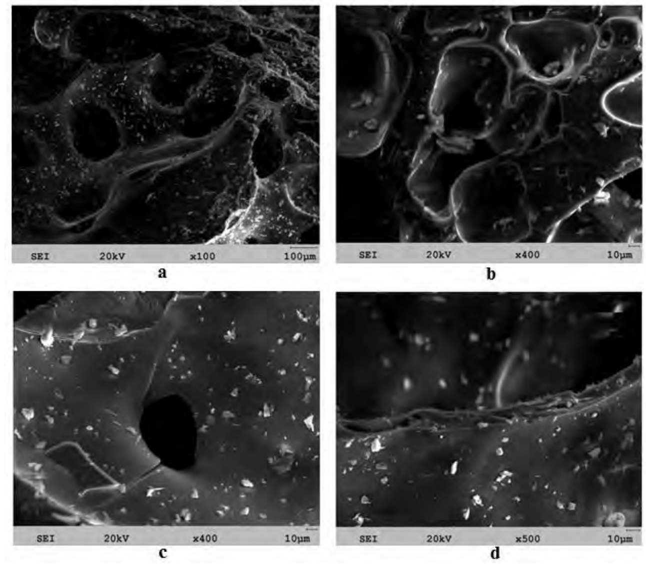


Fig. 4. Images of the surface of Z grade coal treated under microwave radiation.
Magnification of: 100× (a); 200× (b); 400× (c) and 500× (d)

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ТЕРМОХІМІЧНІ ПЕРЕТВОРЕННЯ КАМ'ЯНОГО ВУГІЛЛЯ

Анотація. *Приведені схеми структури органічної маси вугільних макромолекул. Проведено дослідження мікрохвильового оброблення вугілля марки Ж. Побудовано математичну модель впливу мікрохвильового випромінювання на структуру вугільної макромолекули середньометаморфізованого вугілля. Вивчено вплив мікрохвильового оброблення на термохімічні перетворення органічної маси вугілля з використанням скануючого електронного мікроскопу.*

Ключові слова: *макромолекула вугілля, хімічні зв'язки, органічна маса, мікрохвильове оброблення, вугільне зерно, термохімічні перетворення.*