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COMPOSITION AND STRUCTURE OF COAL ORGANIC MASS. 2. KINETIC MODELS OF METAMORPHISM

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Abstract. Regularities of changes in solid fuel elemental composition during metamorphism have been investigated. A mathematical model describing these regularities as functions of C^{daf} has been developed. Experimental data of artificial coalification confirm that it is an experimental model of natural metamorphism.

Keywords: metamorphism, coal, chemical structure.

1. Introduction

In accordance with the existing conceptions [1], during natural coalification, which generates fuel chemical potential, gaseous and liquid products of metamorphism leave the "reaction zone", which is followed by the decrease of fixed residue mass and alteration of its elemental composition (mass contents of carbon (q_C), hydrogen (q_H), oxygen (q_O), nitrogen (q_N), and sulphur (q_S)) as a result of different reactions rates of the mentioned elements.

In search of the metamorphism general regularities two hypotheses regarding its motive force are considered separately:

1. In any area the main factor forming variety of the coals chemical composition, structure and properties is the time from the beginning of "geological history" of maternal vegetable residues.

2. At any stage of "geological age" even in close areas the coals of different "chemical age" may be formed owing to different intensity of natural effects, primarily temperature and pressure.

The analysis of numerous theories concerning coal-formation and fuels metamorphism, as well as of experimental results directly or indirectly characterizing the coals composition, structure and properties testifies to the validity of both theories. The first one asserts the natural process of fossil fuels transformation towards their coalification, while the second one corresponds to the statistic background beside this regularity reflecting the real

variety of maternal vegetable residues, conditions of their depositing and decomposition, temperatures and pressures, and oxidative or reducing character of medium in different areas. Since the latter practically cannot be identified with the lapse of time, the qualitative description of metamorphism is carried out by the establishment of temporary regular changes in the elemental composition against a background of its "incidental" though causal variability (caused by the varying conditions of coals occurrence).

2. Experimental

In the analysis of the dependence between carbon content in the solid fuel and its occurrence depth the data given in [2, Table 1] were used.

To estimate the parameters of metamorphism model of solid fuel, determined by the change of its elementary composition, the testing results of the coals of all metamorphism stages from Donetsk, Kuznetsk, Karaganda, and Pechorsk basins were used. These data are represented in Fig. 1 as dependencies of hydrogen, oxygen, nitrogen, and sulphur mass contents upon carbon mass content.

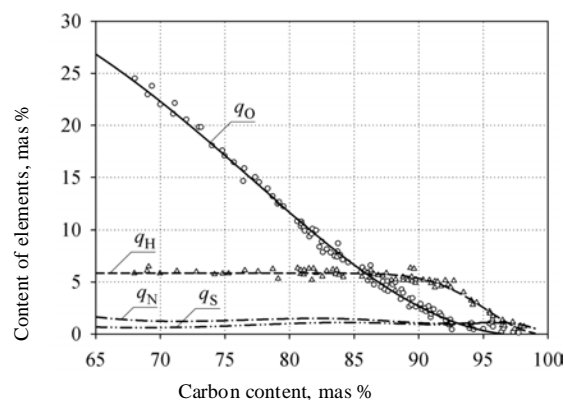


Fig. 1. Dependence of hydrogen, oxygen, nitrogen, and sulphur contents in fuel upon carbon content

Within the ambit of “external addition” principle [3] the obtained model was tested using the data unused earlier: results of brown coal investigations (smut, dull and bright coals) [4] and H, G and K types coals investigations [5].

As a source of the facts for kinetic investigations the

data of artificial coalification as an experimental model of natural metamorphism were used. The process is described in [1] and the experimental results are represented in Table 1.

The data from Table 1, like in [2], are bound to the scale of maximum paleosinking (according to Levenstein).

Table 1

Reflectance, mass loss and elemental composition during brown coal coalification

Occurrence depth, km	R_0 , %	Conversion of coal organic matter, %	C	H	N	S	O
0.10	0.28	0.0	65.6	4.83	0.60	0.41	28.56
0.15	0.31	3.6	65.9	4.76	0.71	0.30	28.33
0.49	0.47	11.8	69.3	4.69	0.69	0.20	25.12
1.48	0.59	21.7	75.0	5.00	0.79	0.52	18.69
2.90	1.00	33.9	83.2	4.86	0.91	0.41	10.62
4.25	1.89	42.0	90.7	3.75	1.01	1.34	3.20
4.60	2.73	45.0	92.9	2.96	0.83	1.03	2.28

3. Results and Discussion

3.1. Fuel Elemental Composition and Regularities of Natural Metamorphism

To describe the metamorphism rate for carbon it is considered that at the time when solid deposit is identified as carbided material, the effect of natural conditions is considerably weakened by the increased degree of isolation from environment due to the increase of occurrence depth. Taking into consideration that carbon as a component of “reaction system” represents itself in an excess amount, metamorphism rate is considered to be equal to the rate of zero-order reaction:

$$\frac{dq_C}{dt} = K_C \quad (1)$$

On the assumption of the fact that degree of metamorphism developing with time increases with the increase of occurrence depth [2, 3] and taking into consideration its connection with metamorphism features, Eq. (1) is represented as follows:

$$\frac{dq_C}{dH_l} = \hat{K}_C \quad (2)$$

The integration of Eq. (2) gives:

$$q_C = (q_C^0 - \hat{K}_C \cdot H_l^0) + \hat{K}_C \cdot H_l \quad (3)$$

where q_C^0 , q_C , H_l^0 and H_l – are initial and current values of carbon content in the coal (mass parts) and occurrence depths (km), respectively.

In accordance with the data [2] it was found that $(q_i^0 - \hat{K}_C \cdot H_l^0) \cdot 100 = 67,17 \text{ mas \%}$; $\hat{K}_C = 5.53 \text{ mas \% / km}$ and

the diagram was plotted (Fig. 2) showing the accordance between Eq. (3) and the used data, confirming the validity of (1).

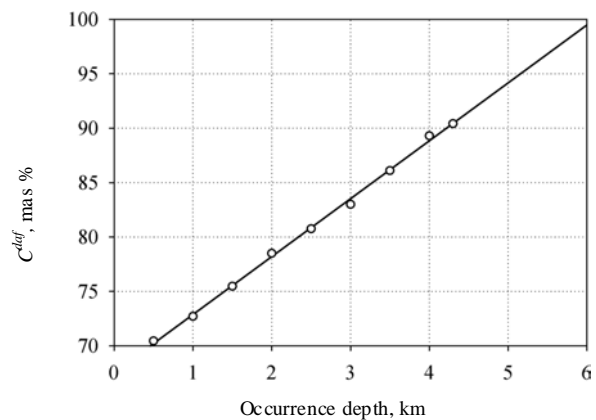


Fig. 2. Dependence between carbon content in coal and its occurrence depth.

Describing the metamorphism rate for oxygen we assumed the primary role of its mass in the mass of elements leaving the “reaction area”. The general direction of metamorphism due to the paramount rate of oxygen mass loss is determined by less stability of oxygen-containing compounds in aliphatic row compared to that of oxyaromatic compounds; hence the decomposition of the first ones anticipates the decomposition of the second ones increasing the carbon content in the residue. Under natural conditions the heat effects of decomposition reactions of oxygen-containing aliphatic and heterocyclic compounds, as well as aromatics cyclization with the participation (for example by B. Rakovsky) of coumarone have different

signs. That is why only time can give the general direction of coalification process in the conditions of opposite effects to the temperature action. Therefore, the oxygen loss rate during metamorphism is represented as a value proportional to its residue and a certain function of carbon mass content:

$$-\frac{dq_O}{dt} = K_O(\hat{q}_O - q_O) \cdot f_O(100 - q_C) \quad (4)$$

where \hat{q}_O – extreme mass content of oxygen in the fuel, %.

Describing the kinetics of hydrogen mass loss during metamorphism the following factors were taken into consideration:

1. Evaluation of the ratio between aromatic and aliphatic compounds amount (using IR-spectroscopy) as decomposition products of plastic mass in centrifugal field and initial coals indicates the absolute predominance of aliphatic structures [5, 6].

2. In aromatic structures the C–C bond is stronger than C–H bond; in aliphatic structures C–C bond is weaker than C–H bond.

3. The mass content of hydrogen is small compared to that of carbon and oxygen.

All the mentioned facts determine the low rate of hydrogen mass loss at earlier stages (from peat to young coals inclusive). Only after achieving close contents of oxygen and hydrogen (time interval corresponding to the middle-age coals) the hydrogen content begins to decrease. Later on the sharp decrease of hydrogen content obviously takes place due to the detachment of aromatic nucleus hydrogen determining the coalification intensity at the final stages of metamorphism. From this point the equation having the same structure as Eq. (4) was used to describe the metamorphism kinetics for hydrogen mass content:

$$-\frac{dq_H}{dt} = K_H(\hat{q}_H - q_H) \cdot f_H(100 - q_C) \quad (5)$$

In view of impossibility of quantitative identification of fuel elemental composition in time the latter was excluded from Eqs. (3), (4) and (5) by division of the second and third equation by the first one.

The obtained expressions after transformation and integration were supplemented by the functions q_S and q_N of q_C [10] and constituted a mathematical model of metamorphism determined by the changes in fuel elemental composition in the conditions of its natural occurrence.

$$q_O = \hat{q}_O \left[1 - e^{-\frac{K_O}{K_C} \cdot F_O(100 - q_C)} \right] \quad (6)$$

$$q_H = \hat{q}_H \left[1 - e^{-\frac{K_H}{K_C} \cdot F_H(100 - q_C)} \right] \quad (7)$$

$$q_S = q_N \left[a + b(100 - q_C) \right] \quad (8)$$

$$q_N = \frac{100 - q_C - q_H - q_O}{(1 + a) + b(100 - q_C)} \quad (9)$$

Using experimental results of all coals from Donetsk, Kuznetsk, Karaganda, and Pechorsk basins it was found for hydrogen: $\hat{q}_H = 5,85$, $b_0^H = -1778 \cdot 10^{-5}$ and $b_1^H = 5236 \cdot 10^{-5}$; for oxygen $\hat{q}_O = 38$, $b_0^O = -3847 \cdot 10^{-6}$ and $b_1^O = 2221 \cdot 10^{-6}$; and for nitrogen and sulphur $a = 1.0520$ and $b = -0.0184$.

The obtained model of metamorphism is stable and adequately describes not only experimental data used for calculation of numerical values of b_0^H , b_1^H , b_0^O , b_1^O , a and b (“internal” adequacy) but previously unused results (principle of “external addition”).

Moreover, calculating the oxygen content as the most changeable parameter during metamorphism, the dependence between calculated and actual values taken from different sources was drawn (Fig. 3).

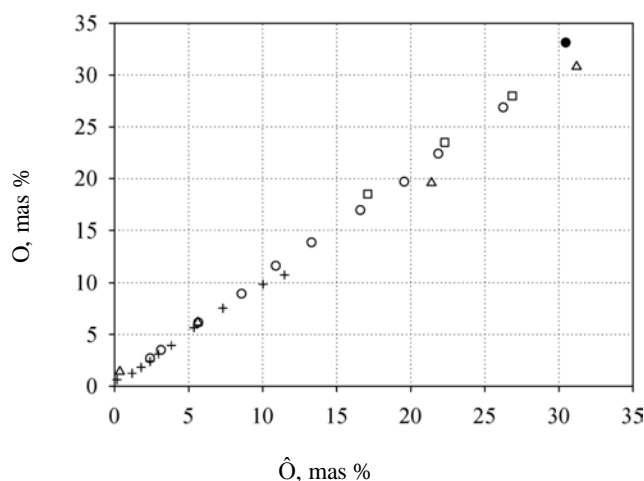


Fig. 3. Dependence between calculated and actual content of oxygen in the coals according to the data: ○ – [4, Table 1]; × – [11, Table 1]; Δ – [11, Table 3]; ● – peat [12]; □ – brown coals [4].

The given results confirm the general character and prognostic capabilities of the obtained equations.

3.2. Artificial Coalification as an Experimental Model of Metamorphism

We tried to create a model of metamorphism kinetics using time factor. The following requirements for the mathematical model of metamorphism temporary regularities were formulated:

1. The model structure must be sufficiently general with respect to different properties of fuel, whose change is used as metamorphism feature.

The model must contain:

2. Temperature-time factor t as a motive force of energy exchange between investigated object and environment.

3. Parameter of thermochemical stability E of investigated object (fuel substance) as an analog of energy barrier (activation energy).

4. Real motive force of metamorphism as a difference between achieved (y) and extreme values raised to some power n , which determines the dependence of the process rate upon the number of particles (molecules) which interact during synthesis or are formed during destruction.

5. Parameter K_0 describing the average action level of unaccounted properties of the investigated object and environment and acting as a scalable factor at the same time.

6. The model must reflect the opposite simultaneous effect of the temperature-time factor increase and the real motive force decrease on the metamorphism rate. Fulfilling of this condition results in the appearance of extremum at metamorphism rate curve while corresponding integral curve asymptotically verges toward extreme value.

As an expression satisfying all the mentioned requirements the Eq. (10) was suggested. In many respects it is similar to the main equation of formal kinetics.

$$-\frac{dy}{dt} = K_0 \cdot e^{-\frac{E}{t}} (\hat{y} - y)^n \quad (10)$$

To describe the coalification kinetics the concept of conditional time t was introduced. This value determines the value of temperature-time factor in accordance with the expression (11):

$$t = 8.314 \cdot (373 + 50t) \quad (11)$$

Conditional character of time means the ability to choose its measurement units depending upon coalification duration: at the laboratory plants – minutes, at the commercial plants – hours, during artificial coalification – years, and during natural metamorphism – millions of years.

The following values of Eq. (10) parameters were found:

– by the change in solid residue yield $G_o(0) = 51.05$, $E_g = 39460$, $K_{0g} = 137.8$, $n_g = 2$, $S_g = 1.44$ with $f = 3$;

– by the change in carbon content $C_c(0) = 100$, $E_c = 39900$, $K_{0c} = 114$, $n_c = 2$, $S_c = 0.96$ with $f = 3$;

– by the change in vitrinite reflectance $E_R = 39900$, $K_{0R} = 114$, $n_R = 2$, $R_0(0) = 0.28$, $S_{R_0} = 0.0426$ with $f = 4$.

The corresponding curves are represented in Fig. 4.

One can see from Fig. 4 that the mass loss rate or change in solid residue yield (which is the same) is described by the curve with a maximum of

$r_{\max} = 13.289$ %/year achieved at the 3rd year of coalification ($t_{\max} = 2.93$). The carbon content in the coalification solid residue growth curve also has a maximum of $r_{\max} = 7.974$ %/year achieved at $t_{\max} = 3.61$.

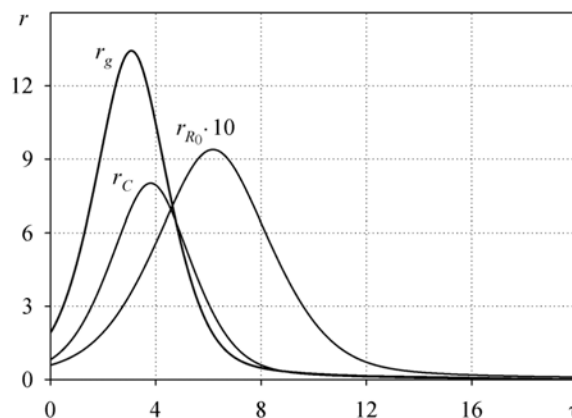


Fig. 4. Rates: r_g – loss mass; r_c – changes in carbon content in the solid residue; r_{R_0} – changes in vitrinite reflectance.

The plot of vitrinite reflectance variations rate with time during coalification also has a maximum equalled to 0.939 achieved in 6 years. It means that solid residue physical properties forming the value R_0 are changed with increasing rate during the whole main period of coalification, right up to the anthracite stage, which makes this value different from the other.

3.3. Structural-Chemical Transformations during Metamorphism

Using the equation obtained for the description of the carbon content changes in the solid residue of artificial coalification, the conditional time t was introduced into the model of natural metamorphism and the curves represented in Fig. 5 were calculated.

Oxygen is the main “active element” during coalification (when estimation according to the dynamics of elements mass parts is made).

Let us note that at the time axis, within the relatively narrow area close to t , at which mass parts of oxygen and nitrogen are equal, the majority of black coals and all well-baking coals are situated. This fact is the most important sign of structural-chemical transformations leading to the appearance of new quality – fuel ability to plasticize and cake. To estimate the combined character of the main elements mass content changes with time the following parameter was introduced:

$$a(t) = \frac{q_o(t) - q_H(t)}{q_c(t)} \cdot 100 \text{ mas \%} \quad (12)$$

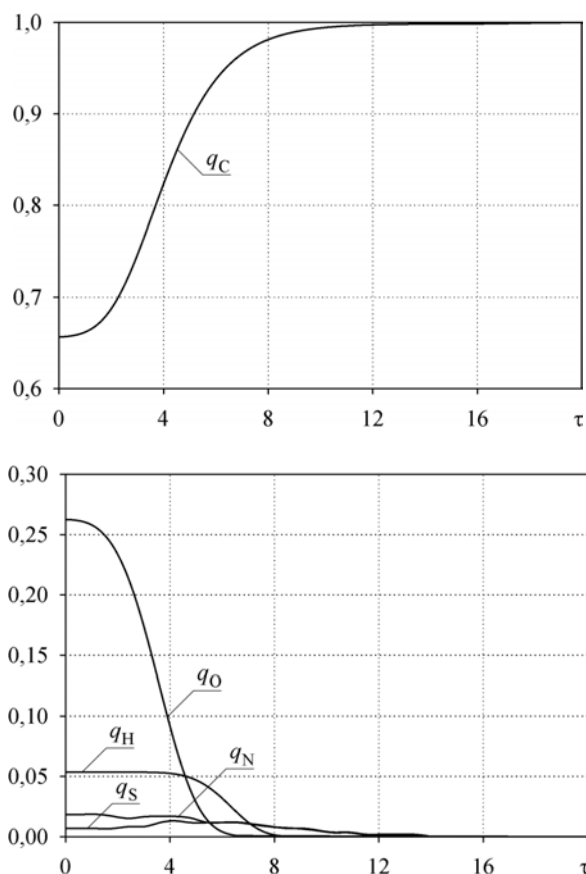


Fig. 5. Changes in carbon, hydrogen, oxygen, nitrogen, and sulphur contents in the solid residue.

The analysis of the mentioned parameter shows the following:

1. At some moment t_1 (Fig. 6), when $q_O(t) = q_H(t)$, $a(t)$ reduces to zero, thus at $t < t_1$ $a(t) > 0$ and at $t > t_1$ $a(t) \leq 0$.

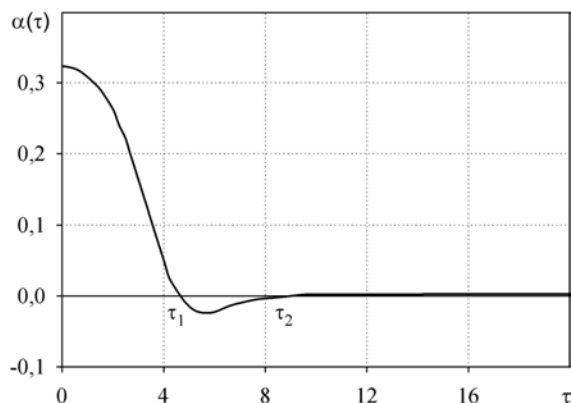


Fig. 6. Changes in α -parameter character during coalification.

2. The curve described by Eq. (12) may return from the area of negative values to zero at the moment t_2

corresponding to the full loss of oxygen and nitrogen by the fuel, i.e. at $q_O(t_2) = q_H(t_2) = 0$. Logically, the moment t_2 is the end of coalification (metamorphism): the following effect of temperature-time factor may cause only physical processes of structure ordering in the solid residue.

3. Till the moment t_1 some averaged unit of fuel chemical structure (“molecule”) has 16 hydrogen atoms for every oxygen atom.

The number of atoms in the coal “molecule” containing N_{10} carbon atoms was calculated in accordance with the formula:

$$N_i(t) = \frac{N_C(0) \cdot M_C}{q_C(0)} \cdot q_{s.r.}(t) \cdot \frac{q_i(t)}{M_i} \quad (13)$$

Using elements atomic masses M_i (amu) and taking as an example the coal “molecule” containing $N_{10} = 100$ carbon atoms, the curves of artificial coalification were calculated. They are represented in Fig. 7.

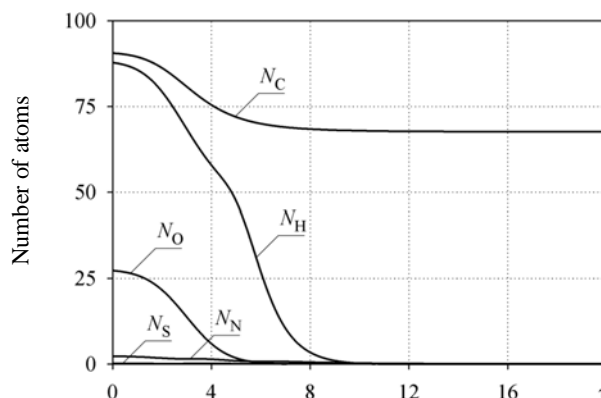


Fig. 7. Change in number of chemical elements in the coal “molecule” containing 100 carbon atoms.

In atomic expression the rate of hydrogen loss either exceeds or is equal to the rate of oxygen loss till $t \cong 5$. Here the oxygen content in the solid residue becomes practically exhausted. After this the rate of hydrogen loss increases sharply.

It was found that the condition $N_H/N_O = 16$ (or $a = 0$) is met at $t = 4.51$, when the solid residue transforms to the composition $q_C(t_1) = 0.866$; $q_H(t_1) = 0.052$; $q_O(t_1) = 0.052$; $q_N(t_1) = 0.016$ and $q_S(t_1) = 0.014$. If $N_C(0) = 27.170$ then the following number of atoms in the solid residue “molecule” will correspond to this mass composition at $t_1 = 4.51$: $N_C(t_1) = 22.026$; $N_H(t_1) = 15.994$; $N_O(t_1) = 0.998$; $N_N(t_1) = 0.355$ and $N_S(t_1) = 0.125$.

The number of atoms in the brown coal “molecule” ($\tau = 0$) is: $N_C(0) = 27.170$; $N_H(0) = 26.34$; $N_O(0) = 8.18$; $N_N(0) = 0.69$ and $N_S(0) = 0.13$.

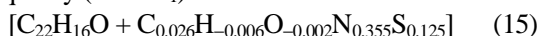
Using all the mentioned data the following formulas may be assigned to the hypothetically averaged

“molecular” structures of the fuel solid component (with a division into integer and fractional numbers):

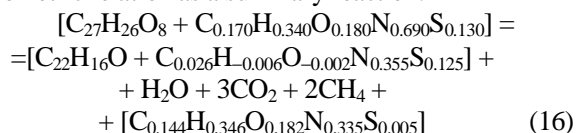
– at the beginning of coalification (at $t = 0$)



– at the moment of hydrogen and oxygen mass contents equality (at $t = t_1$)



If now we suggest that transformation of (14) into (15) takes place during dehydration, decarboxylation, demethylation, and dehydrogenation then the connection between the initial fuel and coalification products for the period from t_0 to t_1 may be described by strict stoichiometric relation as a summary reaction:



In integer numbers the Eq. (16) takes the form of Eq. (17):



The coalification curve expressed by means of “molecular” mass (for 27.17 carbon atoms at the moment t_0) is represented in Fig. 8.

One can see that the mass decreases twice from 498 to 247 amu during the transformation from initial state to the end of coalification. The “molecular” mass of substance described by Eq. (15) is ~306 amu.

It is necessary to note the agreement between experimental data concerning elementary chemical structures and their molecular masses, which are given in [1] in the discussion of the “guest-master” model, as well as peculiarities of metamorphism interval near $R_0 = 0.9$ with the results of our model of artificial coalification. Thus, at $n = 22$ the $C_nH_{2n-28}O$ coincides with theoretically averaged

structure $C_{22}H_{16}O$ of the coal with $R_0 = 0.9$, characterized by equal mass contents of hydrogen and oxygen. The essential fact is that molecular mass of the mentioned compound is 305 amu. The value is practically in the centre of the molecular masses range of the compounds which are the main part of organic matter “molecular phase” (“guest”).

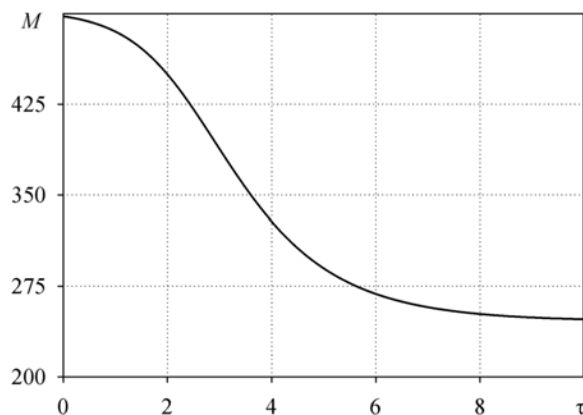


Fig. 8. Coalification kinetics according to the fuel “molecular” mass

In addition, the estimation of “molecular phase” content in the coals agrees with the yield of gaseous and free-running products of pyrolysis in centrifugal field and the data about the content of aromatic and aliphatic hydrocarbons – with their ratio by the results of IR-spectroscopy for initial coals and free-running products [12].

Denoting the expressions with fractional number of atoms in square brackets (Eq. (16) as I, II and III respectively, we made a material balance of artificial coalification for the period t_0-t_1 represented in Table 2.

Table 2

Material balance of artificial coalification

Income			Consumption				
Compound	amu	mas %	Compound	amu	mas %	mas %	according to [11]
$C_{27}H_{28}O_8$	479.000	96.1693	$C_{22}H_{16}O$	297.000	59.6290		
I	19.080	3.8307	II	9.244	1.8559	2.57	1.036
			H_2O	18.000	3.6139	9.38	3.787
			CO_2	132.000	26.5018	68.81	27.779
			CH_4	32.000	6.4247	16.68	6.734
			III	9.836	1.9747	2.57	1.036
Total:	498.080	100.0000	Total:	498.080	100.0000	100.00	40.372

Note: We normalized the last column with an assumption that metamorphism solid residue was also 59.629 mas % [11].

In the next to last column of Table 2 brown coal conversion products composition is given. According to Eq. (16) water and gases are formed at its coalification. Comparison of these values with the results from [11] concerning Donetsk basin coals shows their agreement in spite of different investigation methods and initial data [3].

4. Conclusions

The artificial coalification may be considered as an experimental model of natural metamorphism. Concerning the theory of oil formation given in [11], it is necessary to admit that stoichiometry of Eq. (17) and the data from Table 2 reserve only balance items II and III for the formation of oil as brown coal metamorphism product.

Natural solid fuel consists of the variety of different “molecular” structures (whose averaged models are compounds (14) and (15)). They determine the chemical potential of solid fuels, which sequentially decreases with the increase of coalification (metamorphism) depth.

At the axis of natural metamorphism the coking coals are concentrated near the point at which H/O ratio is equal to 16.

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ПРО СКЛАД І БУДОВУ ОРГАНІЧНОЇ МАСИ ВУГІЛЛЯ. 2. ПРО КІНЕТИЧНІ МОДЕЛІ МЕТАМОРФІЗМУ

Анотація. Досліджено закономірності зміни в ході метаморфізму елементного складу твердого палива та побудовано математичну модель, що описує ці закономірності як функції від C^{daf} . За допомогою експериментальних даних штучної вуглефікації показано, що вона є експериментальною моделлю природного метаморфізму.

Ключові слова: метаморфізм, вугілля, хімічна будова.