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COMPOSITION AND STRUCTURE  
OF COAL ORGANIC MASS.  
3. DINAMICS OF COAL CHEMICAL  
STRUCTURE DURING METAMORPHISM

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*Received: January 28, 2011 / Revised: March 15, 2011 / Accepted: May 26, 2011*

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**Abstract.** Dynamics of coal chemical structure during metamorphism has been evaluated using mathematical model of metamorphism kinetics attached to the time axis in accordance with artificial coalification data.

**Keywords:** metamorphism, coal, chemical structure.

## 1. Introduction

The result of generalization of actual facts and theoretical positions concerning modern conceptions of solid fuels chemical structure is that peculiarities of carbon physico-chemical properties of various geologic age are considered as one of the major criteria of their objectivity.

Thus in the polyconjunction theory [1], where the ratio between its implementers is the main element (hydrogen bonds in younger coals and EDA-interaction in old coals), three "jumps" in the coal properties are emphasized.

The first "jump" is a caking capacity which takes place during LF→G transition (from long-flame coal to gas coal). The amount of carbonyl groups essentially decreases, and consequently the hydrogen bonds strength that ensures the high strength and porosity for young coals decreases too.

The second "jump" is achieving of maximum caking and solubility. It takes place during G→F transition (from gas coal to fat coal). The polyconjunction system is developing toward declining in hydrogen bonds and increasing in donor-acceptor interaction. It weakens interactions between macromolecules, decreases coals porosity and strength, create "liquid-like" structure.

The third "jump" is disappearance of caking and ability to transfer into soluble state. It takes place during C→LB→L transition (coke coal→lean-baking coal→lean coal). The extensive polyconjunction system is formed and strong C–C bonds appear between macromolecules. The coal strength and porosity increase.

In the theory of self-associated multimer [2] the ratio between EDA-interactions is the main one. These interactions are stimulated by heteroatoms (mainly by oxygen atoms) in young coals and byaromatic fragments in old coals. Using "self-association factor"  $c$  [3] the mentioned second "jump" is found as a proof of identity of developing conception.

However, to our opinion, more grounded approach exists to explain the mentioned peculiarities of physico-chemical properties of solid fuel. It has to include the average but practically observed kinetics, stoichiometry and material balance of metamorphism. Moreover, the indispensable condition must be preservation of equality between a form (structure and strength of bonds between atoms) and a content (fuel elemental structure).

We used such approach to detect the "jumps" of physico-chemical properties of solid fuel and realized it by means of mathematical model definition and analysis of artificial coalification kinetics [4].

## 2. Experimental

To ascertain parameters of kinetic models and "special" points detected by means of the model, we carried out experiments with all types of coal using standard procedure. The results are represented in Tables 1-3.

Table 1

## Petrographic and elemental composition of investigated objects

Investigation object	Rank of coal by DSTU 3472-96	Average value of vitrinite reflectance, $R_0$ , %	Petrographic composition (without mineral additives), %					Sum of mineral fillers, $\Sigma MF$ , %	Elemental composition (dry ashless state), %					$\alpha^1$ , mas %
			$V_t$	$S_V$	$I$	$L$	$V_t+L$		$C^{daf}$	$H^{daf}$	$N^{daf}$	$O_d^{daf}$	$S_t^d$	
Alexandrine deposit	B <sup>2</sup>	0.25	95	0	3	2	97	3	70.3	6.0	0.5	19.0	4.2	18.4
Trudovska mine	LF	0.52	87	0	8	5	92	8	78.6	5.4	1.6	12.8	1.6	9.4
Kurakhovska mine	LFG	0.57	81	0	11	8	89	11	81.8	5.9	1.3	10.2	0.8	5.25
Dopropolska concentrating mill	G	0.77	84	0	13	3	87	13	83.0	5.5	1.6	7.7	2.2	2.6
Proletarska concentrating mill	F	1.05	91	1	7	1	92	8	86.6	5.4	1.6	4.0	2.4	-1.6
Kolosnikovska concentrating mill	C	1.28	92	1	7	0	92	8	88.5	5.0	1.6	2.9	2.0	-2.3
Kolosnikovska concentrating mill	LB	1.44	90	0	10	0	90	10	89.1	4.9	1.6	2.6	1.8	-2.5
Mospinska mine	L	1.85	82	2	16	0	82	18	91.5	4.4	1.5	1.9	0.7	-2.7
Komendantska concentrating mill	A <sup>3</sup>	5.03	93	0	7	0	93	7	95.4	1.5	0.7	0.8	1.6	-0.7

Notes: <sup>1</sup>  $a = \frac{O_d^{daf} - H^{daf}}{C^{daf}} \cdot 100\%$ ; <sup>2</sup> brown coal; <sup>3</sup> anthracite

Table 2

## Yield and quality of coal destruction products in centrifugal field

Investigation object	Rank of coal by DSTU 3472-96	Destruction products	Yield of destruction products in centrifugal field ( $\gamma$ ), %	Technical analysis				Elemental composition (dry ashless state), %				
				$W_f^a$	$A_f^d$	$S_f^d$	$V_f^{daf}$	$C_f^{daf}$	$H_f^{daf}$	$N_f^{daf}$	$O_{df}^{daf}$	$S_{fj}^d$
Dopropolska concentrating mill	G	liquid	19.1	2.4	3.8	1.58	34.2	86.00	5.30	1.70	5.40	1.60
		solid phase	53.2	1.9	13.8	1.79	7.1	91.30	2.70	1.90	2.30	1.80
		gas phase*	27.7					64.98	11.02	0.96	19.66	3.38
Proletarska concentrating mill	F	liquid	27.8	1.3	4.3	2.25	32.1	87.10	5.20	1.60	3.80	2.30
		solid phase	46.7	1.7	15.4	1.78	6.5	91.80	2.60	1.70	2.10	1.80
		gas phase*	25.5					76.53	10.75	1.42	7.70	3.60
Kolosnikovska concentrating mill	C	liquid	23.5	0.6	5.6	2.49	20.8	89.60	4.80	1.60	1.50	2.50
		solid phase	59.6	1.2	12.7	1.69	5.6	92.50	2.70	1.70	1.40	1.70
		gas phase*	16.9					72.86	13.39	1.25	10.14	2.36
Kolosnikovska concentrating mill	LB	liquid	6.8	0.8	4.7	1.53	19.0	90.60	4.20	1.60	2.10	1.50
		solid phase	76.7	0.7	10.8	1.50	5.5	92.00	2.60	1.60	1.60	2.20
		gas phase*	16.5					75.00	15.88	1.60	7.46	0.06

\* Defining the elemental composition of gas phase we issued from the mass balance:  $q_{ij} = q_{ij}^l g_i^l + q_{ij}^s g_i^s + q_{ij}^g g_i^g$ , where  $i$  and  $j$  are numbers of coal and elements, respectively. Hence,  $q_{ij}^g = \frac{q_{ij} - q_{ij}^l g_i^l - q_{ij}^s g_i^s}{I_i^2}$ . Using experimental data we found elemental composition of a gas-vapor phase.

Table 3

Characteristics of solid fuel using IR-spectroscopy data

Rank of coal		Parameter			
		$b^*$	$h_1 = D_{3040}/D_{2920}$	$h_2 = D_{2920}/D_{1690}$	$h_3 = D_{2920}/D_{1600}$
B			0.11	9.0	1.30
LF			0.30	1.5	0.80
LFG			0.33	4.0	0.60
G	Initial	1.33	0.33	3.0	0.50
	Liquid phase		0.40	4.0	1.00
	Solid phase		0.38	3.0	2.00
F	Initial	2.10	0.21	7.3	0.27
	Liquid phase		0.24	4.2	0.67
	Solid phase		0.50	2.0	0.77
C	Initial	2.00	0.32	6.3	0.13
	Liquid phase		0.33	4.0	0.66
	Solid phase		0.38	2.0	1.30
LB	Initial	0.25	0.40	2.5	0.33
	Liquid phase		0.75	0.5	0.43
	Solid phase		0.60	2.0	1.60
L			0.50	2.5	0.26
A			0.85	1.6	1.35

$$* b = \frac{h_2(l)}{h_2(s)}$$

### 3. Results and Discussion

#### 3.1. Metamorphism “Jumps” Accordingly to Artificial Coalification Data

The analysis of kinetic models of solid fuel coalification showed the following:

1. Bright brown coal formation is a completion of lignite stage corresponding to the maximum of mass loss rate ( $r_{\max(1)} = 13.28$  % per year) at  $t_1 = 2.93$  year. Bright brown coal is identified in accordance with standard values of carbon mass content (75 mas %) and reflectance (0.55 %). Accordingly to artificial coalification data 5 hydrogen atoms are for every oxygen atom. We may suppose that so high value of mass loss rate is achieved due to the reactions of carbon dioxide formation and partially due to water formation [cf. 4, Table 1].

These assumptions are in agreement with the scheme of fuel aliphatic part decomposition by the reactions of dehydration, decarboxylation and cyclization suggested by V. Rakovsky at the analysis of coking chemism. We took it as a hypothesis when we considered the chemism of natural metamorphism [5].

Table 3 also represents  $b$  parameter, which we introduced as a measure of intermolecular interaction between structures of liquid and solid phases. Accordingly to the “guest-master” conception it is necessary to differentiate them as mobile component and “filtering lattice”. The same differentiation of coal structural fragments (but in less definite form) is the basis for self-

conjunction theory and theory of self-associated multimer [3].

2. The beginning of metamorphism lignite stage corresponds to the maximum of rate of carbon mass content increase in the solid residue ( $r_{\max(2)} = 7.974$  % per year) at  $t_2 = 3.61$  year. This beginning is in the view of transition of fuel composition, structure and properties from LF to LFG rank ( $C^{daf}(t_2) = 81$  % and 8 hydrogen atoms are for every oxygen atom).

The fact that the maximum change of carbon content is achieved after the maximum of mass loss ( $t_2 > t_1$ ) confirms once more that at the examined stages of metamorphism the solid residue coalification takes place due to the primary proceeding of dehydration reactions and decarboxylation reactions particularly.

3. The crossing of curves of hydrogen and oxygen mass changes depending on time points to the completion of chemical structures metamorphic formation. Such structures ensure the good caking of coal residue during its coking. Taking into account the data of artificial coalification the curves crossing is in  $t_3$  point at time axis, between G and F coals.

The peculiarity of fuel chemical structure and composition is a parameter  $a(t_3) = 0$  (cf. (12) in [4]). Therefore, the chemical structures designating the coal properties are characterized by the atomic ratio between hydrogen and oxygen inversely proportional to their atomic masses. In accordance with artificial coalification data,  $t_3 = 4.51$  and  $C^{daf}(t_3) = 86.59$ . Thus, the atomic ratio hydrogen:oxygen is approximately 16.

4. The minimum of the curve  $a(t_4)$  corresponds to the boundary between baking coals and anthracites and falls on metamorphism stage of free-burning coal of L rank. The approaching to this minimum is determined by chemical structures transformation toward the increase of hydrogen atoms number ( $> 16$ ) per one oxygen atom with continuous decrease of their total amount. At the same time the carbon mass content increases,  $t_4 \approx 6$  years,  $a(t_4) = -2.89$ ,  $C^{daf}(t_4) = 92.50$  and 50 hydrogen atoms are for every oxygen atom.

5. The reversion of  $a(t)$  curve to  $a(t_5) = 0$  characterizes the transition of L coal to graphite across the anthracites area. Taking into account that equality  $a(t_5) = 0$  is a condition of complete loss of hydrogen and oxygen by the solid residue, the upper limit of this interval is  $a(t_5) = -1.145$  with corresponding  $C^{daf}(t_5) = 96.15$ .

### 3.2. Regularities of Physico-Chemical and Structural Properties Changes for Solid Fuel during Metamorphism

One can see from Table 1 that there are “jumps” (change of direction or rate of changes) in metamorphism row by the sum of baking (and free-burning) microcomponents from B to LF, from G to F, from LB to L, from L to A. For  $R_0$  only L→A transition has a “jump”. The change of sign of parameter  $a$  is observed for G→F transition.

Comparing the data concerning elemental compositions and vitrinite reflectance presented in Table 1 and results of artificial coalification we see their agreement.

From Table 2 one can see that yields of liquid and gas phases of F coal are equal. Moreover, coals form a group by gas phase yield: G and F coals from the one side, and C and LB coals – from the other. Obviously these facts explain the “jump” between F and C coals by  $V^{daf}$ . The difference between G and F coals is the interchange between yields of yield and gas phases. The same difference is between C and LB coals but with other numerical values. We restricted our investigations only by these coals because LF and LFG coals have a very low yield of liquid phase; the yields of B, L and A coals practically are absent.

Carbon is the main element of all phases though its content is minimal in the gas phase of all coals. Hydrogen and oxygen are mainly in the gas phase; nitrogen is present in all phases. The greatest content of sulphur is in the gas phase, except LB coal.

To confirm the possibility of artificial coalification use as an experimental model of natural metamorphism we compared corresponding dependencies between carbon content  $C^{daf}$  and vitrinite reflectance  $R_0$ .

Fig. 1 shows the full agreement between curves of artificial coalification and natural metamorphism. Therefore, kinetic equations obtained by us, need only changes in  $t$  scale. Averaging the coals geologic age given in literature, the transition period from brown coals to anthracites is 300 millions years. Hence, the unit of conventional time  $t$  in (11) (see [4]) is 50 millions years.

As distinct from volatile components yield, the thickness of plastic layer directly shows the G→F transition (the third “jump”) as a maximum of the curve (Fig. 2). The beginning of curve sharp raise founded itself at the transition from brown dull coal to long-flame coal coincides with the predicted second “jump”. The crossing of its descending branch with  $C^{daf}$  axis points to the beginning of L→A transition (the forth “jump”).

The “jumps” which were determined using the thickness of plastic layer, are also on the curves of metamorphic change of baking microcomponents sum. The fact that the same peculiarities of natural metamorphism are identified by the values based on phenomena of different nature reveals the founded kinetic regularities.

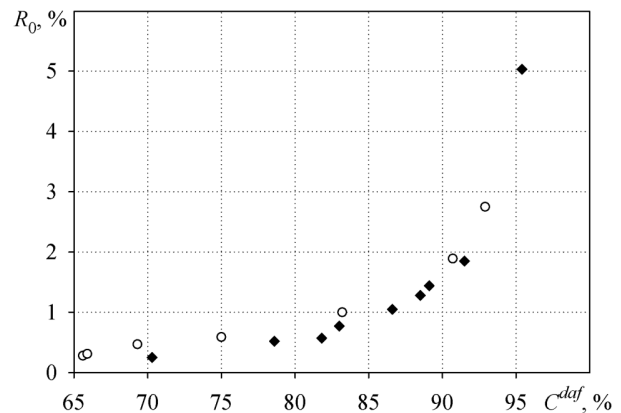


Fig. 1. Dependence of  $C^{daf}$  on  $R_0$  in accordance with the data of artificial coalification (o) and natural metamorphism (♦)

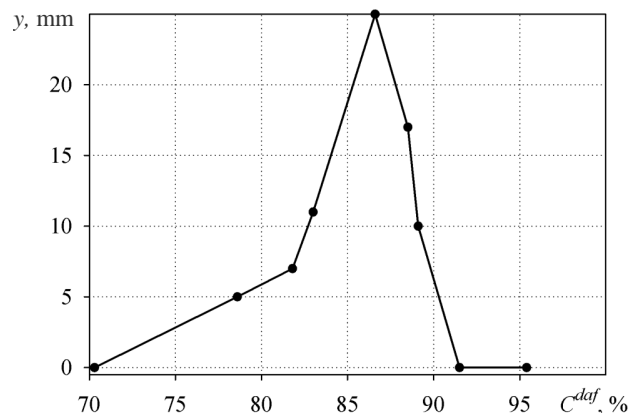


Fig. 2. Plastic layer thickness vs carbon content

Taking into account the results of coal elemental analysis the values of  $\alpha$  parameter (see Table 1) were calculated. The change of parameter during metamorphism is shown in Fig. 3: the curve crosses X-axis in the point corresponded to G→F transfer (the third “jump”) and its minimum indicates the end of coal and beginning of anthracite stage of metamorphism, the same as during artificial coalification.

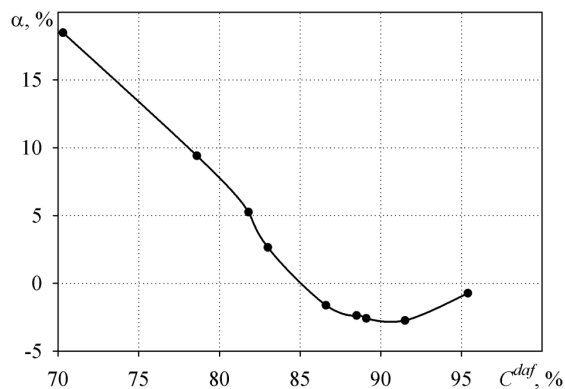


Fig. 3. Elemental-structural parameter  $\alpha$  vs carbon content

The study of the changing character of phases elemental composition (according to the pyrolysis data in a centrifugal field) during metamorphism at the stage of caking coals shows that structure transformation of coal in the area of the third “jump” is influenced by the change of elemental character of the gas phase. At the stage before F coal there is an active loss of oxygen mainly with  $\text{CO}_2$  compounds; at the stage after F coal – active loss of hydrogen mainly with  $\text{CH}_4$  and oxygen (bounded with more heavy coal structures) – with  $\text{H}_2\text{O}$ .

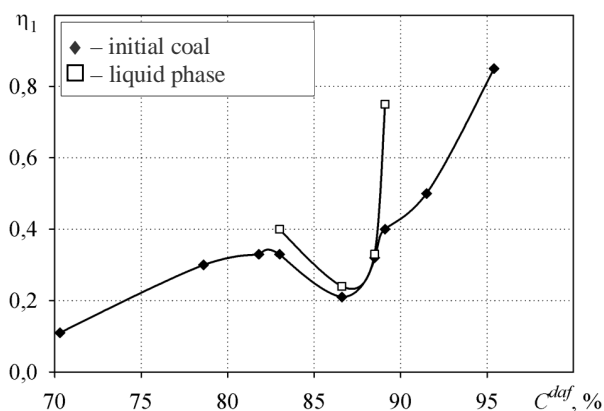


Fig. 4. Change of  $h_1$  parameter with the increase of carbon content

Assuming that the change of spectral parameter  $h_1$  (Fig. 4) during metamorphism indicates the change of ratio between aromatic and aliphatic structures, the latter ones predominate over others in young coals. The part of

these structures decreases while the period before the stage of gas coals, but then this tendency is not valid. The transfer from gas coals to fat ones is accompanied by the decrease of aromatic structures part. The minimum of  $h_1$  located between “states” is the beginning of the new period of OMC intensive aromatization, the rate of which does not decrease during the period till anthracite formation.

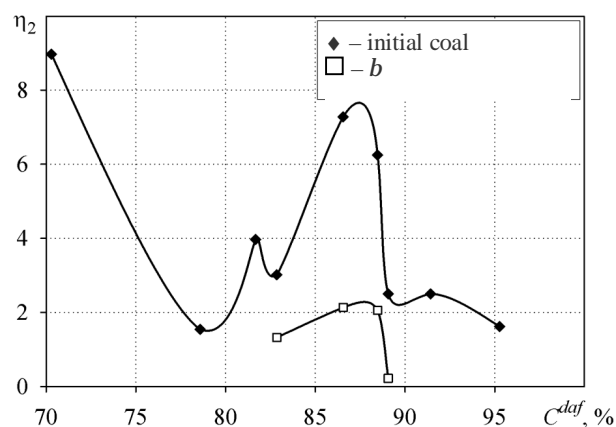


Fig. 5. Change of  $h_2$  parameter with the increase of metamorphism degree

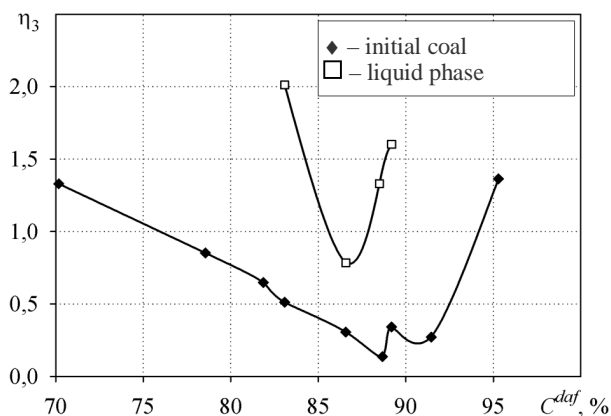


Fig. 6. Change of  $h_3$  parameter during metamorphism

The changes of parameter  $h_2$  during metamorphism (Fig. 5) are connected with the change of ratio between amounts of strong aliphatic C–H bonds and C=O bonds, taking into account that such parameter characterizes the degree of intermolecular interaction [1]. In accordance with experimental data we may assume that the intensive oxygen loss at the stage including B-dull, B-bright and C coals is accompanied by the formation of new C=O bonds with participation of residual oxygen at practically constant amount of aliphatic C–H bonds. The increase of  $h_2$  value at the stage of C→F transfer is connected with further oxygen loss but with C=O bond rupture. Here the atomic ratio hydrogen:oxygen is approximately 16. Under

mentioned conditions the reactions leading to the accelerated decrease of hydrogen mass content are dominant due to the rupture of aliphatic C–H bonds.

Obtained data concerning  $h_3$  (Fig. 6) indicate the dominant rupture of aliphatic C–H bonds during the period till the stage of caking coals. In the area of F coal the rupture rate of C=C bonds is predominant over that of C–H bonds. It means the minimum at the  $h_3$  curve not only for original coals but for liquid phase too. Such treatment of the experimental data supposes that C=C bonds refer to aliphatic fragments of coal, that is in agreement with the data concerning its aromatization during the same period.

#### 4. Conclusions

The end of lignite stage is the formation of brown bright coal (5 hydrogen atoms for every oxygen atom). The beginning of metamorphism coal stage is a LF→LFG transfer (8 hydrogen atoms for every oxygen atom). Both phenomena take place due to decarboxylation leading to the hydrogen loss in the form of molecular hydrogen and methane.

While transferring from G to F coal the metamorphic formation of chemical structures ensuring the good caking of residual coal at coking leads to the atomic ratio hydrogen:oxygen  $\approx 16$  due to the dominant dehydration reactions.

The transfer from caking to free-burning coals is determined by the reactions of methane and water formation which increase the atomic ratio H/O ( $\geq 50$ ) at the constant decrease of their total amount.

The transformation of chemical structures at the stage of noncaking coals (L→graphite transfer) takes place only due to the hydrogen loss of solid fuel aromatic structures.

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#### ПРО СКЛАД І БУДОВУ ОРГАНІЧНОЇ МАСИ ВУГІЛЛЯ.

#### 3. ОЦІНКА ДИНАМІКИ ХІМІЧНОЇ БУДОВИ ВУГІЛЛЯ В ХОДІ МЕТАМОРФІЗМУ

*Анотація.* За допомогою математичної моделі кінетики метаморфізму, що прив'язана до осі часу за даними штучної вуглефікації, виконана оцінка динаміки хімічної будови вугілля в ході метаморфізму.

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