

Vadim Barsky¹, Gennady Vlasov² and Andriy Rudnitsky¹

COMPOSITION AND STRUCTURE OF COAL ORGANIC MASS. 4. GENERALIZED CONCEPTION OF THE COMPOSITION OF SOLID FUEL MOLECULAR STRUCTURES AND CHEMISM OF METAMORPHISM PROCESS

¹ *Ukrainian State Chemico-Technological University, Dnepropetrovsk, Ukraine*

² *JSC "Avdeevskiy KHZ", Avdeevka, Ukraine*

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Abstract. "Jumps" in structure composition and properties of solid fuel have been determined using the model of metamorphism dynamics. For these "moments" of the geological age the elemental composition and structural peculiarities of "molecules" have been determined and approved by stoichiometric equations of the reactions, material balances of the stages and the agreement between the combustion heat of model compounds and coals of similar elemental composition.

Keywords: metamorphism, coal, chemical structure.

1. Introduction

Analyzing the results of modern conceptions about coals chemical structure [1] and data of our previous investigations [2, 3] we assume the following positions within which the models of solid fuel molecular structure should be constructed:

1. The model must correspond to the real object (coal) by its absolute atomic composition.

2. As far as possible, to take into account the values of IR-parameters h_1 , h_2 and h_3 , and first of all, the ratio between aromatic and aliphatic C–H bonds.

3. To describe maximally the amount and nature of functional groups and relatively small sizes of aromatic nuclear of average statistic coal "molecule". The latter results from the fact that in accordance with Haber first rule [4] the decomposition of the initial compound under environmental influence (temperature, pressure, physico-chemical and catalytic properties of the additives and environment) proceeds *via* the least deformation of the initial molecular structure. Therefore, the chemical structure of individual compounds identified in gas-vapor products of coal and charge pyrolysis (in coke-oven gas and resins of coking and semi-coking) is considered to be

possible fragments of average statistic "molecule" of solid fuel.

4. To take into account the modern conceptions about the change of character and type of intermolecular interaction during metamorphism, as well as their influence on physico-chemical properties of solid fuel.

5. Being at variance between continuity of average statistic regularities of the elemental composition change and discontinuity of molecular structures by number of atoms and bonds between them, the model must describe all periods when slow quantitative changes of fuel composition results in quick ("spasmodic" in the terms of geological age) changes of its molecular and permolecular structure.

6. The model molecular structures of solid residue (solid fuel) together with main gaseous and liquid products produced during metamorphism between adjacent "jumps" must meet the requirements of strict (with the accuracy to integer number of atoms) stoichiometric equivalence.

7. The material balance of metamorphism must coincide with the sum of material balances of the mentioned stages.

8. In accordance with classic organic chemistry regulations about the agreement between the structure and combustion heat of organic compounds the calculated values of model structures combustion heat must be adequate to experimental values of combustion heat of the corresponding coals.

2. Experimental

To determine the number of elements atoms in averaged "molecules" of solid fuel we found the elemental composition of the coals corresponding to the special points ("jumps") of metamorphism.

To establish the structural peculiarities of averaged “molecules” we determined h_1 , h_2 and h_3 parameters using IR-spectroscopy. We also determined the combustion heat of corresponding coals, because it is one of the

most important parameters used in the organic chemistry to establish the structural peculiarities of organic matters [5-7].

All these data are represented in Table 1.

Table 1

Parameters of elemental composition, IR-spectroscopy and coal combustion heat

Investigation object	Rank of coal by DSTU 3472-96	Elemental composition (dry ashless state), mas %					a^1 , mas %	IR-spectroscopy ²			The highest combustion heat Q_s^{daf} , MJ/kg
		C^{daf}	H^{daf}	N^{daf}	O_d^{daf}	S_r^d		h_1	h_2	h_3	
Alexandrine deposit	B	70.3	6.0	0.5	19.0	4.2	18.4	0.11	9.0	1.30	20.23
Trudovska mine	LF	78.6	5.4	1.6	12.8	1.6	9.4	0.30	1.5	0.80	31.94
Kurakhovska mine	LFG	81.8	5.9	1.3	10.2	0.8	5.25	0.33	4.0	0.60	32.90
Dopropolska concentrating mill	G	83.0	5.5	1.6	7.7	2.2	2.6	0.33	3.0	0.50	34.28
Proletarska concentrating mill	F	86.6	5.4	1.6	4.0	2.4	-1.6	0.21	7.3	0.27	35.41
Kolosnikovska concentrating mill	C	88.5	5.0	1.6	2.9	2.0	-2.3	0.32	6.3	0.13	35.75
Kolosnikovska concentrating mill	LB	89.1	4.9	1.6	2.6	1.8	-2.5	0.40	2.5	0.33	35.62
Mospinska mine	L	91.5	4.4	1.5	1.9	0.7	-2.7	0.50	2.5	0.26	35.75
Komendantska concentrating mill	A	95.4	1.5	0.7	0.8	1.6	-0.7	0.85	1.6	1.35	33.33

Notes: B – brown coal; LG – long-flame coal; LFG – long-flame gas coal; G – gas coal; F – fat coal; C – coke coal; LB – lean-baking coal; L – lean coal; A – anthracite;

$$^1 a = \frac{O_d^{daf} - H^{daf}}{C^{daf}} \cdot 100\% ; \quad ^2 h_1 = D_{3040}/D_{2920}; h_2 = D_{2920}/D_{1690}; h_3 = D_{2920}/D_{1600} [3]$$

3. Results and Discussion

3.1. Dynamics of Intermolecular Bonds and Structural Peculiarities

The dependence between parameters a (for elemental composition) and h_1 (for chemical structure of coal matter) is represented in Fig. 1.

Metamorphism row is divided by the mentioned parameters into two sequences:

- the first one consists of coals from brown to gas inclusive; it is characterized by slow increase of h_1 parameter practically in all positive region of parameter a variation;
- the second one involves coals from fat to lean inclusive; it is characterized by high rate of increase of h_1 parameter in a narrow negative region of parameter a variation.

Perhaps anthracites form one more branch of the second sequence in the region of h_1 values corresponded to a parameter reset from negative value to zero.

We also estimated the connection between a parameter and combustion heat of coals.

One can see from Fig. 2 that in accordance with such a property all brown and black coals form almost straight line **1** with the increase toward high-metamorphized fuels.

All given facts may be interpreted as following:

During the main part of geological time the change of elemental composition of solid fuel is accompanied by slow increase of ratio between amounts of aromatic and aliphatic structures. The approximation of such quantitative changes to the equality of oxygen and hydrogen mass concentrations results in weakening of heteroatoms role (oxygen, first of all) in the conjugation system. It is destroyed in jumps (in terms of geological time) forming additional amounts of aliphatic fragments with small aromatic structures as nuclei. The appearance of such fragments, the same as appearance of crystal nuclei in oversaturated solution (the analogy was prompted by G. Skripchenko's conception [9, 10]), stimulates the exaggerated growth of aromatic structures amount due to the cyclic non-aromatic formations and end-groups. The partial loss of end-groups in the form of gases and vapors accompanies this process, eliminates spatial disturbances for packing of structural units and increases the aromatization degree of the coal matter forming its sequence from F to A inclusively.

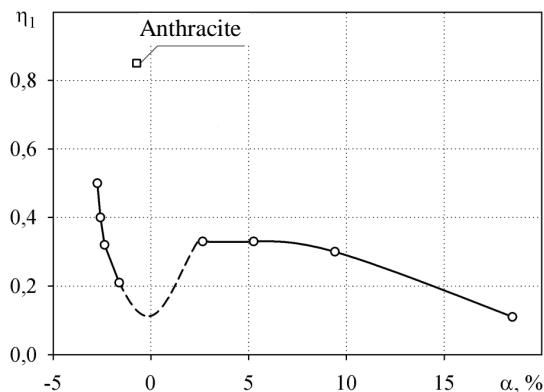


Fig. 1. Connection between parameters of composition (α) and chemical structure of coal matter (h_1)

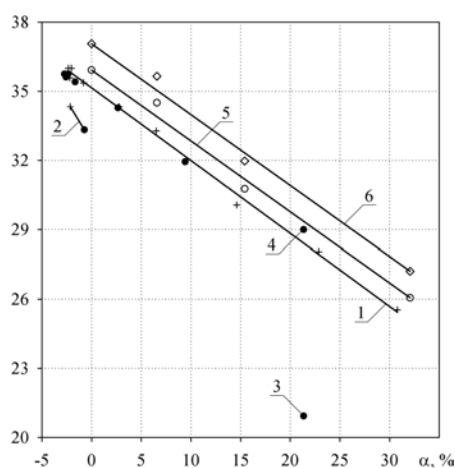
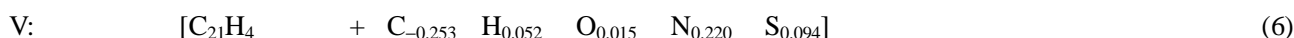
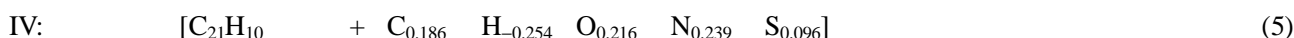
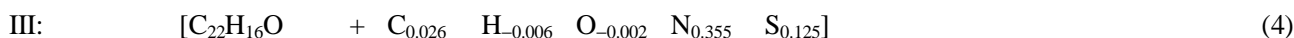
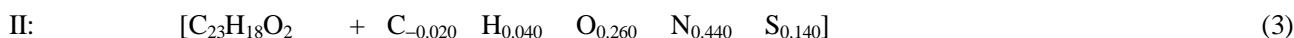
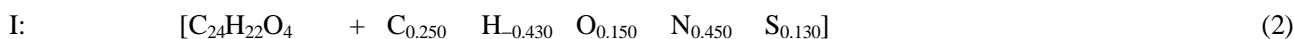
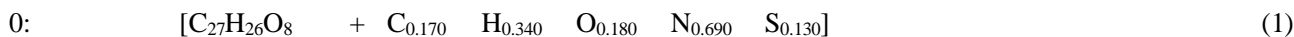


Fig. 2. Change of coal combustion heat depending upon the parameter α value: experimental data [3, Table 1] (\bullet); data of thermochemical calculations of Q_i^{daf} and Q_h^{daf} (\circ and \diamond , respectively) for the model structures 0, I, II, III; averaged data from [8] ($+$). 1 – line of brown and black coals; 2 – line of anthracite; 3 – Q_h^{daf} value for brown dull coal from [3, Table 1]; 4 – point 3 after correction (the correction was done assuming too high humidity and ash content of brown coal sample); 5 and 6 – lines of thermochemical estimations of Q_i^{daf} and Q_h^{daf} , relatively



Studying the dynamics of nitrogen and sulphur content in solid fuel we suppose that these elements are in all main macrocomponents of the initial plant material: cellulose, proteins, alkaloids, waxes and resins, lignin.

3.2. Models of “Molecules” and Chemism of Solid Fuel Metamorphism

Table 2 represents mass elemental composition of the fuel characterizing it in the special points (in “jumps”). Numbers of elements atoms corresponding to the mass compositions were found using kinetic regularities established earlier [2, 3]. The model molecular structure of minimal size which contains one oxygen atom and 16 hydrogen atoms corresponds to the “jump” No.3 ($a = 0$, see Table 3). In Tables 2 and 3 the initial stage (“0”) corresponds to the brown smut.

Table 2

Elemental composition of solid fuel in special points of metamorphism (mas %)

“Jump” No.	C^{daf}	H^{daf}	O^{daf}	N^{daf}	S^{daf}
0	65.591	5.299	26.330	1.943	0.837
I	74.725	5.539	17.051	1.618	1.068
II	80.963	5.297	10.617	1.809	1.315
III	86.590	5.240	5.240	1.620	1.310
IV	92.836	3.559	1.262	1.222	1.122
V	95.998	1.562	0.093	1.188	1.160

Table 3

Numbers of elements atoms in the “molecule” of fuel at different stages of metamorphism

“Jump” No.	N_C	N_H	N_O	N_N	N_S
0	27.170	26.340	8.180	0.690	0.130
I	24.250	21.570	4.150	0.450	0.130
II	22.980	18.040	2.260	0.440	0.140
III	22.026	15.994	0.998	0.355	0.125
IV	21.186	9.746	0.216	0.239	0.096
V	20.747	4.052	0.015	0.220	0.094

These data allow to present the following formulae for the averaged “molecular” structures of solid fuel of metamorphism different degrees.

Cellulose consists of oxygen by half and decomposes into carbonic acids, carbon dioxide, water and methane too quickly. So it cannot be considered as a main precursor of coal.

Proteins completely decompose by bacteria (to aminoacids) still at the beginning of plant residues transformation into peat.

Waxes and resins of plants are transformed into bituminous part of the coal. At the same time waxes are represented by ethers of higher alcohols C₆–C₄₀ of the paraffin row and carbonic acids; resins are mainly represented by isoprenoids: mono-, di-, tri- and sesquiterpenes, sterols and stilbenes having polycyclic condensed alicyclic structure [11].

Lignin mainly consists of the residues of substituted phenol alcohols and forms huminic acids *via* splitting off carbonic acids (humification). Due to the hydroxyl and carboxyl groups lignin is inclined to condensation with acids and alcohols of fatty row and forms branched structures with one, two or three aromatic nuclei in the centre. After splitting off methoxyl groups and water it forms humin which is insoluble in the alkali and may be the initial compounds for further carbonization [12].

Sulphur is present in two of twenty one aminoacids (cysteine and cystine) and apparently stays in the coal in the structure of stable five- or six-membered heterocyclic compounds of aromatic nature.

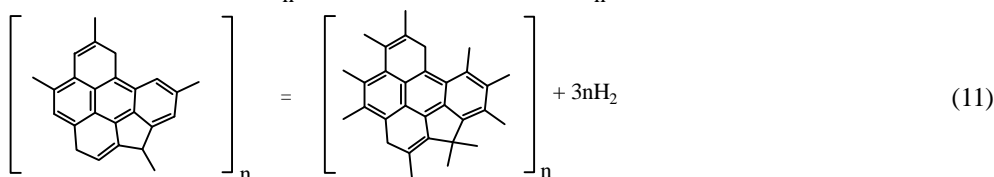
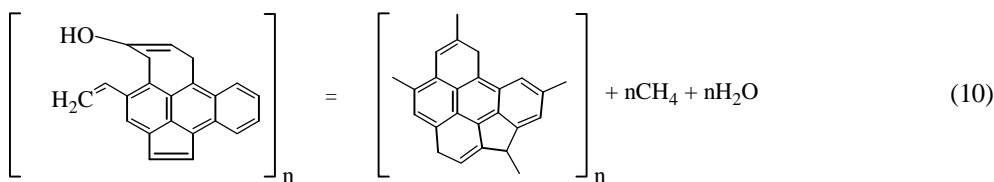
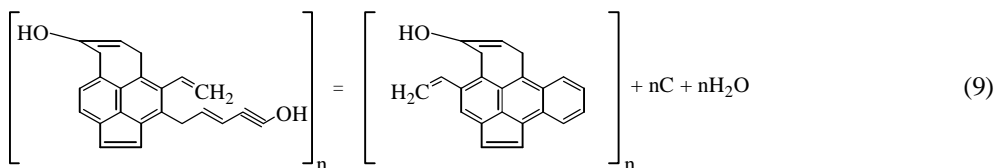
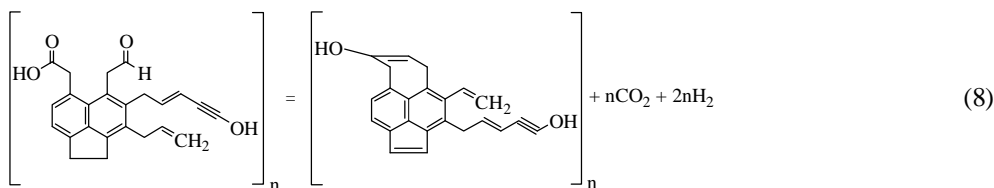
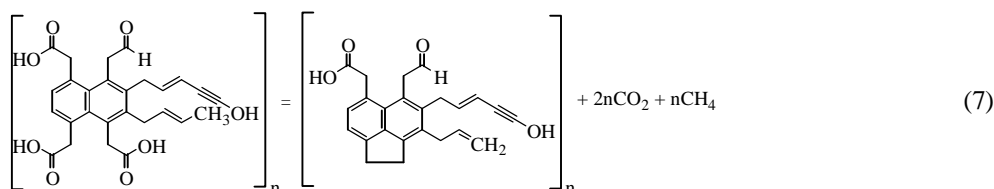
Nitrogen of plant matters is represented by protein aminogroups and heterocyclic compounds of quinoline,

pyrazole, imidazole, indyl and pyridine rows in the structure of chlorophyll, vitamins and alkaloids. Aminogroups are oxidized to elemental nitrogen by bacteria and nitrogen of heterocyclic compounds which are stable to oxidation probably is turned into coal [13].

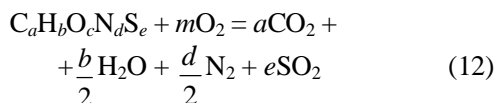
Thus, we may consider that the main amount of nitrogen and sulphur is lost by the initial plant material at the initial stages of decay during pre-lignite period. As a result, till the “beginning” of metamorphism the solid residue has small amount of the mentioned components included in the most stable chemical structures as heteroatoms. The additional confirmation is the fact that nitrogen and sulphur content slightly changes during all metamorphism period: in the case of 0 only one of 7.69 “molecules” contains one sulphur atom, and in the case of V – only one of 1.063 “molecules”.

So, further we included to the conception of model average statistic molecular structure only “molecules” without nitrogen and sulphur.

Taking into account above-mentioned assumptions we constructed model “molecular” structures and stoichiometric equations describing the transformation of solid fuel at stages with peculiarities of metamorphism kinetic curves discovered by us:



Combustion of fuel by general formula $C_aH_bO_cN_dS_e$ is described by the following stoichiometric equation:



where

$$m = \frac{1}{2} \left(2a + \frac{b}{2} + \frac{d}{2} + 2e - c \right) \quad (13)$$

Here we used the analogy with ammonia oxidation at which only one reaction is thermodynamically preferable among three possible ones. It proceeds without a catalyst with the formation of elemental nitrogen [14, 15]. At the same time, even on condition that elements are completely burned, the formation of SO_2 (not SO_3) must be supposed, because the rate of interaction between sulphurous anhydride and oxygen is negligibly low without a catalyst or oxygen "sender".

Heats of formation (enthalpies) of compounds participating in Eq. (12) were taken from [14] and [16] and calculated using Chem3D program. They are represented in Table 4.

Table 4

Heats of formation ΔH_{298_j} (kJ/mol)

Compound	Phase	
	Gas-vapor	Liquid
CO ₂	-393.70	
H ₂ O	-241.94	-286.02
N ₂	0	0
O ₂	0	0
SO ₂	-297.10	
0	-967.00	
I	-213.00	
II	480.00	
III	321.00	

In accordance with Eq. (12) and Table 4 combustion heats of model molecular structures are represented by the following equations (MJ/kg):

$$Q_{l_j}^{daf} = \frac{1}{M_j} (393.70 \cdot N_{C_j} + \frac{1}{2} \cdot 241.94 \cdot N_{H_j} + 297.10 \cdot N_{S_j} + \Delta H_{298_j}) \quad (14)$$

$$Q_{h_j}^{daf} = \frac{1}{M_j} (393.70 \cdot N_{C_j} + \frac{1}{2} \cdot 286.02 \cdot N_{H_j} + 297.10 \cdot N_{S_j} + \Delta H_{298_j}) \quad (15)$$

where $Q_{l_j}^{daf}$ and $Q_{h_j}^{daf}$ are low and high heat values of initial j -component; signs are placed in such a way that combustion heat should be equal to the change of enthalpy

in Eq. (12) taken with the opposite sign; M_j and ΔH_{298_j} are molecular mass and heat of formation of burned j -component; numbers of atoms N_{C_j} , N_{H_j} and N_{S_j} are taken from Table 3.

The results are present in Table 5 and Fig. 2 (curves 5 and 6). The curves are almost parallel to the line 1 describing the character of changes of experimental combustion heats of the coals with different metamorphism degree.

Table 5

Combustion heats of fuel model structures

Compound	Q_l^{daf}	Q_h^{daf}
0	26.062	27.230
I	30.769	31.989
II	34.501	35.669
III	35.921	37.076

This fact is the evidence of "molecular" structures of solid fuel given in Eqs. (7)-(9) typical for 0, I, II and III metamorphism periods. The observed systematic exceeding of calculated values of combustion heats over experimental values may be explained by overstating of calculated values of heat of formation for large molecular fragments by Chem3D program. Moreover, using Chem3D program it is impossible to calculate the heats of formation for fragments IV and V (see Eqs. (10) and (11)) because it should be necessary to take $n \gg 1$, i.e. enclose unsaturated valency bonds and make "molecules" too large.

Given in [1-3] and founded in this paper theory of metamorphic formation of the structure and composition of coal organic matter (COM) found its practical application for the estimation of coals chemical potential and search of new ways and methods of yield increase of gas-vapor products at the production of metallurgical coke [17]. It also shows inadmissibility of annihilation of COM pyrolysis products which are valuable unrecoverable natural resources by their burning at "two-product" coke plants [17].

Moreover, the obtained results allow to give a comparable estimation of reserves of solid, liquid and gaseous energetic and chemical raw materials which are formed during metamorphism as a natural process of solid fuel coalification.

In connection with the fact that development prospects of any branch of industry are determined by the presence of corresponding raw material, the special literature is full of evaluations of main energy resources reserves – coal, oil and gas, which are raw materials for all branches of chemical industry at the same time [21-31]. Actually in all cases the authors conclude that reserves of unrecoverable resources catastrophically decrease [22].

Data represented in [2] show that primary reserves (mas %) of COM should be 85.33 mas %, oil organic matter – 5.45 and methane of natural gas – 9.19 (to calculate for the sum of metamorphism solid residue, entries II, III and methane). Taking into account that all estimations given in the literature include to reserves the mineral impurities of coal (~25 mas %), oil (~10 mas%) and associated to methane gases (~7 mas %) [32], we have the following values of reserves formed during metamorphism (mas %): coal 87.05; oil – 4.92 and natural gas – 8.03.

Thus, we agree that gas reserves are greater than oil reserves [22] but to our mind the ratio coal–(oil + gas) essentially shifts to the latter ones compared with previously published information in which the share of coal reserves approaches to 95 % and oil and gas – to 5 %.

The transfer to reserves expressed in absolute values faces the essential difficulties because the published estimations of world reserves and storage are very different [33-39]. The difference is caused by different standards, nonidentity of predicted methods and requirements presented to the certainty of reserves in different countries [21].

However, in accordance with official reports the situation in 1980 was following: the general geologic reserves of coals are 14300 billion tons, explores reserves are 3705 billion tons and proven reserves are 1367 billion tons [21]. It should be noted that data published during the following years are in accordance with given estimations. For example, values concerning general geologic reserves are (billion tons): 11000 [35], 14800 [38] and 12500 [39]. Being oriented on coal reserves of 14300 billion tons we find the general primary geologic reserves: oil – 808.32 billion tons, gas – 1319.12 billion tons (or 1691.2 trillion m³ if the average density of gas is 0.78 kg/m³ [32]). These values are considerably greater than the existing statement about the primary reserves of oil and gas [36].

4. Conclusions

1. The presence of metamorphic reconfiguration “jumps” of fuel structure was shown by means of theory and experiments. The change of ratio between chemical bonds of different nature was determined. On this basis the generalized conception was formed in accordance with which the dynamics of intermolecular bonds in solid fuel is determined by advance a decrease of EDA-interactions and hydrogen bonds role. Nascent minimum of permolecular structure strength accounts for the stage of coking coals.

2. The models of averaged “molecules” of solid fuel were proposed. They characterize its chemical

structure during the periods of metamorphism discovered “jumps”. The adequacy of proposed models was confirmed by stoichiometric equations of the reactions, material balances and agreement between combustion heats of model compounds and coals of closed elemental composition.

3. The main items of developed theory about chemism of metamorphism process were used for the estimation of chemical potential of coals and search of its application in the production of metallurgic coke, as well as for comparable estimation of coal, oil and gas primary reserves.

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ПРО СКЛАД І БУДОВУ ОРГАНІЧНОЇ МАСИ ВУГІЛЛЯ.

4. УЗАГАЛЬНЕНА КОНЦЕПЦІЯ БУДОВИ МОЛЕКУЛЯРНИХ СТРУКТУР ТВЕРДОГО ПАЛИВА ТА ХІМІЗМ ПРОЦЕСУ МЕТАМОРФІЗМУ

Анотація. За допомогою моделі динаміки метаморфізму виділені “стрибки” будови структури і властивостей твердого палива. Для цих “моментів” геологічного часу визначено елементний склад і структурні особливості “молекул”, які підтверджені стехіометричними рівняннями реакцій, що протікають, матеріальними балансами стадій і узгодженістю теплот згоряння модельних речовин та вугілля близького елементного складу.

Ключові слова: метаморфізм, вугілля, хімічна будова.