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Thermogravimetric Study of Coal Vitrinites at Different Metamorphic Stages in the Oxidizing Medium

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Abstract

A thermogravimetric study of vitrinites of bituminous coals of different metamorphic stages was carried out in the oxidizing medium. It was demonstrated that with increasing the metamorphic grade of vitrinites, the temperature range of the oxidation process rose, while the maximum decomposition rates were shifted to higher temperature region. A strong correlation of the ignition temperature of vitrinites and organic (C^{daf}) and aromatic (C_{ar}) carbon content therein, and also of vitrinite reflectance values ($R_{o,r}$) and volatile matter yield (V^{daf}) was revealed.

Keywords: bituminous coal, vitrinite, stages metamorphism, thermogravimetric analysis, ignition temperature

INTRODUCTION

The current stage of development of ideas on chemical technology and technological processes of conversion of solid fuels is characterised by improving knowledge of transformation stages of coal substances. Organic matter of solid fuels is thermodynamically unstable formations that undergo deep transformations when heated. The nature of thermodynamic transformations of coal is determined by the presence in their structure: 1) a significant number of units of aromatic and heteroaromatic rings; 2) aliphatic bridges and saturated cycles; 3) polar groups and heteroatoms; 4) hydrate-bound water; and also donor-acceptor interaction between the organic mass of coal and mineral impurities. Such differences make their contribution to the characteristics of decomposition of their organic matter at high temperatures in both inert and oxidizing media [1–6].

Oxidation is one of the areas of deep processing of coals that allows implementing their chemical potential. Oxidation decomposition of solid fossil fuels by different oxygen-containing reagents is widely used to determine their chemical structure and increase reactivity in various conversion processes. Coal energy potential is assessed according to the index of the heat of combustion [7, 8] and their reactivities during combustion [9, 10]. Despite the sufficient study of oxygen interaction process with solid fuels, there are still open issues of assessing parameters and mechanisms of thermal-oxidative transformations of coal organic matter.

Work purpose was to find the dependence of temperature boundaries of thermal-oxidative coal vitrinite decomposition on the metamorphic stage.

EXPERIMENTAL

Vitrinite concentrates were isolated by delamination of humus coals at different metamorphic stages in a mixture of CCl_4 and benzene (solution density of 1.27 g/cm^3). Solution density selection is based on the fact that vitrinitized inclusions are maximally concentrated in fractions floating in liquids with a density of lower than 1.3 g/cm^3 [2, 4, and 11]. Samples with a particle size less than 0.2 mm were subjected to analytical studies.

Technical analysis of the selected fractions was carried out by standard methods. Organic matter composition was determined by elemental analysis methods.

The petrographic analysis was carried out using the automated complex of evaluation of the SIAMS-620 system (Russia) for grade coal composition in oil immersion medium. The calculation of micro-components was carried out automatically with the reflected light, magnification of 300 times.

High-resolution ^{13}C NMR spectra in the solid state were recorded on Bruker Avance III 300 WB instrument using standard techniques of cross-polarization with magic angle rotation and CPMAS proton decoupling with a frequency of 75 MHz. Contact time is 1500 μs; accumulation is 4096 scans; scan delay is 2 s; sample rotation frequency is 5 kHz. To acquire quantitative data, modelling of spectra was carried out using Dmfit software. In spectra, there were distinguished ranges corresponding to resonance absorption of the following groups of carbon atoms, ppm: 187–171 – carbon atoms of carboxylic groups and their derivatives (COO–); 171–148 – carbon atoms of the aromatic system connected to an oxygen atom ($C_{ar}O$); 148–93 – carbon atoms of aromatic systems, substituted and non-substituted hydrogen atom ($C_{ar} + CH_{ar}$); 67–51 – carbon atoms of methoxyl groups (OCH_3); 51–0 – carbon atoms of alkyl fragments (C_{alk}). The degree of aromaticity $f_a = (C_{ar} + CH_{ar})/(C_{ar} + CH_{ar} + C_{alk})$.

Thermal analysis was carried out using Netzsch STA 409 thermoanalyzer under the following conditions: sample mass 35 mg; platinum-iridium crucible; heating up to 700 °C with a rate of 10 °C/min in an oxidizing medium (a mixture of nitrogen and oxygen, a flow of 40 and 10 cm^3/min). During analysis, there were registered: mass loss (TG), mass loss rate (DTG), and differential thermal analysis (DTA) curves. The temperature range of the main oxidative degradation in the TG curve was determined by the method of tangents using Netzsch Proteus software: T_1 is particle ignition temperature, T_{max} is the temperature at which the maximum oxidation rate is reached; V_{max} is the maximum rate at

TABLE 1

Petrographic composition of the studied samples of vitrinites

Sample	Petrographic parameters, %				$R_{o,r}$, %	σ_R	Metamorhism stage
	Vt	Sv	I	ΣOK			
1	96	1	3	4	0.63	0.04	I
2	92	1	7	8	0.72	0.07	I–II
3	95	1	4	5	0.82	0.05	II
4	92	2	6	7	0.84	0.05	II
5	78	2	20	21	0.98	0.04	II–III
6	79	6	15	19	1.27	0.04	III–IV
7	75	9	16	22	1.31	0.05	IV
8	81	7	12	17	1.41	0.06	IV

Note. Vt is vitrinite, Sv is semivitrinite, I is inertinite, ΣOK is sum of the fusainized components, $R_{o,r}$ is vitrinite reflectance, σ_R is standard deviation.

TABLE 2

Characteristics of the studied samples of vitrinites

Sample	Technical analysis, %			Elemental composition, % per daf (dry, ash-free)			Atomic ratio	
	W^a	A^d	V^{daf}	C	H	(O + N + S)	H/C	O/C
1	1.9	3.6	43.0	82.2	6.0	11.8	0.88	0.11
2	1.1	2.8	42.2	83.2	6.0	10.8	0.87	0.10
3	0.9	4.9	39.1	85.3	6.0	8.7	0.84	0.08
4	0.9	4.6	36.2	85.7	5.9	8.4	0.83	0.07
5	0.8	4.4	35.7	86.3	5.8	7.9	0.81	0.07
6	0.5	1.4	22.5	88.7	5.3	6.0	0.72	0.05
7	0.5	1.7	22.6	88.6	5.3	6.1	0.72	0.05
8	0.8	1.5	21.5	88.5	5.3	6.2	0.72	0.05

Note. W^a is analytical moisture, A^d is ash content, V^{daf} is volatile matter yield, daf is dry ash-free sample condition.

the point of inflection, T_2 is the final temperature at which coke residue burning occurs.

RESULTS AND DISCUSSION

Tables 1 and 2 give the characteristics of the studied samples. As demonstrated by the analytical data, samples of vitrinite concentrates are related to different metamorphic stages (I–IV), vitrinite reflectance ($R_{o,r}$) varies from 0.63 to 1.41 %. All samples are low-ash ($A^d < 5$ %). Volatile matter yield (V^{daf}) decreases with increasing vitrinite reflectance in coal samples, carbon content increases from 82.2 to 88.5 %, respectively, the content of oxygen and heteroatoms in organic matter decreases from 11.8 to 6.2 %.

As demonstrated by ^{13}C NMR spectroscopy data (Table 3), the degree of aromaticity (f_a) of the studied samples increases from 0.69 for sample No. 1 to 0.86 for sample No. 8. This is related to a decrease in the number of aliphatic carbon in structural fragments in the 25–51 ppm range.

It is believed that during dust-like burning of solid fuel, the degree of its thermal chemical transformation is determined by a series of parameters of consecutive-parallel processes, in particular: the rate of release and combustion of volatile matter, and the rate of combustion of the non-volatile residue [12–14]. Paper [14]

TABLE 3

Fragmentary composition parameters of samples of vitrinites according to ^{13}C NMR spectra

Sample	$R_{o,r}$, %	Carbon atoms distribution by their structural groups, rel. %							f_a
		CH_3	CH_2	CH_3O	$C_{alk}O$	$C_{ar}H + C_{ar}$	$C_{ar}O$	COOH	
		Resonance absorption range, ppm							
		0–25	25–51	51–67	67–93	93–148	148–171	171–187	
1	0.63	5.31	24.36	2.56	0.71	62.51	4.22	0.33	0.68
2	0.72	5.51	24.05	2.05	0.65	63.17	4.20	0.37	0.68
3	0.82	6.72	23.73	0	0.34	65.12	3.78	0.31	0.68
4	0.84	7.06	21.48	0	0.01	67.04	4.13	0.28	0.70
5	0.98	7.52	21.35	0	0.16	67.46	3.24	0.26	0.70
6	1.27	5.00	12.83	0	0.16	79.07	2.56	0.38	0.82
7	1.31	5.00	12.83	0	0.41	80.03	2.19	0.21	0.84
8	1.41	4.91	10.62	0	0.21	81.91	2.21	0.14	0.86

Note. f_a is degree of aromaticity equal to $C_{ar} + CH_{ar}/(C_{ar} + CH_{ar} + C_{alk})$.

proposed a physicochemical model of thermal transformation of organic fuel, which included several independent parallel-sequential multistage stages: drying and heating of the particle before the release or ignition of volatile; the release and combustion of volatile substances near the particle; combustion of the non-volatile (coke) residue consisting of organic and mineral parts.

Figure 1 demonstrates typical curves of thermogravimetric analysis (TGA) carried out in the oxidizing medium for samples of vitrinite at different metamorphic stages (on the example of samples No. 1, 6, and 9 with $R_{o,r}$ of 0.63, 0.98, and 1.41 %, respectively). It can be seen that mass loss related to the release of hygroscopic moisture is recorded during heating of all samples to a temperature of about 150 °C.

There is a certain increase in sample mass for all vitrinite samples in the 200–315 °C temperature range: from 1 % for sample No. 1 with $R_{o,r}$ = 0.63 % and up to 2.5 % for sample No. 8 with $R_{o,r}$ = 1.41 %. Apparently, this is due to the oxygen chemisorption process in their surface. It is known that the primary oxidation products of coal organic matter are peroxide compounds, during decomposition of which new free radicals are generated [9, 15]. Decomposition reactions of peroxides and the interaction of radicals are accompanied by the release of a certain amount of heat, whereby heating of coal mass and its ignition occur. The begin-

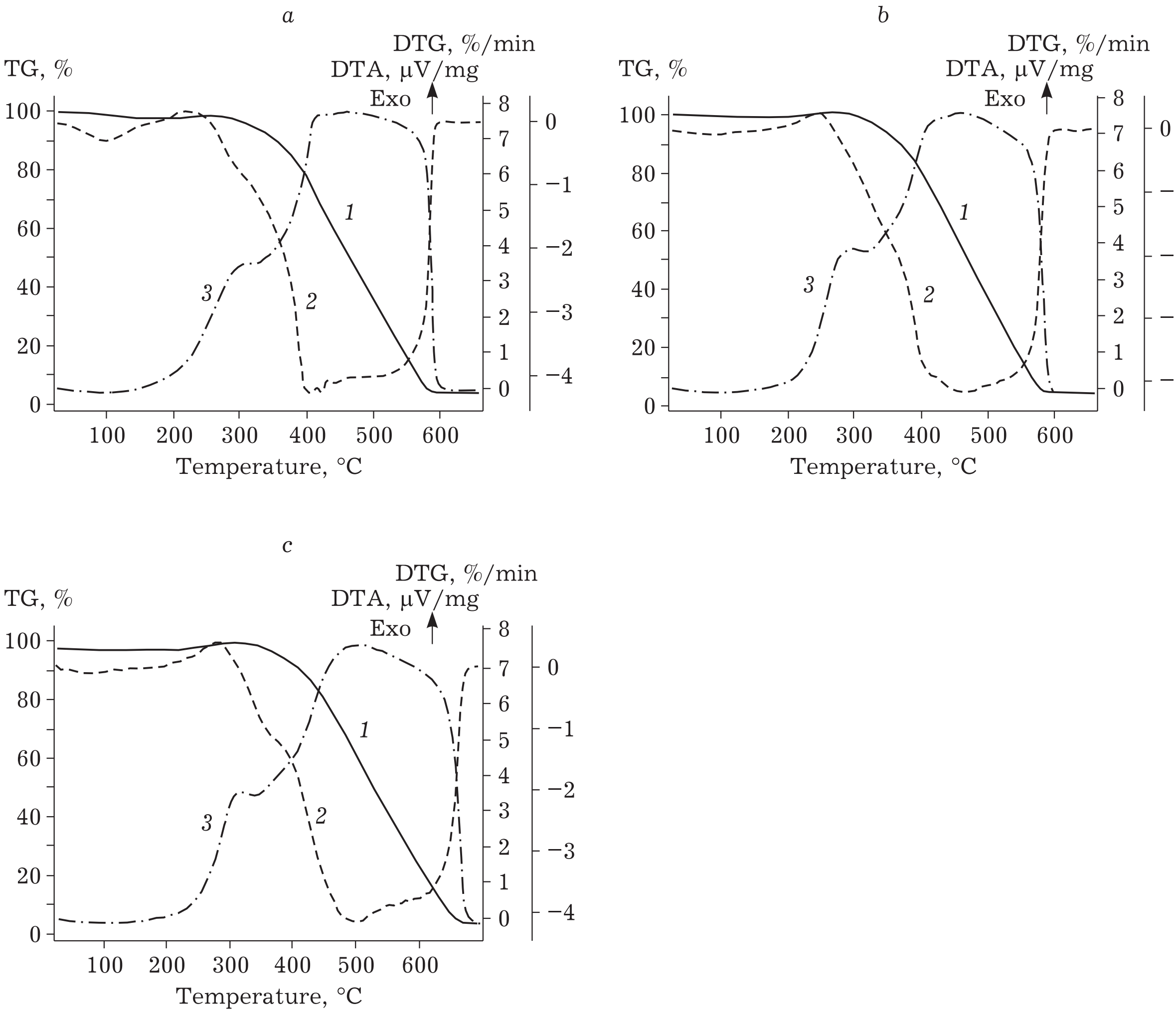

Fig. 1. Thermogravimetric analysis curves carried out in the oxidizing medium, vitrinites at different metamorphism stages. $R_{o,r}$, %: 0.63 (*a*), 0.98 (*b*), 1.41 (*c*). *1* – TG mass loss curve, *2* – DTG mass loss rate, *3* – DTA curve.

ning of the exothermic effect is recorded in the DTA curve in this temperature range.

The main mass loss by samples of vitrinite concentrates occurs in the 340–650 °C temperature range. It is worth noting that DTG curves in intense oxidation area have a typical shape repeatable from sample to sample (see Fig. 1). The beginning of oxidation is characterized by by an increase in mass loss rate; during the further temperature increase, the former is stabilized and changes in a minor way until complete combustion of coal material organic matter.

Intense mass loss of samples in all experiments is accompanied by substantial heat release. In the DTA curve, there are two exothermal effects: there is the first maximum in the of 300–320 °C temperature range, the maximum temperature of the second exothermic peak increases with an increase in the metamorphic degree of coal samples and is recorded in the 400–440 °C temperature range. These effects are supposedly related to different stages of oxygen interaction with coal matter. In the first case – with the decomposition of carbon-oxygen complexes, oxygen-containing functional groups and the direct interaction of the oxidizer with the side chains of the coal substance macromolecules and, as a consequence, the ignition of volatile substances. High-temperature maxima in the DTA curves are probably determined by the thermo-oxidative destruction of the nuclear (condensed) portion of organic matter macromolecules.

Table 4 demonstrates the results of processing of TG-curves. Comparative analysis of the findings showed that in a series of metamorphisms of the studied coal samples, the temperature range of oxidative decomposition of their organic matter increases naturally with a simultaneous shift of decomposition rate maxima to higher temperature region. This effect may be explained by the fact that the degree of aromaticity of organic matter in the studied vitrinite concentrates increases with a rise in the metamorphic stage (see Table 3). Figure 2, *a* observes a proportional correlation between their aromaticity indicator (f_a) and the final temperature of the oxidative process (T_2). For the studied vitrinites with $R_{o,r} \leq 1.41$ %, this dependence may be expressed by the first order equation. The graphical analysis also revealed a clear linear relationship between the number of carbon atoms in aromatic systems of C_{ar}^{*} ($C_{ar}^{*} = C_{ar} + CH_{ar}$), on the one hand, and the final temperature T_2, on the other one (see Fig. 2, *b*).

It is believed that according to the ignition temperature of solid fuel, one may judge of its behaviour in various technological processes [16, 17]. Figure 3 gives graphic dependencies of the ignition temperature T_1 determined using TGA against the main indicators of organic matter properties of vitrinite concentrates (C^{daf}, C_{ar}^{*}, $R_{o,r}$, and V^{daf}). It can be seen that all dependencies are linear. As demonstrated by analysis of equations and their statistic evalu-

TABLE 4

Results of thermogravimetric analysis of samples of vitrinites conducted in the oxidizing medium

Sample	V_{max}, %/min	Temperature boundaries the main decomposition, °C				Δm, mass %,
		T_1	T_{max}	T_2	$\Delta t = T_2 - T_1$	at $\Delta t = T_2 - T_1$, °C
1	4.27	355	404	587	232	85.4
2	4.10	366	491	587	221	84.6
3	4.12	378	493	607	228	84.6
4	4.15	377	510	604	227	84.5
5	4.16	382	483	609	227	84.3
6	4.17	401	496	653	252	89.9
7	4.07	404	503	658	254	89.6
8	4.16	404	500	651	247	89.0

Note. T_1 is ignition temperature of coal particles; T_{max} is temperature, at which the maximum oxidation rate is reached; T_2 is final temperature at which the coke residue is burned out; V_{max} is the maximum oxidation rate at T_{max}; Δt is oxidation temperature range; Δm is mass loss in the corresponding temperature range.

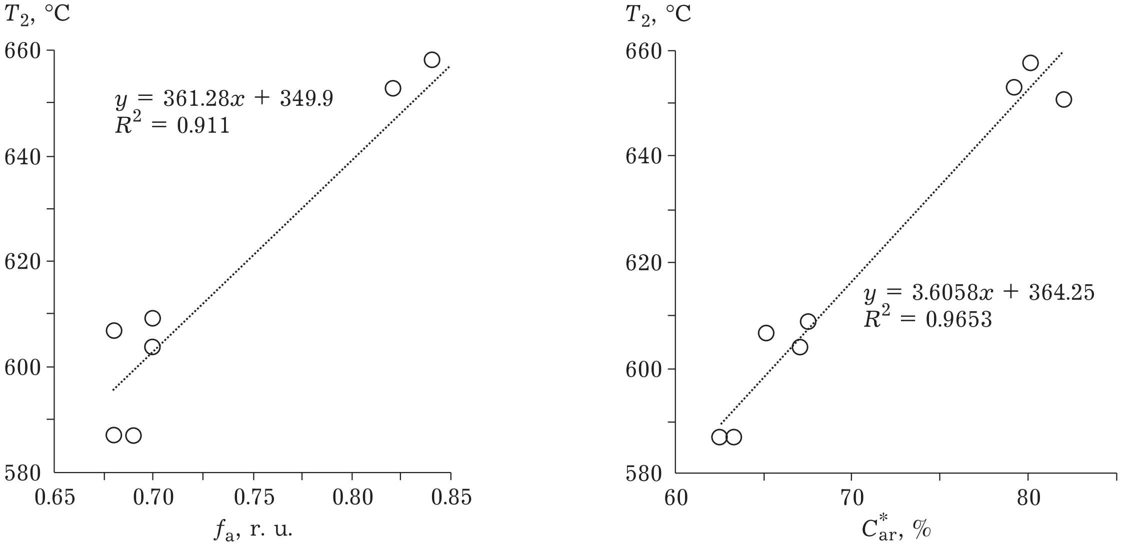

Fig. 2. Final oxidation temperature (T_2) versus aromaticity factor (f_a) (*a*) and number of carbon atoms in aromatic structures (C_{ar}) in organic matter of vitrinites (*b*) at different metamorphic stages.

ation, the studied dependencies are characterized by high correlation (0.92–0.99) and determination (0.86–0.97) coefficients.

Hence, the ignition temperature of vitrinite concentrate species depends on carbon content and structure order strength of their organic matter. An increase in its absolute value is related to a rise of the total (C^{daf}) and aromatic (C_{ar}^*) carbon in the studied samples. The ignition temperature also increases with a rise in vitrinite reflectance ($R_{o,r}$) and a reduction in organic matter yield (V^{daf}). It is worth noting that these indicators also indirectly provide evidence of structural features of organic matter in the vitrinites studied. For example, volatile matter yield reflects the thermal stability of coal organic matter (COM) that depends on the fraction of aliphatic and aromatic components of COM macromolecules [16, 17].

Paper [18] gives ignition temperature range for unoxidized coke coal of different grades and groups (Table 5). The ignition temperatures of vitrinite concentrates in the oxidizing medium determined by us using TGA are in a satisfactory agreement with the data of [18] (see Table 5).

TABLE 5

Ignition temperature (T_1) of coke coal of various grades [18] and studied vitrinites

Data of [18]			Our work	
$R_{o,r}$, %	V^{daf}, %	T_1, °C	$R_{o,r}$, %	T_1, °C
0.60–0.69	38–44	353–366	0.63	355
0.70–0.79	36–42	357–371	0.72	366
0.80–0.89	33–39	364–378	0.82	378
0.80–0.89	33–38	366–378	0.84	377
0.90–1.19	28–36	371–397	0.98	382
1.04–1.19	28–30	385–397	n/d	n/d
1.20–1.49	18–28	389–418	1.27	401
1.20–1.49	18–28	389–418	1.31	404
1.20–1.49	18–28	389–418	1.41	404

Note. n/d means no data available.

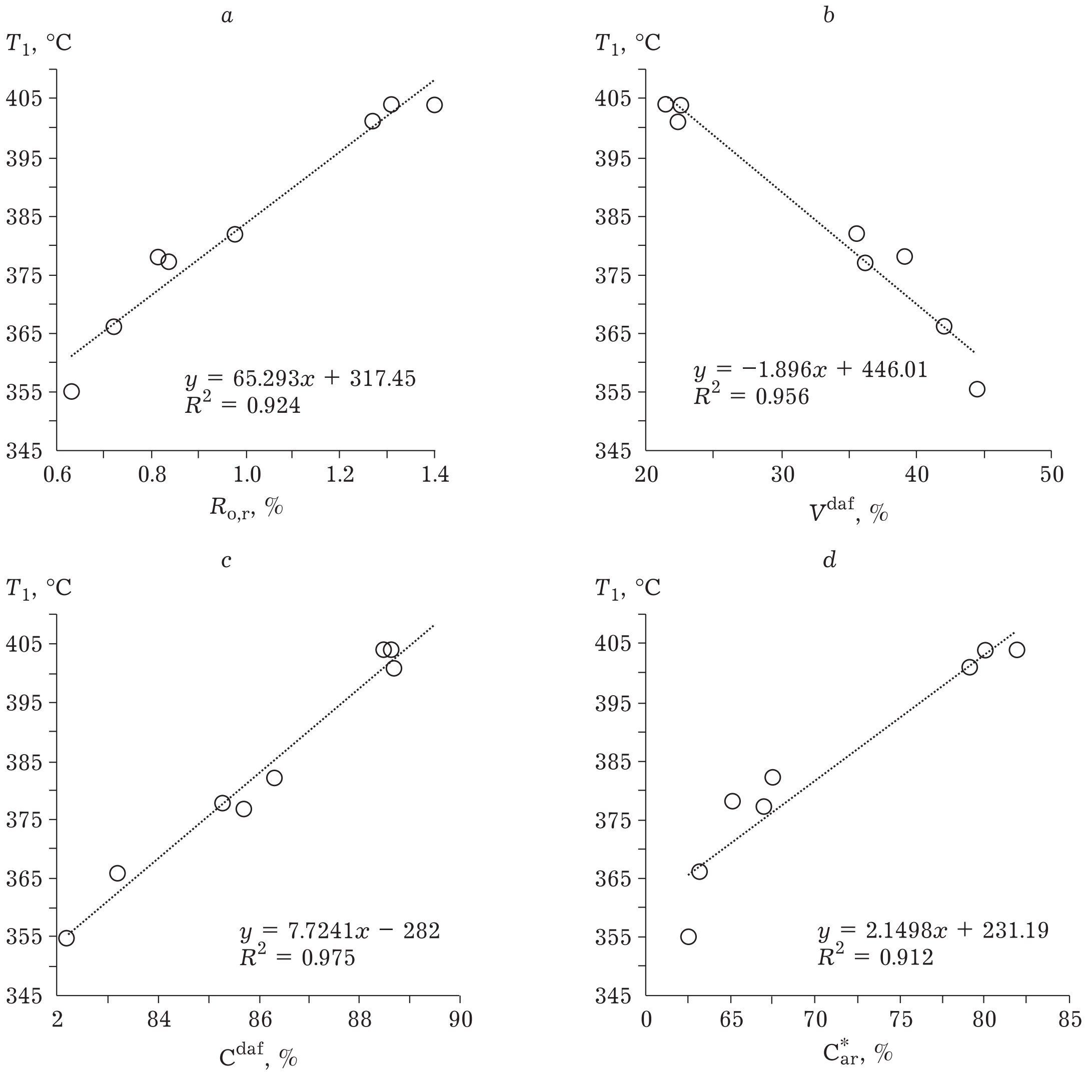

Fig. 3. Ignition temperature (T_1) of vitrinites at different metamorphic stages versus their qualitative characteristics: *a* – vitrinite reflectance ($R_{o,r}$), *b* – volatile matter yield (V^{daf}), *c* – organic matter content C^{daf}, *d* – number of carbon atoms in aromatic systems (C_{ar}).

CONCLUSION

A thermogravimetric study of eight samples of vitrinite concentrates isolated from coals at different metamorphic stages with vitrinite reflectance ($R_{o,r}$) from 0.63 to 1.41 % was carried out in the oxidizing medium. Temperature boundaries of oxidative decomposition of organic matter of the studied samples were determined. It was demonstrated that there were a natural increase in the temperature range of the oxidative process and a simultaneous shift of decomposition rate maxima to higher temperature region. A strong correlation of the ignition temperature of vitrinite concentrates and the main indicators of properties of their organic matter was revealed. It was demonstrated that the ignition temperature of the studied samples increased with a rise in their metamorphic stage ($R_{o,r}$), total (C^{daf}) and aromatic carbon (C_{ar}*) content.

As a whole, the acquired regularities are crucial and may be considered during the prognosis of the behaviour of coal and its petrographic components in oxidative conversion processes.

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