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Thermogravimetric Study of Coal Vitrinites of Different Metamorphic Stages

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Abstract

The paper presents the results of a thermogravimetric study of coal vitrinites of different metamorphic stages. It was demonstrated that initial mass loss temperature increased, the rate of gum formation and gassing decreased, and maximum thermal decomposition of coal material shifted in the DTG curve to a higher temperature region with an increase in metamorphic grade of vitrinites during their pyrolysis in inert atmosphere at 300–600 °C temperature range. When studying the effect of heating rate for the destruction process of vitrinite organic matter it was found that an increase in the maximum rate of thermal decomposition happened in the DTG curve and temperature, whereby it was reached with its increasing (from 5 to 40 °C/min) in the 300–600 °C temperature range..

Kew words: coal, vitrinite, metamorphic stages, thermogravimetric analysis, pyrolysis

INTRODUCTION

In various technological processes, including coking, coal is affected by high temperatures. Therefore, to ensure their more efficient uses characteristics of properties of coal of different genetic types and metamorphic grade characteristics of thermal properties of coal should be defined.

Fossil coal is a complex natural system of organic microcomponents (macerals) and mineral inclusions. Out of four groups of microcomponents (vitrinite, semivitrinite, inertinite, and liptinite), composing the organic matter of coal, vitrinite that is responsible for sintering ability and cokability of coal, the solubility in organic solvents, physicomechanical properties, *etc.* is of defining value for technological properties [1, 2].

The thermogravimetric method, through which one may capture certain differences in sample properties, in particular the petrographic components of coal, is one of the fastest and most convenient methods for the study of substances behaviour under conditions of constant temperature increase, which is of special interest for coal chemistry.

The purpose of the work is to find the dependence of temperature limits for thermal decomposition of coal vitrinites on a metamorphic stage.

EXPERIMENTAL

Vitrinite concentrates that were obtained by delamination of humic coal of different metamorphic stages in a mixture of carbon tetrachloride and benzene with a density of 1.27 g/cm^3 were used as study objects. Selection of solution density was defined by the fact that the maximum content of vitrinite inclusions was concentrated in fractions that float in liquids with a density of <1.3 g/cm^3 [2–4]. Samples with particle size less than 0.2 mm were subjected to analytical studies.

Technical analysis of isolated fractions was carried out by standard methods. Organic matter composition was defined by elemental analysis methods.

Petrographic analysis was performed using an automated complex for assessment of the grade composition of SIAMS-620 system (Russia) coal in oil immersion medium. Counting microcomponents was carried out automatically at an increase in reflected light of 300 times.

The degree of aromaticity (f_a) was calculated by the van Krevelen formula [5, 6] derived with regard to coal:

$f_a = (100 - V^{daf}) \cdot 12 \cdot 100/(1240C^{daf})$

where C^{daf} is coal carbon content, mass %; 12 is carbon atomic mass, 1240 is the conditional molecular mass of coke residue.

There are several methods for assessment of aromaticity degree of coal; however, the above method based on the data of thermogravimetry and elemental analysis is simplest.

Thermal analysis was carried out using Netzsch STA 409 thermal analyser under the following conditions: platinum-iridium crucible;

TABLE 1

Petrographic composition of the studied samples of vitrinite

Sample code	Petrographic parameters, %				Vitrinite reflectance		Metamorphic stage
	Vt	Sv	I	ΣFC	$R_{0,r}$, %	σ_R	
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–II
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 – vitrinite, Sv – semivitrinite, I – inertinite, ΣFC – the sum of the fusainized components, $R_{0,r}$ is vitrinite reflectance, σ_R – the standard deviation.

TABLE 2

Characteristic of the studied samples of vitrinite

Sample code	Technical analysis, %			Elemental composition, % per daf			Atomic ratio		f_a
	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	0.66
2	1.1	2.8	42.2	83.2	6.0	10.8	0.87	0.10	0.67
3	0.9	4.9	39.1	85.3	6.0	8.7	0.84	0.08	0.69
4	0.9	4.6	36.2	85.7	5.9	8.4	0.83	0.07	0.72
5	0.8	4.4	35.7	86.3	5.8	7.9	0.81	0.07	0.72
6	0.5	1.4	22.5	88.7	5.3	6.0	0.72	0.05	0.85
7	0.5	1.7	22.6	88.6	5.3	6.1	0.72	0.05	0.85
8	0.8	1.5	21.5	88.5	5.3	6.2	0.72	0.05	0.86

Note. W^a is moisture in the analysis sample, A^d is ash content, V^{daf} is volatile matter yield, daf is dry ashless condition of the sample.

heating to 1000 °C in helium medium with different heating rates that are 5, 10, 20, and 40 °C/min. The mass loss (TG) and the mass loss rate (DTG) were recorded during analysis. The following indicators were used to characterise thermal decomposition: T_{max} is temperature of maximum degradation rate; V_{max} is the rate of decomposition at the inflection point. The temperature range of the major decomposition peak in the DTG curve was determined using the tangent method: T_1 is the beginning of the process; T_2 is the end of the major thermal decomposition. The mass loss (Δm) was calculated in temperature ranges of the most intensive sample decomposition.

RESULTS AND DISCUSSION

Characteristics of studied vitrinite concentrates are given in Tables 1 and 2. The analytical findings demonstrate that vitrinite concentrates from the I to the IV metamorphic stages with index of reflection of vitrinite ($R_{0,r}$) from 0.63 to 1.41 % were studied. The degree of aromaticity of their organic matter increases, the yield of volatile matters and H/C and O/C atomic ratios decrease (see Table 2) with increasing the metamorphic stage (a rise of $R_{0,r}$ indicator).

Typical thermogravimetric curves for the resulting samples of vitrinite concentrates are presented in Fig. 1 on an example of samples Nos. 1, 6 and 9 with $R_{0,r}$ of 0.63, 0.98 and 1.41 %. Thermal decomposition for all samples is characterised by several stages, which defines the presence of several maxima in the DTG curve. The first peak in it corresponds to moisture removal; the major mass loss by samples driven by destruction of carbon-carbon bonds with isolation of volatile products and the formation of semicoke happens at higher temperatures (in 300–600 °C range). The mass loss by samples in a high-temperature region (750–900 °C) is minor and a clear peak is not observed in the DTG curve.

The results of thermogravimetric analysis carried out at a 10 °C/min heating rate of vitrinite concentrate samples are given in Table 3.

The fact that the rate of gassing and gum formation decreases, temperature of the beginning of mass loss T_1 increases, and the maximum thermal decomposition T_{max} of coal material

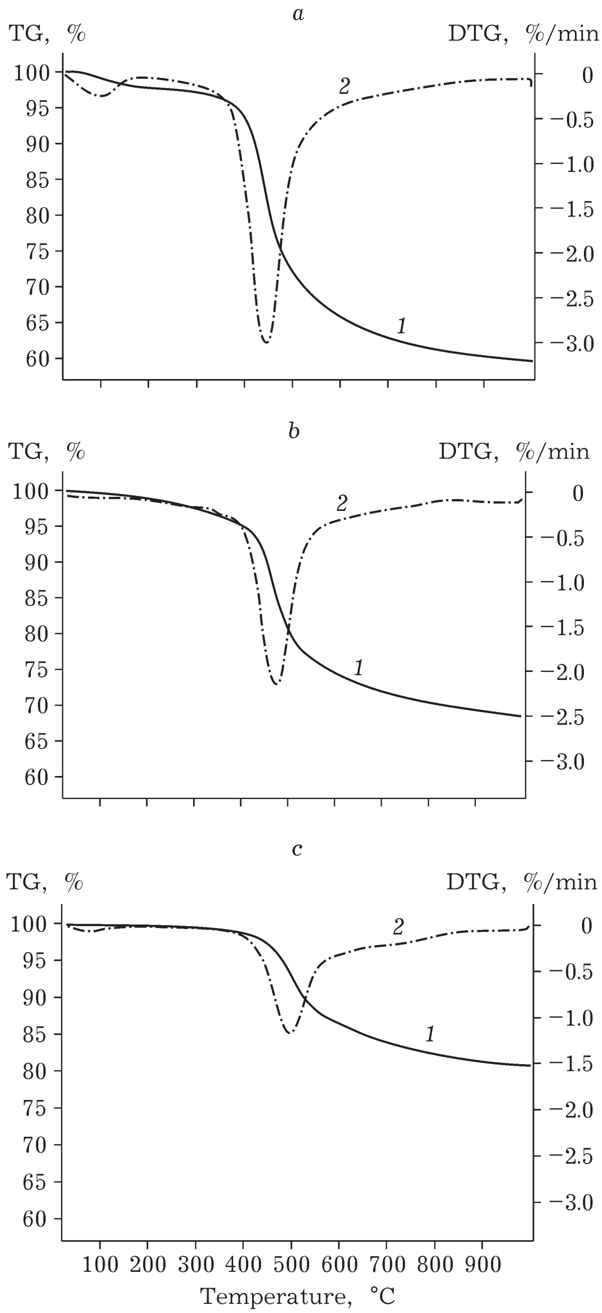

Fig. 1. Thermogravimetric curves (vitrinites of different metamorphic stages). $R_{0,r}$, %: 0.63 (*a*), 0.98 (*b*), 1.41 (*c*); *1* – mass loss curve in TG, *2* – mass loss rate in DTG.

shifts to a high temperature region with increasing metamorphic grade is typical for pyrolysis of the above samples of vitrinites. It is noteworthy that herewith, the temperature range of the major decomposition ($\Delta t = T_2 - T_1$) increases with increasing the degree of metamorphism. Maximum temperature (T_{max}) at the DTG curve probably has a quite certain physi-

TABLE 3

Results of thermogravimetric analysis of vitrinite samples carried out at heating rate in 10 °C/min

Sample code	V_{max}, %/min	Temperature limits of the main decomposition, °C				Δm, mass %, at temperatures, °C	
		T_1	T_{max}	T_2	$\Delta t = T_2 - T_1$	$\Delta t = T_2 - T_1$	260–900
1	3.21	404	446	506	102	31.6	37.4
2	3.05	412	458	514	102	30.1	35.5
3	2.61	423	471	526	103	25.3	31.7
4	2.50	427	472	530	103	24.4	29.5
5	2.29	430	474	537	107	21.5	29.0
6	1.43	449	486	566	118	16.0	19.4
7	1.29	446	494	568	122	14.7	19.1
8	1.21	451	496	576	125	14.3	18.1

Note. T_1 is temperature of onset of the main decomposition; T_{max} is maximum decomposition temperature, T_2 is main decomposition final temperature, Δt is main decomposition temperature range, V_{max} is maximum mass loss rate in main decomposition temperature range, Δm is mass loss in an appropriate temperature range.

cal meaning: it is the quantitative measure of the thermal stability of organic matter in vitrinite concentrates. Indeed, from the data of Fig. 2 it can be seen that there is a proportional relationship between vitrinite reflectance index and maximum temperature of DTG. This dependence could be expressed by the first order equation for the studied vitrinites. Graphical analysis also demonstrated that there was also a clear straight-line correlation between $R_{0,r}$ from one side and the maximum rate of the main period of mass loss – from another (Fig. 3).

Vitrinite reflectance ($R_{0,r}$, %) was compared with mass loss defined in the gravimetric curve in 260–900 °C temperature range (Fig. 4). Analysis demonstrated that there was a direct correlation between these parameters (correlation coefficient is 0.979).

To study the effect of the rate of an increase in temperature of the pyrolysis process on characteristics of thermograms the following indica-

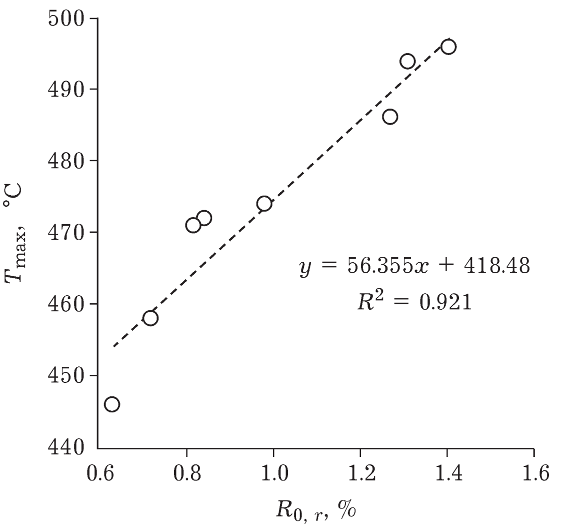

Fig. 2. Maximum temperature (T_{max}) of mass loss in the DTG curve *vs*. metamorphic stage of vitrinites ($R_{0,r}$).

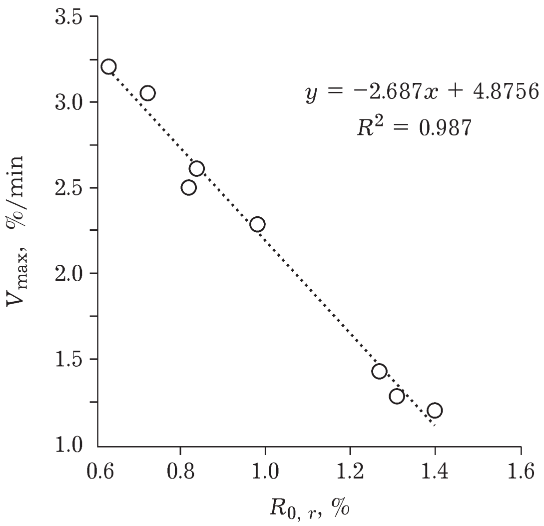

Fig. 3. Maximum rate of the main period of mass loss (V_{max}) *vs*. metamorphic stage of vitrinites ($R_{0,r}$).

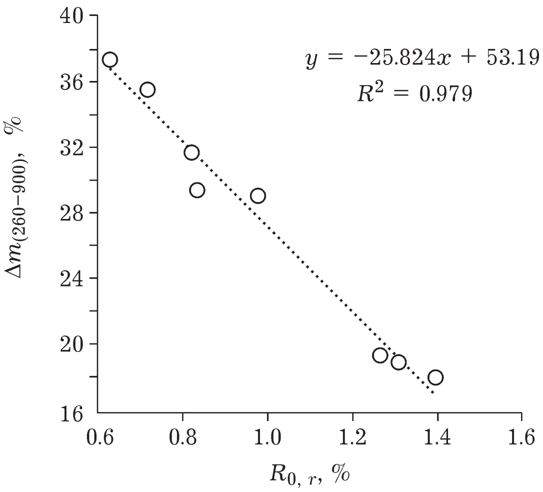

Fig. 4. Mass loss (Δm) in the 260–900 °C temperature range *vs.* metamorphic stage of vitrinites ($R_{0,r}$).

tors were studied: temperature (T_{max}), maximum destruction rate (V_{max}) and the temperature range of the main decomposition ($\Delta t = T_2 - T_1$). The results of processing of thermogravimetric curves obtained at different heating rates (5, 10, 20, and 40 °C/min) are given in Fig. 5.

Analysis of findings demonstrates that an increase in the rate of temperature rise during thermal destruction of all samples of vitrinite concentrates results in an increase in the maximum rate of thermal decomposition V_{max} (Figs. 4 and 5, *a*) and temperature T_{max}, whereby it is reached (see Figs. 4 and 5, *b*). The curves of the dependence of the temperature interval on the heating rate have a more complicated form (see Figs. 4 and 5, *c*). Broadening of the temperature range of the major decomposition of their organic matter is observed for all samples of vitrinite concentrates at 10 °C/min heating rate. However, a trend to decreasing its value is noted at higher heating rates (20 and 40 °C/min). Maximum narrowing of temperature ranges is observed for vitrinite concentrates of samples Nos. 4 and 5 with the $R_{0,r}$ index of 0.82 and 0.84 %, respectively.

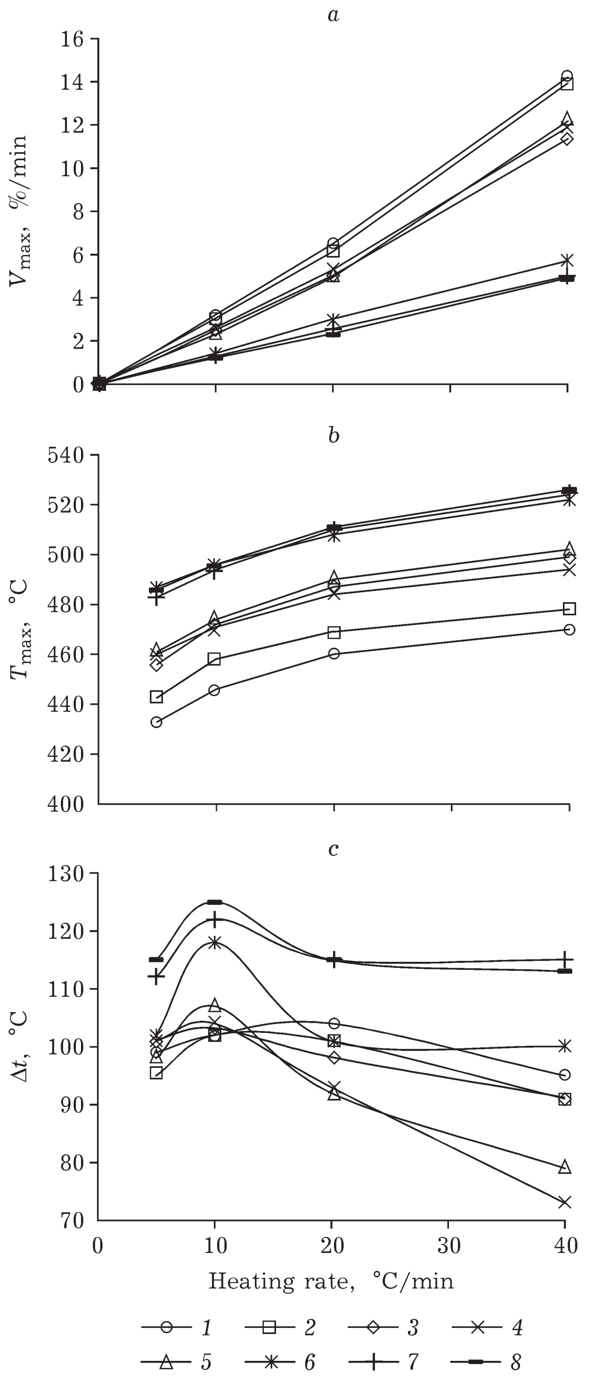

Fig. 5. Effect of heating rate on the maximum rate (*a*), temperature of reaching the maximum rate (*b*), and temperature range of the main decomposition (*c*) during thermal destruction of vitrinite organic matter of different metamorphic stages (curve number corresponds to sample number in Table 1).

CONCLUSION

A thermogravimetric study of eight samples of vitrinite concentrates isolated from coal of different metamorphic stages was carried out. It was demonstrated that temperature of onset of mass loss increased; the rate of the main period of gum formation and gassing decreased, and maximum thermal decomposition of coal material in the DTG curve is shifted to a higher temperature region with an increase in the metamorphic grade of vitrinites during their pyrolysis in inert atmosphere in the 260–600 °C temperature range.

When studying the effect of heating rate on the destruction process of vitrinite organic matter it was found that an increase in the maximum rate of thermal decomposition happened in the DTG curve and temperature, upon which it was reached, happened with a heat rate increase (from 5 to 40 °C/min) in 260–600 °C temperature range. Herewith, temperature range value of the main decomposition of organic matter had a trend to reduction for all samples in 20 and 40 °C/min heating rates.

The dependence for the maximum rate of the main period of gum formation and gassing on metamorphic grade can be used as the basis for preliminary assessment of coal from new fields. As a whole, the obtained regularities are important when predicting coal behaviour and its petrographic components in various coal refining processes (laminar coking, production of moulded coke, medium temperature coking, *etc.*).

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