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INFLUENCE OF THE COMPOSITION, STRUCTURE, AND PROPERTIES ON THE IGNITION'S TEMPERATURE OF COAL

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Abstract

The reactions of coal with the materials used in determining the ignition temperature of unoxidized coal according to Ukrainian State Standard DSTU 7611:2014 are analyzed. The ignition temperature of various types of coal from Ukraine, Russia, Canada, Australia, the Czech Republic, Poland, and Indonesia is determined. The influence of the composition, structure, and properties of the coal on its ignition temperature is assessed. The ignition temperature of the unoxidized coal is found to be closely related to the content of organic carbon C^{daf} and aromatic carbon C_{ar}, the structural parameter δ characterizing the degree of saturation of the coal's organic mass, and also the vitrinite reflection coefficient R_0 and the yield of volatiles V^{daf}.

Keywords: coal; ignition temperature; properties of coal; mathematical formulas.

1. Introduction

The lowest temperature at which coal can be ignited is referred to as the ignition temperature. The ignition temperature for a certain coal is variable under different conditions because of the complexity of the ignition process. For the convenience of comparison, the ignition temperature is specified in terms of specific conditions. Table 1 shows the ignition temperatures of different types of coal. Table 2 presents the range of ignition temperature $t_{ig.un}$ of unoxidized coking coal according to [1].

Table 1. Ignition temperatures of different types of coal

Coal type	Ignition temperature, °C
Lignite	250–450
Bituminous	400–450
Anthracite	700–800

Table 2. Ignition temperature of unoxidized coal samples

Coal rank	Ignition temperature, °C
G	320–340
Zn	350–360
K	365–370
OS	375–380

Note that the some intervals were not found to include the ignition temperatures of any unoxidized coal in [1]: in particular, 340–350°C, 360–365°C, and 370–375°C. In our view, these gaps would be filled if further tests were conducted. In addition, the classification adopted by the authors included no information regarding the quality of the coal ranks. For example, for coal of each specific rank, no information was provided regarding the range of the mean vitrinite reflection coefficient, volatile matter, or the plastic-layer thickness.

Accordingly, given the continuing introduction of oxidation measurements in the quality control of incoming coal at Ukrainian coke plants, our goal in the present work is to study the

factors that affect the ignition temperature of unoxidized coal, for a wide range of coal samples. It should be noted that the effect of the mineral part of the coal on its ignition temperature in this work has not been investigated.

2. Experimental

The introduction of Ukrainian State Standard DSTU 7611:2014 «Coal. Method for the determination of oxidation and degree of oxidation» in the quality control of coal deliveries at coke plants permits characterization of the coal in terms of its ignition temperature.

The installation for determination of coal oxidation is a laboratory complex (Fig.1) comprising electric furnace 1, copper block 2, thermocouples 3 and 4, furnace temperature regulator 5, four sets of test tubes 6, burettes 7, glasses 8, two laboratory supports 9. The main component of the installation is an electric furnace with copper block where the coal sample is heated in order to determine its ignition temperature.

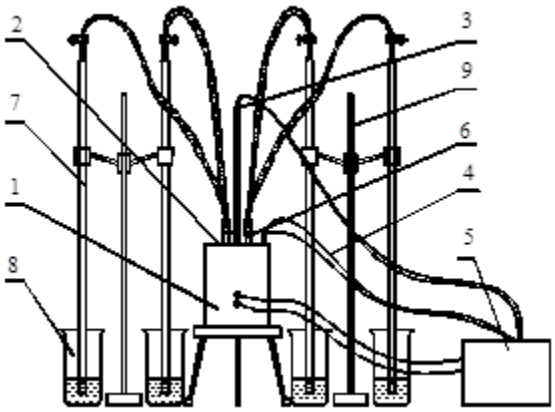

Fig. 1. Installation for determine of coal's inflammation temperature: 1 – electric furnace; 2 – copper block; 3, 4 – thermocouples; 5 – furnace temperature regulator; 6 – test tubes; 7 – burettes; 8 – glasses; 9 – laboratory supports.

To determine the ignition temperature $t_{ig.un}$ of reduced (unoxidized) coal, we mix 0.5 g of coal with 0.25 g of sodium nitrite ($NaNO_2$) and 0.0125 g of benzidine (4,4-diaminodifenyl).

We know that, on heating in the absence of air, coal will undergo thermal destruction; this complex process will depend on the composition and structure of the coal's organic mass and the heating conditions. In the initial stage of heating (up to 350–400°C), we primarily observe decomposition of their organic mass, accompanied by the formation of water, various oxidebearing gases, and low-molecular hydrocarbons [2]. The use of sodium nitrite as an oxidant is based on its ability to melt at 271°C, with subsequent decomposition [3-4]:

$$2NaNO_2 \xrightarrow{t} Na_2O + \cdot NO + \cdot NO_2. \quad (1)$$

In our view, the appearance of the reactive free radicals ·NO and NO_2 (as decomposition products of sodium nitrite) in a mixture with coal provokes oxidation of the coal's thermal destruction products in a free-radical chain [2, 5]. Consequently, in the presence of sodium nitrite, the usual thermal destruction of coal is converted to thermooxidative destruction [5-6]. The process becomes autocatalytic.

According to handbook data, benzidine (4,4'-diaminodiphenyl), with the chemical formula $C_{12}H_{12}N_2$, takes the form of white or pale yellow crystalline needles that darken in the light and in air, are poorly soluble in water, and dissolve readily in alcohol and ether. Its molar mass is 184.24 g/mol, and its melting point is 122–125°C. In its chemical properties, benzidine is a typical aromatic amine [7].

By mixing the coal sample with the oxidant (sodium nitrite) and heating the mixture, we ensure that vigorous coal oxidation on reaching a certain temperature, with the appearance of a flame. The addition of benzidine, which is known to be a reducing agent, neutralizes the

excess free radicals in the reaction mixture. Ultimately, that results in an ignition temperature close to that for fresh unoxidized coal.

The resulting mixture is transferred into a dry test-tube. The test-tubes are closed up with rubber stoppers with glass tubes inserted into, which are connected to burettes with rubber (silicone) tubes; burettes are filled with water and then the open end is immersed into a glass of water to a depth of 20–30 mm. The system is checked for leaks. The burette is connected to a test-tube turning the tap.

The test-tubes are dropped into a block of a device which enables simultaneous heating of the four test-tubes. In the center of the block a recording unit of thermocouple is set which generate heating at a rate of 5°C/min. At the moment of explosion (ignition of the coal sample), which is accompanied by a sharp decrease of the water level in the burette as a result of the pressure of gases evolved, the registration of temperature is taken.

3. Results and discussion

In all, we consider 170 coal samples: 50 from Ukraine; 78 from Russia; and 42 from elsewhere (the United States, Canada, Australia, the Czech Republic, Poland, and Indonesia).

Table 3–5 presents the maximum, minimum, and mean values of the technological, petrographic characteristics, ultimate composition and structural parameters of the coal samples [8–10]. We see in table 3 that the samples are characterized by low analytical moisture (which indirectly indicates lack of oxidation) and ash content. The ignition temperature increases with increase in the metamorphic development of the coal.

Table 3. Technological properties of coal samples

Value	Technical analysis, %				Ignition temperature of unoxidized coal $t_{ig.un}$, °C
	W^a	A^d	S^d_t	V^{daf}	
Maximum	3.8	12.4	3.26	43.4	418
Minimum	0.2	3.7	0.13	16.7	341
Mean	1.4	8.4	0.83	30.0	384

Table 4. Petrographic characteristics of coal samples

Value	Mean vitrinite reflection coefficient *Ro*, %	Petrographic composition, %				
		Vt	*Sv*	*I*	*L*	*ΣFC*
Maximum	418	99	4	77	10	79
Minimum	341	20	0	1	0	1
Mean	384	71	0.8	26	1,6	26.5

Table 5. Elementary composition and structural parameters of coal samples

Value	Ultimate composition, %					Structural parameters	
	C^{daf}	H^{daf}	N^{daf}	S^d_t	$O_d{}^{daf}$	δ	C_{ar}, %
Maximum	99	4	77	10	79	10.42	35.19
Minimum	20	0	1	0	1	7.62	14.30
Mean	71	0.8	26	1,6	26.5	9.18	23.03

The petrographic characteristics in table 4 indicate that the coals are not identical in petrographical composition. Some coals are characterized by elevated total content of fusinized components (79 %).

Table 5 presents the ultimate composition and structural characteristics of the coals' organic mass. It is evident that the carbon content (C^{daf}) increases uniformly from 80.79 to 91.19 % with increase in the mean vitrinite reflection coefficient (R_0).

The hydrogen content varies from 4.64 to 6.42 %. As a rule, the oxygen content declines at later metamorphic stages. The degree δ of incomplete saturation of unit mass of the coal's organic mass with hydrogen was calculated as:

$\delta = C^{daf}/6 - H^{daf} + N^{daf}/14$, (2)

where C^{daf}, H^{daf}, and N^{daf} are the concentrations of the corresponding elements in the coal's organic mass, %.

The content C_{ar} of aromatic carbon in the coal's organic mass with respect to the total carbon content was calculated as:

$C_{ar} = 3.4 \cdot C^{daf}/(100 - C^{daf})$. (3)

The structural characteristics indicate increase in content of cyclic polymerized carbon in the coal macromolecules as a result of polycondensation in the course of metamorphism. Thus, the structural parameter δ increases from 7.62 to 10.42. An analogous picture is seen for the content of aromatic carbon in the coal's organic mass.

Overall, our analysis shows that the coal samples differ markedly in their technological properties, petrographic and structural characteristics. This will be associated with different ignition temperature of coals.

Table 6 presents pair correlations between individual properties of the coal and the ignition temperature $t_{ig.}$ The significance of the correlation coefficients r is verified by comparison of the product $|r|\sqrt{n-1}$ with its critical value H at the specified confidence level P [11]. For P = 0.999, in the case of 170 samples, H = 3.291. Table 6 presents the r and $|r|\sqrt{n-1}$ values for each correlation.

Table 6. Pair correlation coefficient r and $|r|\sqrt{n-1}$ for the ignition temperature with various coal characteristics

Statistical correlation	V^{daf}	Vt	ΣFC	R_0	C^{daf}	H^{daf}	$O_d{}^{daf}$	δ	C_{ar}
R	-0.915	-0.389	0.410	0.891	0.914	-0.637	-0.113	0.880	0.910
$\|r\|\sqrt{n-1}$	10.763	3.827	4.051	7.878	10.901	6.106	1.218	9.949	7.974

As we see, the highest r values (0.88–0.915) are found for the correlation of $t_{ig.un}$ with V^{daf}, R_o, C^{daf}, C_{ar}, and δ which characterize the composition, structure, and properties of the coal's organic mass. Those correlations also correspond to the highest values of $|r|\sqrt{n-1}$, which indicates their high reliability.

In Figs. 2–6, we plot the ignition temperature $t_{ig.un}$ against the most significant characteristics of the coal. We see that these are linear plots.

On that basis, we may conclude that $t_{ig.un}$ depends on the carbon content and the structural ordering of the coal's organic mass. Increase in $t_{ig.un}$ is associated with increase in the total coal content (C^{daf}) and the content of aromatic carbon (C_{ar}), as well as the degree of saturation of its structure (δ).

The ignition temperature also increases with increase in the vitrinite reflection coefficient R_o and decrease in volatile matter V^{daf}. Note that these characteristics also indirectly reflect the structure of the coal's organic mass. The vitrinite reflection coefficient is associated with the presence of cyclically polymerized carbon in the coal's organic mass. The volatile matter reflects the thermal stability of the coal's organic mass, which depends on the proportions of aliphatic and aromatic components in the macromolecules of the coal's organic mass.

An increase in the ignition temperature with coal rank was clearly observed in findings other authors [12–14].

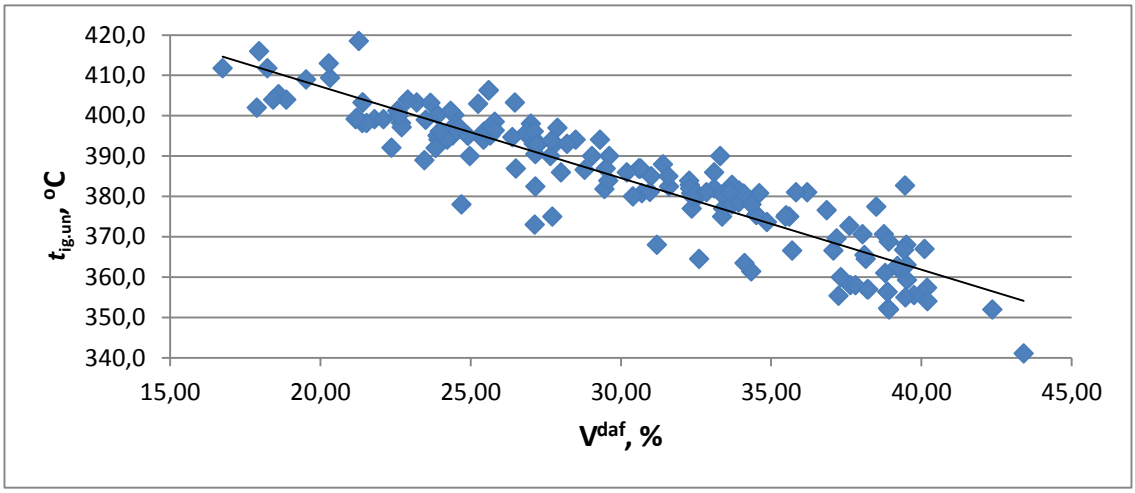

Fig. 2. Dependence of $t_{ig.un}$ on V^{daf}

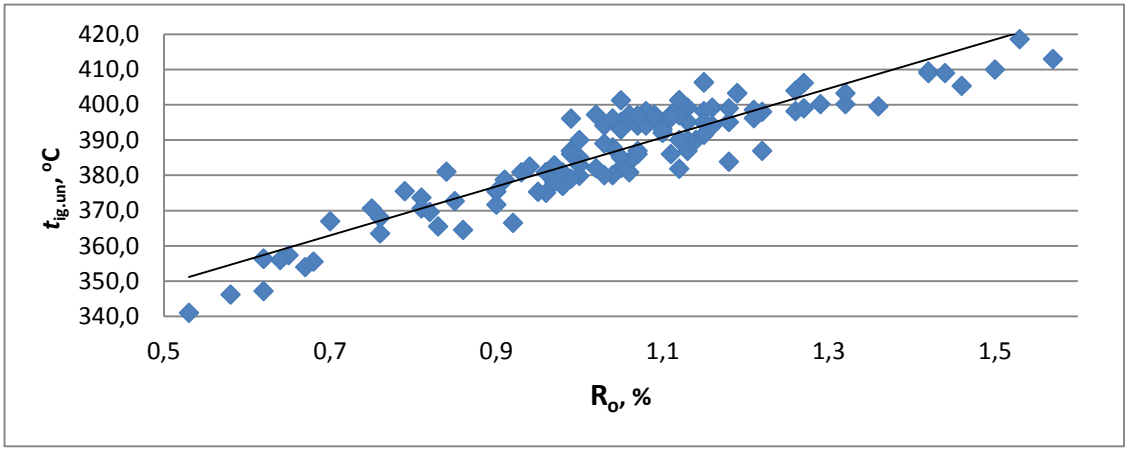

Fig. 3. Dependence of $t_{ig.un}$ on R_0

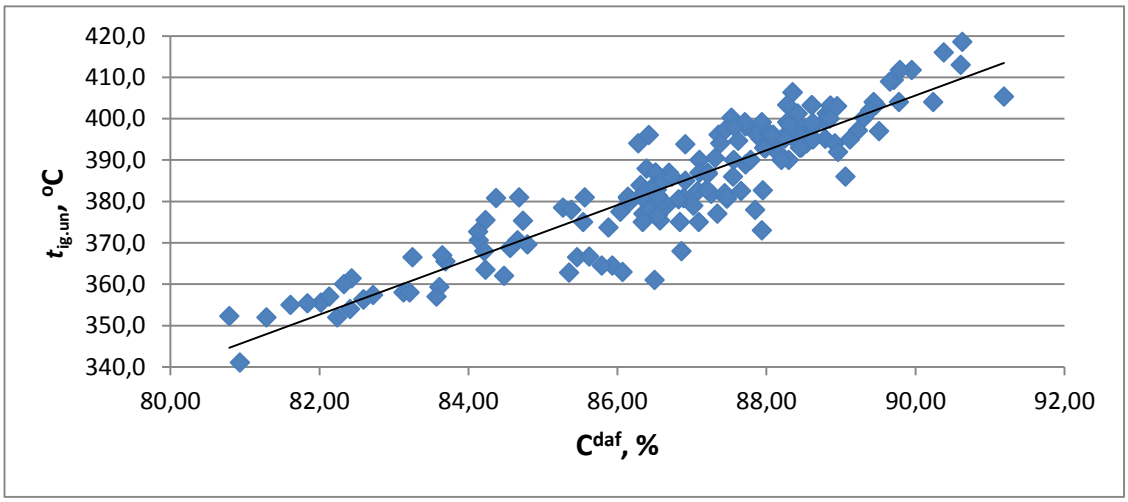

Fig. 4. Dependence of $t_{ig.un}$ on C^{daf}

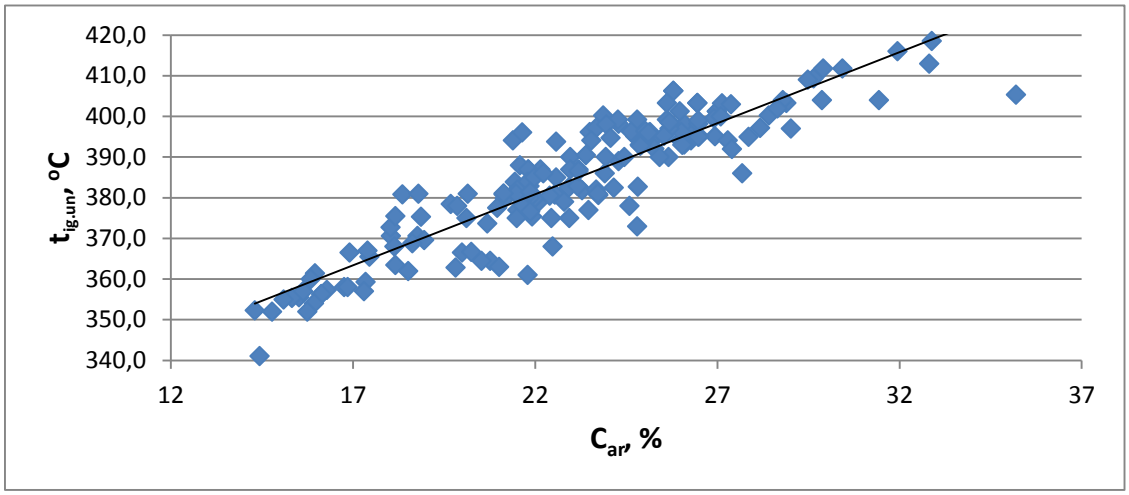

Fig. 5. Dependence of $t_{ig.un}$ on C_{ar}

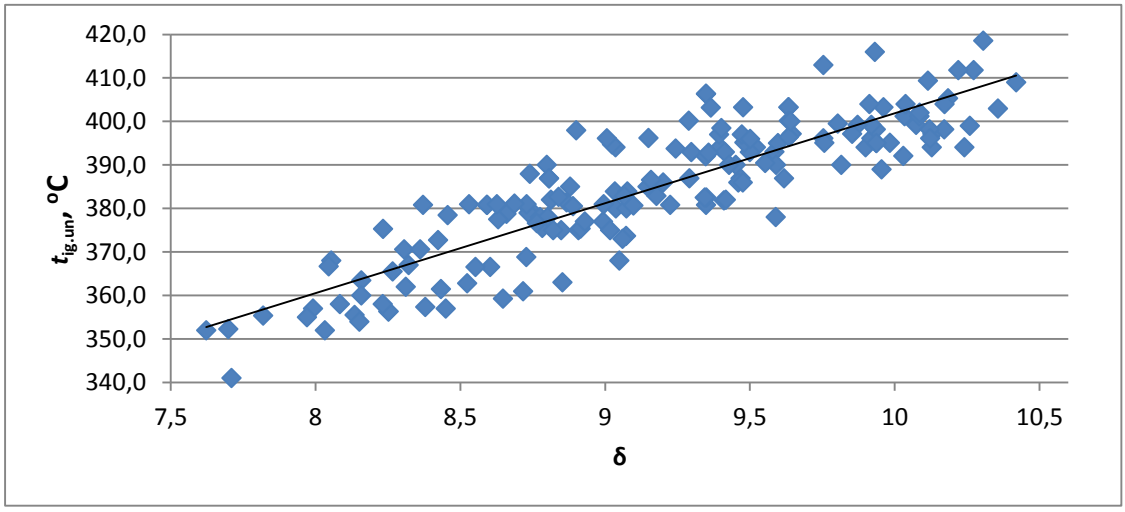

Fig. 6. Dependence of $t_{ig.un}$ on δ

Table 7 describes the dependence of $t_{ig.un}$ on the selected characteristics in Eqs. (4)–(8), with corresponding statistical estimates. Analysis shows high values of the correlation coefficient (0.88–0.92) and the determination coefficient (77.4–84.2 %) for these formulas.

Table 8 presents the ignition temperatures calculated from Eqs. (5) and (4) for different coal ranks and groups in accordance with Ukrainian State Standard DSTU 3472:2015.

Table 7. Mathematical equations and corresponding statistical assessments

Eq.	Mathematical form	Statistical assessment	
		the multiple correlation coefficient, *r*	the determination coefficient, *D*, %
(4)	$t_{ig.un} = -2.2691 \cdot V^{daf} + 452.59$	0.91	83.7
(5)	$t_{ig.un} = 69.31 \cdot R_0 + 314.47$	0.92	84.2
(6)	$t_{ig.un} = 6.6134 \cdot C^{daf} - 189.63$	0.91	83.7
(7)	$t_{ig.un} = 3.4929 \cdot C_{ar} + 304.04$	0.91	82.7
(8)	$t_{ig.un} = 20.673 \cdot \delta + 195.16$	0.88	77.4

Table 8. Ignition temperature of coking coal samples (Ukrainian State Standard DSTU 3472:2015)

Coal	Designation		Mean vitrinite reflection coefficient R_o, %	Volatile matter V^{daf}, %	Ignition temperature, $t_{ig.un}$, °C		
	rank	group			from Eq. (5)	from Eq. (4)	aggregate interval
Gas coal	G	G1	0.60–0.69	38–44	353–366	356–362	353–366
		G2	0.70–0.79	36–42	357–371	363–369	357–371
Lean bituminous gas coal	GZhO		0.80–0.89	33–39	364–378	370–376	364–378
Bituminous gas coal	GZh		0.80–0.89	33–38	366–378	370–376	366–378
Bituminous coal	Zh		0.90–1.19	28–36	371–389	377–397	371–397
Coke-grade coal	K	K1	1.04–1.19	28–30	385–389	387–397	385–397
		K2	1.20–1.49	18–28	389–412	398–418	389–418
Lean coking coal	OS		1.50–1.69	14–22	403–421	418–432	403–432

In Table 8, in contrast to Table 2, values of R_o and V^{daf} are given for each coal rank or group, and there are no intervals within the range that do not contain ignition temperatures.

4. Conclusions

The reactions of coal with the materials used in determining the ignition temperature ($t_{ig.un}$) of coal according to Ukrainian State Standard DSTU 7611:2014 were analyzed. The influence of the composition, structure, and properties of various types of 170 coal samples from Ukraine, Russia, Canada, Australia, the Czech Republic, Poland, and Indonesia on its ignition temperature was assessed.

The influence of the carbon content and the structural ordering of the coal's organic mass on the ignition temperature of coal were determined. Increase in $t_{ig.un}$ (from 341 to 418 °C) with increase in the total coal content of carbon (from 80.79 to 91.19 %) and the content of aromatic carbon (from 14.30 to 35.19 %), as well as the degree of saturation of its structure (from 7.62 to 10.42) were defined. Correspondingly, increase in the yield of volatiles (16.7 to 43.4 %) and decrease in the vitrinite reflection coefficient (1.60 to 0.53 %) with decrease in the ignition temperature were associated.

The ignition temperatures for different coal ranks and groups in accordance with Ukrainian State Standard DSTU 3472:2015 were calculated.

Symbols

W^a	moisture in the analysis sample, %;
A^d	ash content of coal in the dry state, %;
V^{daf}	volatile matter in the dry ash-free state, %;
S_t^d	sulphur of coal in the dry state, %;
C^{daf}, H^{daf}, N^{daf}, O^{daf}	carbon, hydrogen, nitrogen and oxygen in the dry, ash-free state, %;
R_0	mean vitrinite reflection coefficient, %;
Vt	vitrinite, %;
Sv	semivitrinite, %;
I	inertinite, %;
L	liptinite, %;
ΣFC	sum of fusinized components, %;
Δt	oxidation index, °C;
d_0	degree of oxidation, %;

$t_{ig.r}$ ignition temperature of reduced coal, °C;
$t_{ig.o}$ ignition temperature of oxidized coal, °C;
t_{ig} ignition temperature of initial tested coal, °C;
δ degree of saturation of its structure;
C_{ar} content of aromatic carbon, %.

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