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Pore Structure Characteristics and Reactivity of Coal Semicokes

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Abstract

The paper presents research results on the pore structure and the reactivity of semicoke derived from LF, LFG, G, F, and C coal by low-temperature pyrolysis at 600 °C in the Fisher vessel. It is certified that the development of pore structure upon semi coking depends on the nature of the initial raw materials because when the degree of metamorphism is increased, the specific surface area of semicoke derived therefrom is reduced. As demonstrated by comparative analysis, semicoke derived using coal of a higher degree of metamorphism is characterised by reduced reactivity towards oxygen. The correlation between the temperature of the beginning of mass loss (T_1) and that of maximum mass loss rate (T_{max}) of oxidative breakdown for the investigated samples of semicoke vs its specific surface area was found. It is stated that T_1 and T_{max} indicators are reduced when the specific surface area of semicoke increases.

Key words: coal, low-temperature pyrolysis, semicoke, pore structure, thermogravimetric analysis, oxidative breakdown

INTRODUCTION

The ability of coal to undergo chemical transformations upon heating is grounds for all known methods of its pyrogenous processing. Thermal decomposition processes for separate classes of organic compounds that are a part of coal organic matter proceed in the 300–600 °C temperature range, after which structurization processes are prevailing in solid residues from carbonization [1, 2]. This indicates that the process of transformation of coal into semicoke is multistage and coke medium is formed stepwise via the stage of semicoke formation.

Lately, when investigating properties of semicoke, its porosity has attracted particular attention, as it is the latter that determines its reactivity, in particular when melting metals [3–6]. Most research papers explore the pore structure of

high-temperature cokes [7–10], whereas semicoke porosity has been investigated to a lesser extent [11]. However, research in this area allows clarifying regularities of the transformation of pore structure upon coking. The results of such research are also required to improve process procedures for preparation of coal-based carbon sorbents. Traditional techniques of their production involve the carbonisation step of the initial material to make the primary pore structure and the activation stage directly linked to the reactivity of carbonisates towards various oxidizing agents (air oxygen, CO₂, and water vapour) [12].

The paper presents research results on the pore structure of semicoke derived using coal of various matrix compositions and on the determination of its reactivity towards oxygen by thermogravimetric analysis.

EXPERIMENTAL

Five samples of coal were used for low-temperature pyrolysis. The former was sampled in various coal mining enterprises of the Kuznetsk Coal Basin and included grades LF (Alekseevskaya mine), LFG (Kotinskaya mine), and G (Kirov mine), 39 (Karagaylinskoye Mine Management), and 50 (Berezovskaya mine).

Technical analysis of coal was carried out using standard techniques. The composition of coal organic matter was determined by elemental analysis.

Petrographical analysis was performed using an automated system of assessment of coal grade SIAMS-620 (Russia) in the oil immersion medium. Calculation of microcomponents was carried out automatically with 300× magnification in reflected light. Assignment of coal samples to the grade composition was carried out in accordance with the uniform classification of coal and process parameters based on values of vitrinite reflectance ($R_{o,r}$), a sum of fusainized components (ΣFC), and volatile matter yield (V^{daf} , %).

The semi coking of coal was performed in the Fisher vessel by the standard procedure according to GOST 3168-93 (ISO 647:1974). The key point of the standard method consists in the heating of a sample of the test fuel in a glass vessel (100 cm³ capacity) as high as 600 °C and determination of yield of primary resin (T_{sc}) and pyrogenetic water (W_{sc}) followed by their separation, and also the output of semicoke (sC), and gas products (G_{sc}).

The removal of pyrogenetic water was carried out by the Dean-Stark method. The latter assumes the formation of the azeotrope comprising water and a solvent which is distilled off into the Dean-Stark adapter with subsequent separation of water and the solvent after cooling. The content of the primary resin of semi-coking is determined as the difference between the mass of the resulting condensate and pyrogenetic water. The yield of semicoke is determined by the weight method.

The specific surface area value (S_{BET} , m²/g) and pore structure characteristics (total pore volume, V_{Σ} , cm³/g, meso- and micropore volumes (V_{meso} and V_{micro} , cm³/g) of the investigated samples of carbon materials were acquired using analysis of N₂ adsorption/desorption isotherms at -195.97 °C (77.4 K). The latter were measured with an ASAP-2020 vacuum static system. Prior to absorptive measurements, the investigated samples were vacuumed directly in the special port of the device at 350 °C for 15 h until a re-

sidual pressure of about 0.005 mm of Hg. Measurements of N₂ adsorption/desorption isotherms were carried out in the region of equilibrium relative vapour pressures between 10⁻³ and 0.095 P/P_0 . The average pore diameter was assessed according to the formula $D_{av} = 4V_{\Sigma}/S_{BET}$. The macropore diameter was determined *via* the formula $V_{macro} = V_{\Sigma} - (V_{micro} + V_{meso})$.

In order to determine the reactivity of semicoke (particle size of below 0.2 mm) towards air oxygen, the method of thermogravimetric analysis (TGA) is widely used when exploring carbon-containing materials of various structures, surfaces and porosities [3, 13–16]. The technique is notable for experiment simplicity and an opportunity to be used to acquire gravimetric curves of thermal analysers of various brands, a great deal of informativity of the resulting curves of mass loss in a varying temperature field, and also for an opportunity to investigate and compare samples of various heat resistances [17, 18].

Experiments were carried out using the analyser Neltch STA 449 under the following conditions: a sample mass of 35 mg, a platinum/iridium crucible; heating to 800 °C with a rate of 10 °C/min in the oxidizing medium (a mixture of nitrogen and oxygen, channels of 20 cm³/min). The mass loss (by TG), mass loss rate (*via* DTG) and differential thermal analysis (DTA) curves were recorded in the course of the investigation. The temperature range of the main oxidative breakdown in the TG/DTG curve was determined by the maximum-slope method using the Netzsch Proteus software. In order to assess oxidation reactivity, there were used the following indicators: T_1 , the temperature of the beginning of mass loss determined according to the origin of bending of the DTG curve; T_{max} , the temperature, upon which the maximum oxidation rate V_{max} determined according to the origin of bending is reached; T_2 , the final temperature, at which there is burning out the coke residue; and ΔT , the temperature range of mass loss [15].

RESULTS AND DISCUSSION

Tables 1 and 2 report the performance of the petrographic composition of the investigated coal samples. According to petrographic analysis results (see Table 1), this coal is of various degree of metamorphism; vitrinite reflectance ($R_{o,r}$) is varied from 0.58 (D grade sample) to 1.01 % (K type specimen). Coal samples of LF, LFG, G, and F grades contain a significant amount of vit-

TABLE 1

Performance of the petrographic composition of the investigated coal samples

Code of sample	Petrographic parameters, %				Vitrinite reflectance index		Coal grade (GOST25543-88)
	Vt	Sv	I	Σ FC	$R_{o,r}$, %	σ_R	
37	89	2	9	10	0.58	0.02	LF
61	83	4	13	15	0.64	0.04	LFG
40	72	4	24	26	0.75	0.06	G
39	86	2	12	13	0.81	0.06	F
50	31	13	56	64	1.01	0.04	C

Note. Vt - vitrinite, Sv - semivitrinite, I - intertinite, Σ FC - the total amount of fusainized components, $R_{o,r}$ - vitrinite reflectance index, σ_R - standard deviation, LF - long-flame, LFG - long-flame gas, G - gas, F - fat, C - coking.

TABLE 2

Performance of the investigated coal samples

Coal grade	Technical analysis, %				Elemental composition, % per daf			Atomic ratio	
	W ^a	A ^d	V ^{daf}	S _t ^d	C	H	(O + N + S)	H/C	O/C
LF	1.8	9.4	44.4	0.3	79.4	5.6	15.0	0.85	0.14
LFG	2.5	2.5	42.8	0.5	81.9	5.6	12.5	0.82	0.11
G	1.1	4.5	42.2	0.4	83.7	5.6	10.7	0.80	0.10
F	1.1	8.9	33.5	0.3	87.8	5.9	6.3	0.81	0.05
C	1.0	8.1	22.8	0.5	88.9	4.9	6.2	0.66	0.05

Note. W^a - moisture in the analysis sample, A^d - ash content, V^{daf} - volatile matter yield, S_t^d - total sulphur, daf - dry ash-free.

rinite (Vt) components. A sample of LF grade is characterised by the maximum content (about 89 %). The maximum amount of intertinite (I) and fusainized components (Σ FC = 64 %) was found for a sample of C grade.

The ash content of samples is changed from 2.5 % for a sample of LFG grade to 8.9 % for a specimen of F type. When the genetic maturity of samples is increased, volatile matter yield (V^{daf}) and the atomic ratios H/C and O/C are reduced. A sample of D coal contains the maximum amount of oxygen and heteroatoms (see Table 2). A certain degree of oxidation of a sample of CC coal should also be noted, which is indicated by the increased O/C ratio.

Table 3 gives semi-coking results for the tested coals. Poorly-sintered semicoke was formed using LF and LFG coal resulting from low-temperature pyrolysis. The former presented moieties that were destroyed upon minor pressing. G coal yielded sintered and weakly-alloyed semicoke; F and C grades provided relatively swollen semicoke. The yield of semicoke is maximum when using LF coal. When the degree of metamorphism of the investigated coal is increased, the amount of semi-coke generated upon low-temperature-pyrolysis is elevated against the

TABLE 3

Product yield of the semi-coking of coal samples

Coal grade	Yield of semi coking products, % per daf			
	sC	T _{sc}	W _{sc}	G _{sc}
LF	67.2	10.1	7.7	15.0
LFG	70.0	12.1	7.3	10.7
G	70.3	13.4	7.0	9.3
F	73.5	11.3	2.2	13.0
C	84.3	5.6	1.5	8.6

Note. sC - yields of semicoke, T_{sc} - resin, W_{sc} - pyrogenetic water, G_{sc} - gas products and losses.

background of a reduction in resin and vapour gases.

Table 4 presents pore structure parameters computed according to adsorption/desorption isotherms. It can be seen that samples of semicoke derived from LF/LFG-grade coal has a relatively developed specific surface area (over 400 m²/g). Semicoke derived from more mature K coal has the lowest S_{BET} value (almost by 3 times lower, around 30 m²/g). Hence, with an increase in the degree of polymorphism of coal, the specific surface area of semicoke derived therefrom is decreased.

Upon low-temperature pyrolysis, the pore structure of semicoke of all investigated grades is

TABLE 4

Performance of the pore structure of the investigated semicoke (SC) samples

Sample code	S_{BET} , m^2/g	V_{Σ} , cm^3/g	V_{micro} , cm^3/g	V_{meso} , cm^3/g	V_{macro} , cm^3/g	$V_{\text{micro}}/V_{\Sigma}$, %	$V_{\text{meso}}/V_{\Sigma}$, %	$V_{\text{macro}}/V_{\Sigma}$, %	D_{av} , nm
LF	431	0.21	0.11	0.05	0.05	52.4	23.8	23.8	2.0
LFG	415	0.19	0.11	0.03	0.05	57.9	15.8	26.3	1.9
G	287	0.13	0.08	0.01	0.04	61.5	7.7	30.8	1.8
F	328	0.16	0.08	0.03	0.05	50.0	18.8	31.2	2.0
C	131	0.06	0.03	<0.01	0.03	50.0	16.7	33.3	1.9

Note. S_{BET} – the specific surface area; V_{Σ} – total pore; V_{micro} – micropore volume; V_{meso} – mesopore volume; V_{macro} – macropore volume; $V_{\text{micro}}/V_{\Sigma}$ – relative micropore contents; $V_{\text{meso}}/V_{\Sigma}$ – relative mesopore contents; $V_{\text{macro}}/V_{\Sigma}$ – relative macropore contents; D_{av} – average pore diameter.

formed due to the formation of mainly micropores (see Table 4), the fraction of which is around 50 %. The maximum relative micropore content was determined for samples produced using G coal (over 60 %) and LFG analogue (around 68 %). Hence, the investigated samples are micropore ones and have a relatively low volume of meso- and micropores. Thus, the development of micropore structure upon semicoking depends on the nature of the raw materials used because with an increase in the degree of metamorphism of coal, the specific surface area of semicoke derived therefrom is decreased. In other words, each coal precursor displays its own peculiarities of the formation of pore space upon semicoke preparation, which is likely to be due to properties and peculiarities of its organic matter.

Table 5 reports research results of the reactivity of semicoke derived using individual coal. It can be seen that temperatures corresponding to the beginning of the reaction (T_1) and the maximum rate (T_{max}) of the reaction of semicoke with O_2 depend on the nature of the initial coal: the minimum values are typical for semicoke based on low-metamorphosed coal of LF, LFG, and G grades; the maximum ones – for semicoke de-

rived using F and C coal. Thus, semicoke structure based on medium-metamorphosed coal is less reactive towards oxidative exposure.

It is known that the reactivity of coke is directly linked to its chemical composition and physicochemical properties [19–22]. For example, a drastic change in oxidation rate accompanied with coke burning out depends on pore structure and reaction surfaces as demonstrated by the authors of [21].

Figure 1 gives characteristic curves for the temperature of the beginning of mass loss in the oxidation process (T_1) and that of the maximum rate of mass loss (T_{max}) by the investigated semicoke samples vs their specific surface area.

There is the common trend of a decrease in T_1 and T_{max} when S_{BET} of the investigated samples is increased. The characteristic curves are of the linear nature. As demonstrated by the analysis of equations and their statistical assessment, the given interlinks are characterised by high correlation (0.92 and 0.94, correspondingly) and determination (0.86 and 0.88) coefficients.

It is common knowledge that coal of medium degrees of metamorphism (passing to plastic condition) yields semicoke with a high degree of order

TABLE 5

Reactive characteristics of laboratory semicokes (SC) prepared from individual cokes at 600 °C

Sample code	V_{max} , %/min	Temperature boundaries of main decomposition, °C				Δm , mass %, at temperatures, °C
		T_1	T_{max}	T_2	$\Delta t = T_2 - T_1$	
SC LF	4.15	344	490	600	256	80.0
SC LFG	4.39	348	517	618	270	90.0
SC G	4.30	367	538	640	273	87.2
SC F	4.22	386	544	660	274	88.1
SC C	4.34	404	569	680	276	89.2

Note. T_1 – the temperatures of the beginning of mass loss; T_{max} – the point, at which the maximum oxidation rate is reached; T_2 – the final temperature, whereby organic matter is burnt out; V_{max} – the maximum oxidation rate at T_{max} ; Δt – the temperature range of mass loss; Δm – the latest value in the corresponding temperature range.

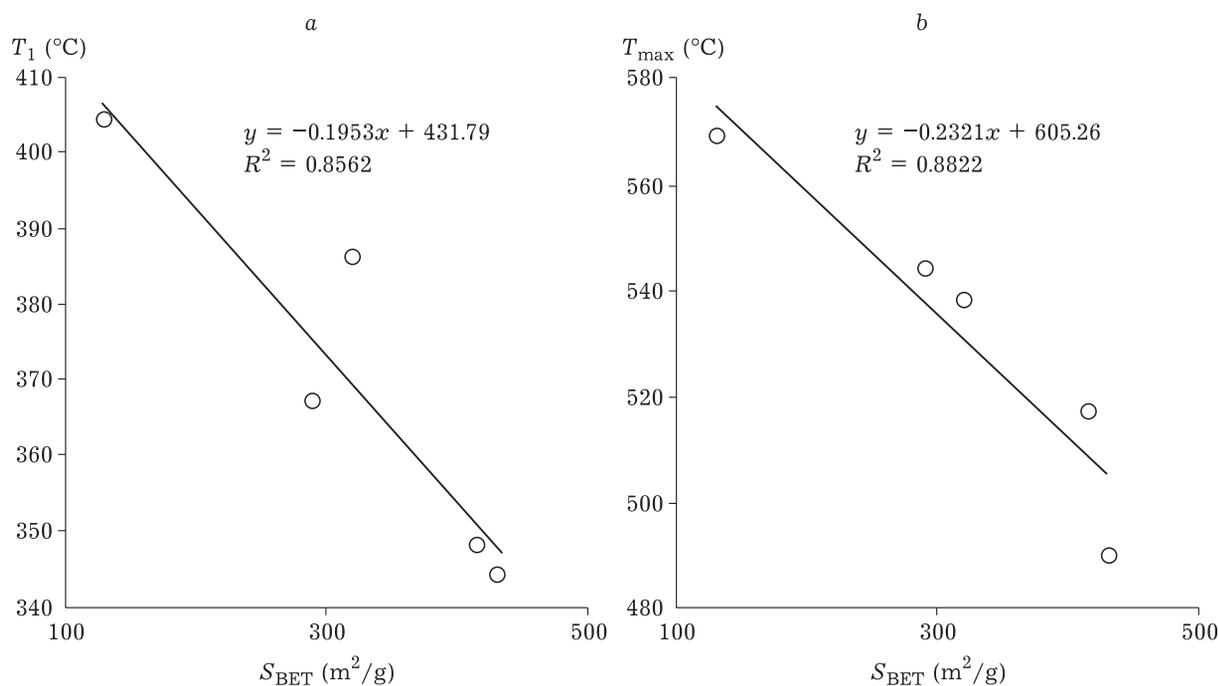


Fig. 1. Specific surface area of semicoke derived from individual coal vs the temperature (T_1) of the beginning of mass loss for the oxidation process (a) and vs the temperature (T_{max}) of the maximum rate of mass loss (b).

of its carbon skeleton and the specific surface area related to macro- and microporosity [1, 19]. Hence, the T_1 indicator for the investigated semicoke is determined by two counteractive factors: the improvement of its structure facilitates an increase in this indicator, whereas increasing the specific surface area leads to a decrease in T_1 .

CONCLUSION

The pore structure and the reactivity of semicoke derived from individual coals with different degrees of metamorphism and vitrinite reflectance ($R_{\text{o,r}}$) of 0.58–1.01 % towards oxygen have been explored. The development of the pore structure upon semi coking depends on the nature of the initial raw materials, as there is a trend towards a reduction in the specific surface area of semicoke derived from coals with a higher degree of metamorphism. The maximum specific surface area has been determined for semi-coke derived from LF coal (431 m²/g). Semicoke obtained using individual coals of a higher degree of metamorphism are characterised by reduced reactivity: higher T_1 and T_{max} values are typical for the former according to the TGA data. The interlinkage between the temperature of the beginning of mass loss (T_1) and that of the maximum rate of the latter (T_{max}) during oxidation with the investigated samples of semicoke vs its specific surface area

has been identified. As shown, when the specific surface area of semicoke is increased, T_1 and T_{max} indicators are reduced. Thus, each coal precursor displays its own peculiarities in the formation of both the porous space and reactivity towards oxygen upon the preparation of semi-coke, which is primarily due to the structure and properties of its organic matter.

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