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Porous Carbons Obtained from Lignite, Anthracite and Graphite in a Bed of Slag and Catalyst Particles

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This paper describes the influence of solid fuel nature and conditions of thermal treatment in a flow reactor with a fluidized and fixed bed of slag and catalyst particles on the porosity of obtained carbon products. Lignite, anthracite and natural graphite were used as starting raw materials. Optimal conditions of thermal treatment providing the formation of porous carbons were selected for the each type of a raw material: pyrolysis with high rate of heating (flash pyrolysis) for lignite, the same combined with steam activation for anthracite and chemical modification and flash pyrolysis for natural graphite.

Keywords: porous carbon, lignite, anthracite, graphite, flash pyrolysis, activation, fluidized and fixed beds, slag and catalyst particles.

Introduction

It is known the pyrolysis of carbon-containing materials results in an evaporation of some fragments of organic matter with the obtaining of porous carbon products. Carbons with the developed porosity are usually produced from raw materials with a significant content of volatile matter at the conditions of high rate heating (flash pyrolysis) [1-6].

Different methods were applied for the technological realization of flash pyrolysis processes. Among them are the processes based on the high rate heating of powdery raw material in a flow of a gaseous carrier.

In order to increase the efficiency of a mass transfer between solid material and gaseous carrier the special technical decisions are used. Some of them supply the fuel particles moving by curvilinear trajectory, for example in cyclone reactors [5, 7]. As it was shown early, the new possibilities for increasing an efficiency of lignite pyrolysis process gives the technology based on the thermal treatment of lignite particles moving through the heating fluidized bed of more big particles of catalytically active material [1, 8, 9].

The conventional approach in production of porous carbons is the activation of carbon raw material by gaseous reagents: water steam, carbon dioxide and oxygen [10-11]. In this case

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the formation of new pores proceeds as a result of gasification of some part of carbon material. These methods are used for activation of raw materials with a high concentration of carbon and with a low content of volatile matter. The good results were obtained using the carbon material activation by steam-air flow in the reactor with a fluidized bed of catalytically active particles [9, 12].

The textural characteristics of produced active carbons are regulated by variation of activation process conditions. When the reactions between gaseous reagents and carbon are limited by the external diffusion they proceed mainly on the external surface of carbon particles. At these conditions the carbons with rather low porosity and surface area are produced. The formation of macro- and mesopores situated close to the surface of carbon particles dominates in carbon products when the internal diffusion limits the activation process [13]. The prevention of diffusion limitations promotes the formation of carbons with the more developed porosity and homogeneous distribution of pores in the particle volume. Besides, the absence of diffusion limitations expand the possibility to produce carbons with the demanded porous texture.

The important direction in the use of a flash pyrolysis technology is the production of thermally expanded graphite and unique carbon materials on its basis [14-16]. The preparation of expanded graphites includes the two main steps – graphite intercalation by chemical reagents and following thermal treatment of intercalated product. The properties of expanded graphites are varied depending on the conditions of intercalated graphite thermal treatment. The use of a flow reactor where powdery graphite particles are moving through a heating bed of the more big particles of thermally resistant material can open the new possibilities for producing of expanded graphites [17].

Aim of the present paper is connected with a selection of optimal operating parameters of thermal treatment of lignite, anthracite and intercalated graphite at flash pyrolysis conditions in fluidized and fixed beds of catalytically active materials.

Experimental

Samples preparation

Some characteristics of initial raw materials are given in Table 1.

Borodinsky lignite of Kansk-Ashinsk basin was taken at Krasnoyarsk Power Station – 2 after its grinding and drying at the industrial conditions. The amount of lignite particles with sizes less 200 mkm was 92 %. The upper size of particles was limited by 315 mkm.

Anthracite was taken from Donetsk basin (Ukraine). The amount of particles with sizes less 200 mkm was 86 % and their upper size – 315 mkm.

The initial pieces of Kureisky graphite with the size 100 – 500 mkm have fine granular structure which includes admixtures of lamellas (mica, chlorite) and rounded (pyrite and calcite) structures. These admixtures have the length 20 – 40 mkm and the width 2 – 4 mkm. Graphite samples after grinding to particles with sizes less 200 mkm were used as starting raw materials.

The same procedure was used for the preparation of Noginsky and Zavalevsky graphites samples with particles sizes less 200 mkm.

The preparation of modified graphite samples included the next steps. Powdery graphite was subjected to magnetic separation. The yield of final fraction was near 97 – 98 % from the weight of the initial one. The graphite samples were demineralized by boiling during 12 h in HCl solution at ratio graphite:HCl:H₂O=1:3:3, then treated by HF during 24 h at ratio graphite:HF=1:2 and by

Table 1. Characteristics of starting carbon-containing materials

Parameters	Borodinsky lignite	Donetsky anthracite	Kureisky graphite	Noginsky graphite	Zavalevsky graphite*
Moisture, % wt	7.2	3.4	1.3	2.7	1.3
Ash content (A ^d), %	9.5	18.6	11.7	16.3	0.1
Yield of volatiles (V ^{daf}), %	50.5	7.2	2.1	2.8	1.9
Total volume of pores, cm ³ /g	0.2	0.08	0.05	0.08	0.06

*This sample was demineralized at industrial conditions on Zavalevsky Plant.

boiling water during 40 min. After filtration the samples were dried at 108 °C until the constant weight. The content of ash in treated samples was varied between 1.2 – 2.4 % wt.

Demineralized samples were intercalated with chloric acid at graphite/HClO₄ ratio 1:5. Step by step procedure of graphite intercalation included the treatment by HClO₄ at 120 °C during 0.5 h, than at 130 °C, 0.5 h at 140 °C, 0.5 h and at 150 °C, 0.5 h. Finally the samples were treated by boiling HClO₄ at temperature 160 °C during 1.5 h with the addition of HNO₃ (5–7 % from HClO₄ content). Intercalated graphite was separated on a glass filter, than it was washed by distilled water until the neutral pH and dried at 105 °C until the constant weight.

The other method of intercalation was based on demineralized graphite treatment by nitric and acetic acids. Concentrated nitric acid (10 cm³) with density 1.5 g·cm⁻³ was added to 25 g of graphite and mixed during 10 min at conditions which supply removing the nitrogen oxides. Then the 100 cm³ of concentrated acetic acid was added and the reaction mixture was mixed during 10 min. Treated graphite was separated on a glass filter, washed by distilled water and dried at 105 °C until the constant weight.

Thermal treatment

Lignite and anthracite samples were thermally treated in a reactor with a fluidized bed [9]. The mixture of powdery raw material and air (or air and water-steam mixture) was blown

through a heated at 700-900 °C fluidized bed of catalyst particles.

The activation of natural graphite was carried out by water steam in a fixed bed reactor at temperature 850 – 900 °C, steam concentration in nitrogen – steam mixture 80 % vol, time of treatment 1.5 h.

Two following procedures of thermal treatment of intercalated graphite were applied. According to the first one the metallic reactor with volume 90 cm³ was heated in the electric furnace up to demanded temperature (400–900 °C). The sample of intercalated graphite with weight 0.1–0.3 g was quickly placed into heated reactor and kept during 60–180 s. Then the reactor with expanded graphite was taken out the furnace and cooled down to room temperature.

The another procedure included the thermal treatment of intercalated graphite in a flow stainless reactor with inner diameter of 2 cm and with high of 20 cm. This reactor was filled by Marting slag particles with sizes 0.5-0.8 mm, which act as a heat accumulators. Owing to the big mass of slag bed a temperature in the reactor was changed only slightly after feeding graphite particles. Graphite particles are moving by curvilinear trajectory between the more big slag particles. The special construction of sprayer allows to organize graphite particles feeding into reactor volume from the center to the wall of reactor. It makes possible to increase the time of particles thermal treatment and to improve the heat transfer conditions in the reactor.

Results and discussion

Lignite and anthracite thermal treatment

The influence of temperature and time of lignite pyrolysis at isothermal conditions on the yield of volatile substances was studied (Fig. 1).

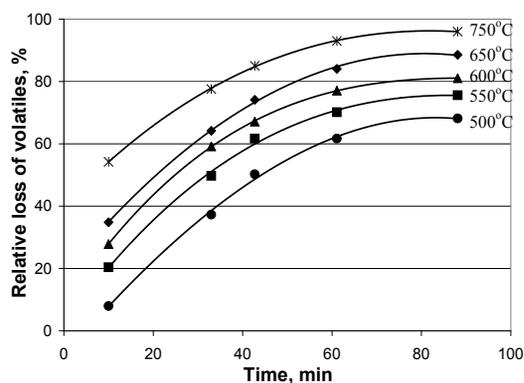


Fig. 1. Influence of temperature and time of lignite thermal treatment at isothermal conditions on the yield of volatiles

The parameters of lignite pyrolysis process were varied in the next range: temperature between 500 – 750 °C, time within 7 – 90 min. The BET surface area of carbonized samples goes up to 90 – 120 m³/g with the increase of temperature and time of lignite pyrolysis. But a total volume of pores was practically the same for the initial and thermally treated lignite samples (0.2–0.25 cm³/g).

It was found that the shrinkage of lignite samples after isothermal treatment reached to 35 % from the initial volume. This fact can indicate that the main part of macro and mesopores which are formed owing to the emission of volatiles from the organic matter of lignite gets closed at the final steps of lignite isothermal treatment. The observed increase of BET surface area is probably connected with opening of the closed micropores of starting lignite.

The pyrolysis experiments with a high heating rate were accomplished in a pilot reactor by means of powdery lignite blowing by air

flow through the fluidized bed of the more big particles of quartz sand, Martin slag and oxidation catalysts. The material of a fluidized bed had the temperature between 400 – 900 °C.

Fig. 2 illustrates the significant increase of semicoke porosity at the rates of lignite particles heating 10³–10⁴ °C per second. The rate of heating in the range 10²–10⁴ °C per second was regulated by variation of lignite particles, according to [5].

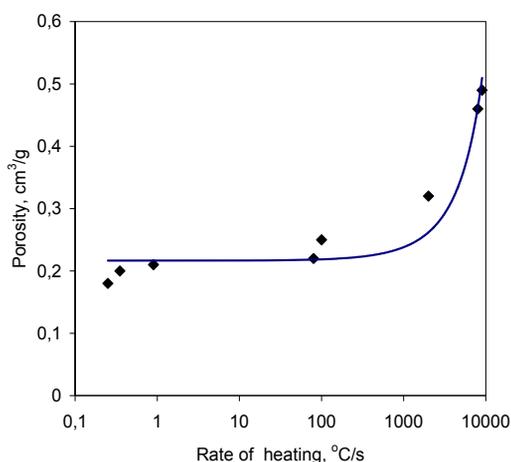


Fig. 2. Influence of the rate of lignite heating to final temperature 750 °C on the total volume of pores in carbon products

No distinct dependence between the heating rate and the specific surface area of obtained semicokes were observed. The BET surface area of all studied semicokes was varied near 120 m³/g (± 30 m³/g). But the significant influence of activating agent composition on the BET surface area of activated semicokes was established. Textural characteristics of the selected samples of activated semicokes were compared. The first sample was activated in the flow of exhaust gases produced at combustion of diesel fuel and the second one – in the flow of exhaust gases with the addition of water-steam. The total pore volume of the both activated carbons was 0.36 – 0.40 cm³/g. But these two samples have the different surface areas: 146

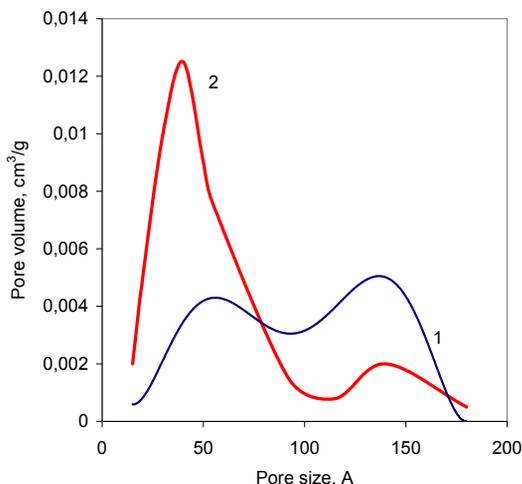


Fig. 3. Distribution of pores in carbon products from lignite activated by exhausted gases at final temperature 700 °C, time of treatment 1.2 s. and rate of heating 10³ °C per second.

Composition of activating gases: 1 - 20±2 % of water-steam, 10±0.5 % CO₂, N₂ – the rest; 2 - 40±2 % of water-steam, 7.5±0.5 % of CO₂, N₂ – the rest

m³/g – for the first sample and 390 m²/g – for the second one.

Fig. 3 demonstrates the different distribution of pores in these activated semicokes. Obtained data show that even at the low time of treatment (less than 2 s) the increase of water-steam concentration in activating mixture promotes the intensive formation of micropores, which are responsible for the higher surface area of the second sample.

Oxidation catalyst with composition (% wt.): 55,9 Al₂O₃, 14,4 CuO, 29,7 Cr₂O₃ was by 2.5 times more active in reactions of combustible gases oxidation than catalyst containing 94,1 Al₂O₃, 2,2 CuO, 3,7 Cr₂O₃. Martin slag has the most low catalytic activity in oxidation reactions at elevated temperatures. As it was shown [12] at the used conditions of lignite thermal treatment the catalyst particles promote the reactions of volatile products oxidation which supply by heat the pyrolysis process. Therefore in the case of lignite, containing the high amount of volatiles

the pyrolysis process goes at autothermal conditions.

Experimental results of anthracite and lignite thermal activation with a high heating rate in catalytic fluidized bed are compared in Table 2. At the comparable temperature of catalyst bed the flow of gaseous products of lignite pyrolysis has the lower temperature on the reactor outlet as compared to that of anthracite pyrolysis. Obviously the two main factors can be responsible for the lower temperature of the flow of gaseous products of lignite pyrolysis. The first one is connected with the higher consumption of heat for evaporating and heating of water, which content in lignite by 2 times large then that in anthracite. The another factor is connected with a heat expenses on the endothermic reactions of char products gasification by steam. At the pyrolysis temperatures used (785-840 °C) anthracite has the lower reaction ability in gasification than that of lignite.

Experiments 1 and 4 (Table 2) demonstrate the differences in the behavior of lignite and anthracite at the same parameters of a thermal treatment. The minimum temperatures, corresponding to the stable conditions of lignite pyrolysis process are 615 °C for active catalyst 1 and 720 °C – for less active catalyst 2. In the case of anthracite the corresponding temperatures are 785 °C for catalyst 1 and 840 °C for catalyst 2.

The reaction ability to activating reagents is very important parameter defining the possibility of coal application for the preparation of carbon sorbents. It is known that the low reactivity of anthracite in activation by such gaseous reagents as water-steam and carbon dioxide limits its wide application as a sorption material.

The reaction ability of thermally treated anthracite was measured by DTA technique under the next conditions: sample weight 35-40 mg, rate of heating 2 °C/min, final temperature 800 °C, air medium. Obtained data are given in Table 3.

Table 2. Parameters of lignite and anthracite thermal treatment in a fluidized bed of catalyst and some properties of obtained carbon products

Parameters	Number of experiment						
	1	2	3	4	5	6	7
Material of fluidized bed	Active catalyst 1			Less active catalyst 2			Martin slag
Fuel type*	L	A	L	L	A	L	A
Air expenditure, m ³ /h	76.3	72.6	98.6	72.3	71.0	79.3	68.2
Raw material expenditure, kg/h	64.9	59.1	116.1	38.1	36.0	56.7	41.6
Temperature of bed, °C	770	785	615	825	840	720	810
Temperature of product flow on reactor outlet, °C	560	650	440	650	715	530	685
Composition of dry gas, % vol:							
H ₂	7.9	0.2	0.1	11.7	0.2	3.4	0.9
CO	5.5	0.7	0.2	7.4	1.0	2.2	1.3
CH ₄	2.9	absent	absent	2.4	absent	1.4	0.2
CO ₂	13.1	13.8	13.1	11.4	12.1	10.3	10.8
N ₂	67.9	81.2	83.8	62.4	81.2	76.6	80.1
O ₂	2.6	4.2	2.9	4.7	4.8	6.1	6.6
Carbon product composition:							
Moisture (W ^b), %	2.1	2.1	4.4	0.3	0.2	2.6	0.3
Ash (A ^d), %	15.6	20.9	11.2	25.9	46.6	13.4	32.1
C ^{daf}	80.2	94.2	72.8	89.1	93.6	77.2	92.8
H ^{daf}	3.2	0.9	4.4	2.1	1.4	3.5	1.4
Heat of combustion (Q _i), MJ/kg	24.3	25.1	22.0	23.1	17.4	23.0	14.7

* L – lignite, A – anthracite

Catalyst 1 – 55.9 % Al₂O₃, 14.4 % CuO, 29.7 % Cr₂O₃Catalyst 2 – 94.1 % Al₂O₃, 2.2 % CuO, 3.7 % Cr₂O₃

Table 3. Characteristics of texture and reaction ability of the initial coals and obtained carbon products

Samples	Porosity* cm ³ /g	BET surface area m ² /g	Ignition temperature °C	Temperature of maximum loss of mass °C	Temperature of complete combustion °C
Lignite	0.19	6.1	240	410	470
Anthracite	0.02	0.4	437	566	617
Carbon products**:					
experiment 3 (L)	0.31	27.0	252	380	460
experiment 4 (L)	0.49	38.9	280	345	425
experiment 5 (L)	0.21	26.0	402	550	600
experiment 7 (L)	0.19	14.1	404	549	605

* measured by kerosene absorption

** numbers of experiments are the same as in Table 2

Curves of the mass loss show that the thermally treated anthracite reacts with air with a much higher rate than non-treated anthracite. The higher reactivity of anthracite and lignite after their thermal treatment is connected with the increase of their porosity. According to the data

of Table 3, the thermal treatment of anthracite in a catalytic fluidized bed increases by 10 times its total volume of pores and by 65 times its BET surface area. In the case of lignite the effect of thermal treatment on porosity and surface area of carbon product was less pronounced.

Table 4. Characteristics of Noginsky graphite before and after activation by water-steam at 900 °C

Parameters	Initial graphite	Activated graphite
Solid product yield, % wt	-	76.50
Ash content (A ^d), %	16.30	23.20
Density, g/cm ³	0.87	0.79
Activity in I ₂ adsorption, %	11.10	15.40
Attrition strength, %	96.00	98.00
Total volume of pores*, cm ³ /g:		
measured by water absorption	0.075	0.217
measured by mercury intrusion	0.070	0.183
measured by N ₂ adsorption	0.098	0.227
Volume of mesopores*, cm ³ /g	0.028	0.044

*from data of N₂ adsorption

Summarizing the obtained results the next conclusions should be made. The pyrolysis of lignite and anthracite at high heating rates promotes the formation of carbeneous materials with the increased porosity and surface area. Semicokes obtained from lignite have the higher ignition temperature and lower temperature of maximum loss of a mass as compared to the initial lignite.

Only slightly variations in chemical composition were observed after the thermal treatment of anthracite despite on a significant growth of its specific surface area. For the thermally treated anthracite the ignition temperature and temperature of maximum loss of a mass is lower in comparison with the initial anthracite.

Graphite thermal treatment

Some characteristics of carbon materials obtained by water-steam activation of natural Noginsky graphite at 900 °C, steam concentration 80 % vol. and time of treatment 1.5 h are given in Table 4.

Obtained results show that activation at 900°C increases by 2.5 times the porosity of graphite. Taking into account the extremely low content of volatile matter in graphite sample, the

increased porosity of activated graphite can be explained by gasification of amorphous fragments and another imperfect places on graphite surface with the formation of the additional pores.

It is known [18] that the porosity of carbon materials with a graphite structure is increased after its chemical modification or intercalation. The following fast heating of intercalated graphite results in some cases in a huge expansion of the carbon network giving the low-density porous carbons.

The treatment of demineralized Kureisky and Nogiusky natural graphites by HClO₄ increases the content of volatile substances to 7–9 % wt. (for initial graphites 2.1–2.8 % wt). The thermal treatment of chemically modified graphites results in a significant increase of their volume. The microscopic analysis of thermally treated samples show that only some part of graphite particles were expanded. The content of expended particles both in Kureisky and Noginsky graphites was near 10-12 %. The main part of graphite particles keeps the initial acute-angled shape.

Zavalevsky natural graphite treated by concentrated nitric acid and then by concentrated acetic acid was expanded in a flow reactor, described in Experimental section.

Specific volumes of thermally expanded samples were calculated from the equation $K = V/m$, where V – sample volume (cm^3) and m – sample mass (g). Three parallel measurements were made for the each sample. The difference in K value for parallel experiments was near 5%. Zavalevsky graphite samples thermally expanded in a stationary reactor have the K value near $200 \text{ cm}^3/\text{g}$. But the K value of expanded graphite samples obtained in a flow reactor was only about $5\text{-}10 \text{ cm}^3/\text{g}$. Expanded graphite samples produced in a stationary reactor have low mechanical strength and they easily decrease their volume at slight press or even at shaking.

It is worth to note that the specific volume of a sample (K) is defined by few factors including the internal porosity of particles and the porosity between particles and their agglomerates. The observed decrease of specific volume of expanded graphite after its mechanical pressing is connected obviously with the reduce of porosity between particles and between particles agglomerates.

The thermal expansion of intercalated graphite in a flow reactor is accompanied by a significant mechanical stress owing to the collision of expanded graphite particles with particles of fixed bed filler (Martin slag) and with walls of a reactor. This results in a destruction of not strong particles of expanded graphite or their agglomerates. Therefore the rather low values of specific volume of expanded graphite samples produced in a flow reactor can be conditioned by destruction and packing processes.

The thermal treatment of intercalated graphite in flow reactor has some advantages as compared to stationary reactor. The expanded graphite produced in a flow reactor has the higher density in comparison with that obtained by heating at stationary conditions. Owing to that the expanded graphite of this type has the more stable properties. Expanded graphite with higher

density is more suitable for transportation and its using decreases the number of steps in mould articles producing under the pressure.

Conclusion

The processes of thermal treatment based on powdery carbon raw material blowing by air flow through a fluidized or fixed bed of more big slag or catalyst particles have their own features for each type of raw material used.

More than 40 % wt of organic mass is removing with volatile compounds in the case of lignite pyrolysis at low rates of heating. But the formation of new pores is accompanied by the decrease of lignite volume which reaches to 35 %. This shrinkage prevents the significant growth of obtained semicoke porosity. The semicokes with an increased porosity were obtained by lignite pyrolysis in a flow reactor with fluidized bed of catalytically active material at high rate of heating ($10^3\text{-}10^4 \text{ }^\circ\text{C/s}$) and short time of treatment (few seconds).

The pyrolysis with high rate of heating promotes mainly the formation of meso- and macropores, therefore the obtained carbon materials have rather low BET surface area. The fast pyrolysis of lignite in catalytic fluidized bed in the presence of water-steam makes it possible to increase the BET surface area of semicoke to $400 \text{ m}^2/\text{g}$ at short time of the process (less than 2 s).

Since anthracite has low content of volatile matter (near 7.2 % wt.) the carbon materials with the increased porosity and BET surface area are produced only after its activation by water-steam at $900 \text{ }^\circ\text{C}$.

The treatment of natural graphites by water-steam makes low influence on their porosity. But the chemical intercalation of graphite with following thermal treatment at conditions of a high rate heating has prospects for producing of carbons with low density and high specific volume.

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