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Production of Activated Carbon Based on the Coal/Pitch System

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Abstract

An opportunity to use Zh, D, and KS coal of the Kuznetsk Basin referred to bituminous coals as raw materials to produce activated carbon was investigated. Formulas of coal/pitch systems were developed using coal-tar pitch as a binder. The optimum coal tar content (5 mass %) in the system was determined. New activated carbons based on coal/pitch systems were produced; parameters of their microporous structure, adsorptive properties, and strength performance were examined.

Key words: coal, coal-tar pitch, activated carbons, pore structure, adsorptive activity, mechanical strength, ash content, grinding, briquetting, milling, activation, carbonization

INTRODUCTION

The production of activated carbon (AC), as an important sector of economy, ensures the work of many industrial sectors. Nevertheless, they play a particularly important part in environmental protection from technogenic and anthropogenic impacts, such as treatment of waste gases, wastewater, and drinking water, and also the detoxication of soils and the protection of human life (anti-gas equipment).

Manufacturing AC is extensively growing in the whole world; the annual increase of the former is 5 %. In order to produce it, only fossil coals have unlimited feedstock resources out of the entire range of carbon-containing raw materials. However, modern systems for activated carbon exploiting, especially in drinking water supply, solvent recuperation, and sanitary gas treatment use AC layers of a large height (1–2 m), which imposes specific requirements not only towards adsorptive activity but also granule abrasion strength [1].

A significant improvement in strength and density properties (and therefore microporosity) of AC may be achieved when using coal gases as a binder, in which coke content is 2.5–3.0 times higher than that in coal tars [2].

To this end, the technology of briquetting bituminous coal raw material and solid binder are used in world practice. Lately, the leader in this area of the production of activated carbon is an American company, Calgon Carbon Corporation (Pittsburgh, PA), has launched a number of plants in Belgium, Japan, China, Thailand, and other countries. Each enterprise has a capacity of 10 thousand t of AC a year.

The main raw materials for the production of AC according to the technique of the coal/pitch system are bituminous coal of the following quality:

– moisture content of not more than 5 %,

– ash content of not more than 3 %,

– volatile matter content of 27–31 %.

The second component is coal–tar pitch with the following performance:

– softening temperature of 90 °C,

– volatile matter content of 55–60 %,
– coke content of 30 %.

Russia has enormous reserves of bituminous coal (Zh, D, G, GZh, OS, and KS grades) in Kuzbass [3]. Large plants of coal tar pitches are concentrated there, too. Therefore the development of the domestic coal-tar pitch technology for producing AC by steam/gas activation was begun precisely on this raw material base.

EXPERIMENTAL

Relying on analysis data for the domestic raw material base of bituminous coal, there were used samples of coal of the following types were used:

– Zh grade from the Yubileinaya mine (the Novokuznetsk city); water content (W^a) of 1.4 %, an ash content (A^d) of 6.5 %, volatile matter yield (V^{daf}) of 34.3 %;

– D grade from the Arshanovskii pit (Khakassia); water content (W^a) of 12.7 %, an ash content (A^d) of 7.7 %, volatile matter yield (V^{daf}) of 35.2 %;

– KS grade from the Koksovii section Ltd (Kiselevsk), water content (W^a) of 1.3 %, an ash content (A^d) of 3.7 %, volatile matter yield (V^{daf}) of 19.9 %.

Granulated coal tar pitch from Altai Coke JCS (the Zarinsk city) was used as a binder. The former had the following characteristics: a softening temperature of 87 °C, coke residue of 65.5 %, and an ash content of 0.1 %.

The processing procedure for producing granular activated carbon based on the coal/pitch system (CPS) involves a number of steps, such as 1) raw material preparation, 2) the combined milling of coal and coal tar, 3) the grinding of a mixture of coal and coal tar, 4) the forming of the coal/pitch system into briquettes, 5) the crushing of briquettes and their screen sizing, 6) the carbonization of crushed particles, 7) the activation of the carbonisate and dust screening, 8) analysis of the finished product.

RESULTS AND DISCUSSION

Determination of the optimum type of bituminous coal

Producing activated milled carbon based on CPS was carried out with laboratory equipment.

The activation of the carbonisate was performed in the medium of water vapour using a retort furnace made of stainless steel with a rate of temperature rise of 10 °C/min and isothermal exposure time of 5–6 h at 800 °C. The temperature mode was controlled by a thermal regulator with a thermocouple.

Gaseous substances emitted during thermal treatment of granules were emitted to the atmosphere through a hydro ozonator.

The resulting activated carbon was sifted out from dust using an AS 200 Retsch screening machine and analysed according to GOSTs and methodical regulations accepted in adsorptive engineering.

Table 1 gives the performance of the resulting AC. It can be seen that a sample of Zh coal-based AC has the best indicators of porous structure and adsorptive properties both in gas (time of protective effect, Θ, for benzene) and liquid phases (adsorptive capacity for iodine and methylene blue). The maximum yield of the finished product characterises this sample, too. The total analysis of the performed investigation allows recommending Zh coal as the basis of the developed coal/pitch system.

Determination of the optimum ratio of coal/coal tar pitch

The types of the investigated Zh, D, and KS coal are different in the content of volatile matter and thus, anthracenites, naphthenes, and anthracenes, which additionally (together with coal tar pitch) ensure the plasticity of coal systems when briquetting. Not only coal tar but also the bitumi-

TABLE 1

Performance of activated carbon (AC) produced from coal of various grades

Grade	Yield, %	Δ, g/dm^3	П, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine, %	for MB, mg/g	
Zh	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
D	24.3	448	84	0.93	0.41	0.37	0.16	80	241	53
SS + T	26.7	453	87	1.02	0.46	0.32	0.15	74	217	50

Note. Here and in Tables 2–6: П, Δ, MB, V_Σ, V_{mic}, and Θ are rub fastness, bulk density, methylene blue, total pore volume, micropore volume, and protective power time, respectively.

TABLE 2

Performance of activated carbon produced at various coal-tar pitch contents in the system

Pitch content, %	Yield, %	Δ, g/dm^3	Π, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine, %	for MB, mg/g	
0	31.7	470	81	0.88	0.41	0.32	0.15	80	217	50
1	31.4	467	84	0.90	0.42	0.35	0.16	82	244	52
3	28.9	464	85	0.90	0.42	0.36	0.17	84	250	54
5	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
7	24.3	438	86	0.94	0.41	0.32	0.14	78	214	51

Note. See symbols in Table 1.

nous portion of coal passes into the liquid state ensuring the good binding of coal particles (dust).

Table 2 gives data for detecting the optimum ratio of Zh coal/coal tar pitch for the coal-pitch technique. It can be seen that the AC sample based on the system with a binder content of 5 % demonstrates the best performance both in gas (time of protective effect, Θ, for benzene) and liquid phases (adsorptive capacity for iodine and methylene blue). The yield of the product and micropore volume are reduced when the content is more than 5 %, which results in worsening adsorptive properties.

On the other side, an increase in product yield is accompanied by worsening strength properties of granules when coal tar content is less than 3 %. The total analysis of the performed investigation allows recommending coal tar content of 5 mass % in the system to produce laboratory samples and optimise the technique.

Determination of carbonization modes of granulated coal tar pitch

Carbonization with a view to removing volatile matter is one of the required steps prior to activation when generating carbon adsorbents using coal-tar raw material. Herewith, there are certain structural variations of the carbon-containing material in the course of carbonization. Further they are likely to have an effect on the quality of the activated carbon generated.

In order to examine the effect of carbonization conditions on the quality of carbon adsorbents using coal-tar raw material, a set of adjusting experiments were carried out and optimum parameters of the carbonization process and the rate of temperature elevation were determined. Relying on literature data, the optimum time of pyrolysis is 30 min. It is the time that was selected for our experiments.

Samples of moulded granules of a mixture of Zh coal and coal tar pitch (5 mass %) with a particle size of 0.5–3.5 mm were produced, their carbonization being carried out in one step under CO_2.

The effect of carbonization temperature at the selected heating rate (10 °C) and isothermal exposure for 30 min, at which the total gas release was ensured and the minimum amount of volatile matter was left in the carbonisate, was initially explored. Table 3 gives the performance of the resulting activated carbon. It can be seen that the optimum carbonization temperature is 600 °C. The maximum quantity of carbon crystallites is laid into carbon matter at this temperature ensuring both the development of high microporosity and the preservation of good strength properties. The effect of the rate of temperature eleva-

TABLE 3

Performance of activated carbon produced at various carbonization temperatures (T_{carb})

T_{carb}, °C	Yield, %	Δ, g/dm^3	Π, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine, %	for MB, mg/g	
500	32.0	437	83	0.71	0.31	0.31	0.13	78	229	51
550	29.4	460	86	0.82	0.38	0.37	0.17	82	240	56
600	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
650	28.1	471	88	0.87	0.41	0.38	0.18	84	250	55
700	26.3	482	89	0.83	0.40	0.36	0.17	81	243	52

Note. 1. See symbols in Tables 1. 2. Isothermal exposure of 30 min, the mass fraction of water in the resulting samples of 1.2 %, ash of 7.8–8.4 %; volatile matter yield of 5.6–9.2 %.

TABLE 4

Performance of activated carbon produced at various rates of temperature elevation (v)

v, °C	Yield, %	Δ, g/dm^3	Π, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine,%	for MB, mg/g	
5	32.4	480	87	0.88	0.42	0.38	0.18	86	252	56
10	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
15	22.1	451	83	0.96	0.43	0.33	0.15	81	244	50
20	20.4	420	80	1.04	0.43	0.29	0.12	74	218	48

Notes. 1. See symbols in Tables 1. 2. Isothermal exposure of 30 min, the mass fraction of water in the resulting samples of 1.2 %, ash of 7.8–8.4 %; volatile matter yield of 5.6–9.2 %.

tion vs properties of the resulting AC was explored at the selected temperature (600 °C) and isothermal exposure of 30 min (Table 4).

As it follows from the data of Table 4, the optimum rate of temperature elevation is 10 °C/min. There is a greater release of volatile matter at a higher elevation rate, which reduces both the yield of the product and qualitative indicators of the latter. On the other side, upon a low heating rate (5 °C/min and lower), the same indicators of quality were acquired. Nevertheless, a drastic increase in process time is not economically viable.

Therefore, the coal/pitch system-based carbonisate derived at carbonization temperature of 600 °C and a rate of temperature elevation of 10 °C/min were selected for the further optimization of the activation process (see Tables 2–4).

Determining the optimum conditions for activation

Gas-vapour activation of carbonised products was carried out in a stationary electric furnace using water vapour as an activating agent. Activation duration was regulated according to reaching total pore volume within 0.90–0.93 cm^3/g.

The effect of activation temperature on the performance of the finished product was initially explored at water steam flow rate of 60 mL/h (per H_2O).

Table 5 gives the performance of the resulting activated carbon adsorbents. It can be seen that the optimum flow rate of water vapour per H_2O is 60 mL/h. When steam supply is increased, product yield is reduced due to more intense scorching. Herewith, adsorptive properties are worsened, too. A decrease in vapour flow rate (less than 60 mL/h) results in the insufficient development of micropores, though product yield remains high.

Thereafter, the effect of activation temperature on the quality of the activated product was explored at the selected vapour flow rate per activation (60 mL/h). Table 6 presents test data. It can be seen that a temperature of 860 °C should be regarded as optimum. Surface scorching is increased when T is higher than 860 °C and therefore the development of the microporous structure is reduced, which worsens adsorptive properties of AC. A decrease in temperature as low as 800 °C allows increasing product yield and preserving qualitative characteristics, however, the activation time is increased significantly (by 1.5–1.8 times).

The performed research has made it possible to determine the optimum preparation conditions for activated carbon based on the coal/pitch system and tghermal processes of their carbonisation and activation:

– initial raw materials: Zh coal,

– the working mixture of the coal/pitch system, 95 : 5 (percentage),

TABLE 5

Performance of activated carbon produced at various steam flow rate (FR, with respect to water) (FR per H_2O)

FR, ml/h	Yield, %	Δ, g/dm^3	Π, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine,%	For MB, cm^3/g	
40	27.9	443	82	0.88	0.39	0.35	0.15	81	233	52
50	28.2	458	86	0.90	0.41	0.35	0.16	83	241	55
60	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
70	24.9	460	84	0.86	0.40	0.36	0.16	83	235	54

Note. See symbols in Table 1.

TABLE 6

Performance of activated carbon produced at various activation temperatures (T_a)

T_a, °C	Yield, %	Δ, g/dm^3	Π, %	V_Σ,		V_{mic}		Adsorption capacity		Θ, min
				cm^3/g	cm^3/cm^3	cm^3/g	cm^3/cm^3	for iodine,%	For MB, cm^3/g	
800	29.4	460	88	0.90	0.41	0.38	0.17	84	249	56
860	28.8	462	88	0.91	0.42	0.39	0.18	85	253	57
950	23.3	444	81	0.96	0.43	0.34	0.15	81	241	53

Note. See symbols in Table 1.

– carbonization of granules at 600 °C,

– a rate of temperature elevation at carbonization of 10 °C/min,

– activation at 860 °C,

– steam flow rate at activation of 60 mL/h with respect to liquid water.

CONCLUSION

Thus, the most rapid build-up of new plants of activated carbon based on domestic coal-tar raw material in Russia (primarily in Kuzbass) would surely give a powerful spur to the development of productive forces and the provision of efficient environmental protection. This entirely fits the concept of sustainable development.

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REFERENCES

1 Mukhin V. M., Tarasov A. V., Klushin V. M. Aktivnyie ugli Rossii. Metallurgiya, Moskva, 2000.

2 Mukhin V. M., Klushin V. N. Proizvodstvo i primenenie uglerodnyih adsorbentov, Izd. Ros. Khim.-Tehn. Un-ta im. D. I. Mendeleeva, Moskva, 2012.

3 Loginov M. I., Starokozheva G. I., XII Vseros. Ugolnogo Sov. "Innovatsionnyie Napravleniya Izucheniya Otsenki i Effektivnogo Ispolzovaniya Mineralno-Syirevoy Bazyi Tverdyih Goryuchih Iskopaemyih" (Thesis of reports), Rostov-na-Donu, 27–29 April 2010. P. 17–20.