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Studying the Effect of Properties of a Petroleum Processing Product Based Binder on the Quality of Extruded Activated Carbon.

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ABSTRACT

Extruded activated carbons are the sorbents that are widely used in the production industry in systems of treating ventilation gases, water and other liquids. Most industrial brands of extruded activated carbons in Russia are produced from carbonaceous raw materials with coal and wood tar used as a binder. Most important characteristics of these binders are viscosity and content of coke residue. At the same time, coal and wood tars are characterized by considerable instability of properties with time, which reduces processability and deteriorates the quality of extruded activated carbons. In this regard, this work is devoted to studying the possibility of using of alternative binders in the extruded activated carbon production, and several products of oil refining have been tested as such. In course of the studies, the main indicators of binder quality were determined: the carbon residue (with the use of the ASTM D 4530-07 method), and viscosity at different temperatures. Next, on the basis of the obtained binders, samples of extruded activated carbons were manufactured. The resulting product was analyzed for the key quality indicators, and detailed study of surface properties was performed. In addition, for updating the temperature regimes of granules heat treatment, thermo gravimetric analysis of raw granules samples was performed. Based on these data, the following conclusions can be made: 1. If petroleum processing products are used individually, the binder features either excessively high viscosity, or insufficient content of the carbon residue. 2. The optimum values of viscosity and carbon residue of the binder may be achieved by the use of compositions of low-viscosity products with low content of carbon residue, and high viscosity and carbon residue products. 3. When activated carbon is obtained using a binder based on compositions of petroleum processing products, sorbents may be obtained, characteristics of which are not inferior to those of activated carbons based on conventional tars.

Keywords: extruded activated carbon, binder, carbon residue, dynamic viscosity, bitumen, asphalt, coal tar.

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INTRODUCTION

Activated carbons are porous adsorbents that mainly consist of carbon. In the industry, active carbons are obtained from various organic materials: solid fuels with various degrees of metamorphism (peat, coal, and anthracite), raw plant materials, etc. Activated carbons belong to the group of graphite bodies and are a kind of microcrystalline carbon. Activated carbons are characterized by the presence of developed porous structure, including all types of pores: micropores with effective radius of 0.6 to 1.6 nm, mesopores (transitional), whose effective radius is in the range between 1.6 and 100-200 nm, and the largest, transport pores (macropores), whose radius exceeds 2,000 nm.

The research was performed in the framework of the decree of the Government of Russia No. 218 dated 09.04.2010 "On Measures of State Support for development of Cooperation Between Russian Universities and Organizations Implementing Integrated Projects on Creating High-Tech Production" on the topic: "Creating High-Tech Adaptive Production of Carbon Sorbents and Filtering Materials as the basis of Russian Sorption, Environmental and Gas-Protection Equipment of a New Generation".

By the shape of granules, activated carbons are divided into powder-like (fine) materials; granular (crushed), with grains of irregular shape, and extruded, made in the shape of cylindrical or spherical pellets of various sizes.

Extruded activated carbons are the sorbents that are widely used in the production industry in systems of treating ventilation gases, water and other liquids [1, 2]. The technology of obtaining extruded activated carbons includes, in addition to the main stages of thermal treatment (carbonization and steam activation), the processes of mixing carbon dust with the binder and extrusion of the resulting paste. The properties of extruded activated carbons and the parameters of the extrusion process are largely dependent on the characteristics and the composition of the binding components.

Most industrial brands of extruded activated carbons (EAC) in Russia are produced from carbonaceous raw materials with the use of coal tar and wood tar as binders [3, 4, 5]. Besides others, a mixture of semi-coke and low-ash coal can be used as carbonaceous raw material in the ratio of 1:0.20-0.40 [6], as well as carbon black [7, 8].

Pyrolysis resin (by-product of steam cracking), petroleum resin, petroleum pitch [9, 10], and bituminous hydrocarbons from sands [11] and sulfite-alcohol bard [12], etc. also can be used in extruded activated carbon production. In addition to varying the coal bases and binders, it is also possible to introduce the third component for improving some properties of coals, in particular, the use of nonoxynols [13] allows to improve the sorption characteristics of extruded activated carbons. In order to increase the mechanical strength of the extruded activated carbon, basalt fibers are used [14, 15].

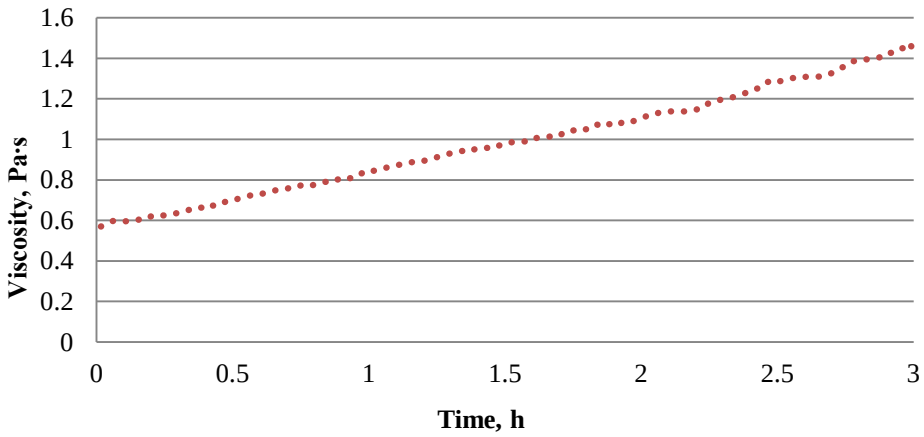

Figure 1: Changing viscosity of coal tar over time at constant temperature (60°C)°

The important characteristics of any binder that ensures forming the coal-resin compositions into granules, and their strength after further thermal modification are viscosity and carbon residue [16]. The

normalized values of binder viscosity ensure the required plasticity of the coal-and-tar composition (CTC), in the absence of which uneven distribution of coal powder throughout the binder may occur, and the process of the coal-tar composition extrusion through a die may be disrupted. Carbon residue in the binder is normalized at about 8-12 wt %. Low carbon residue in the binder may result in insufficient number of carbon bridges generated in the process of heat treatment, which does not ensure the required strength against abrasion of the granules of the resulting activated carbon. At the same time, high carbon residue leads to coking of the pores in the obtained sorbent, thus decreasing its activity as a result.

It should be noted that coal tar and wood tar are characterized by considerable instability of properties. Over time, its viscosity may increase up to 2.5 times (Figure 1), which affects the parameters of the technological process and the quality of the obtained extruded activated carbons.

In this regard, this work is devoted to studying the possibility of using alternative binders in the extruded activated carbons production; and several products of oil refining characterized by high availability [17] and sufficient stability of characteristics have been tested as such.

OBJECTS AND METHODS

In course of the studies, the following petroleum products [18] have been analyzed:

- Asphalt from vacuum residue deasphalting with propane;
- Road bitumen, grade BND 60/90 (BND);
- Heavy gasoil of delayed coker unit (HCG);
- Fuel oil, residue from atmospheric distillation of crude oil;

as well as tars that are traditionally used as binder:

- Coal tar;
- Wood tar.

The carbon residue in the binder was determined with the use of the ASTM D 4530-07 [19] method with carbon residue microanalyzer NMC440 (made by the Normalab company). Viscosity of the binder was determined using modular compact rheometer MCR 102 (from Anton Paar) with the use of the plate-plate measuring geometry 25 mm in diameter (for highly viscous binders) and the "coaxial cylinders" geometry 10 mm in diameter (for low viscosity binders).

The thermogravimetric analysis of raw granules samples was performed using a device for simultaneous thermal analysis made by the NETZSCH company.

The surface properties of extruded activated carbons were determined with automatic high-speed analyzer of porous structures NOVA– 1200e.

RESULTS AND DISCUSSION

Studying raw materials

The characteristics of the petroleum processing products [20] and those of the traditional components of the binder are shown in Table 1.

Table 1: Characteristics of various binder components

No.	Component name	Carbon residue according to method ASTM D 4530-03, wt. %	Viscosity at temperature, Pa·s	
			60°C	80°C
1	Coal tar	26.16	0.983	0.040
2	Road bitumen	18.64	230.360	23.710
3	Asphalt	18.46	89.687	9.537
4	Wood tar	13.59	0.351	0.092
5	Fuel oil	7.31	0.140	0.054
6	Heavy coker gasoil	0.17	0.008	0.005

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However, if these components are used individually, the binder features either excessively high viscosity, or insufficient carbon residue value. Therefore, based on the characteristics of the studied binders, the compositions of low viscosity products with low content of carbon residue and high viscosity products with high content of carbon residue have been made (Table 2).

Table 2: Carbon residue in composite binders

Binder No.	Binder composition		Carbon residue (ASTM D 4530-03), wt. %	Viscosity, Pa·s	
	Component	Content, wt. %		at 60°C	at 80°C
1	Coal tar Wood tar	40 60	19.76	0.259	0.080
2	Asphalt Heavy coker gasoil	60 40	11.32	0.559	0.106
3	Road bitumen Fuel oil	50 50	12.51	1.980	0.470

Compound No. 1 is a conventionally used binder and an extruded activated carbon obtained on the basis of it is used as a reference sample.

The characteristic of used coal dust is shown in Table 3.

Obtaining coal-and-tar compositions and raw granules

Next, on the basis of the composite binders, coal-and-tar compositions were obtained with the use of the dust of non-coking mineral coal [21]. In order to improve molding of these compositions, water in the amount of 5% by weight of the coal-and-tar composition was added to each of them.

The content of coal-and-tar compositions is shown in Table 4.

Table 3: Characteristics of initial coal dust

No.	Characteristics	Value
1	Fractional composition, %, mass fraction of the residue on a sieve with mesh: No. 010 (0.1 mm) No. 0063 (0.063 mm) No. 0040 (0.040 mm) on the tray	 0.3 16.4 57.6 25.7
2	Mass fraction of water, %	5.5
3	Mass fraction of ash, %	4.5
4	Mass fraction of volatile substances, %	38.0

Table 4: Content of coal-tar compositions

CTC No.	Components	Amount, wt. %	Activated carbon grade
1	SSOM grade coal dust Binder No. 1	73 27	SS-KA
2	SSOM grade coal dust Binder No. 2	73 27	SS-ATGC
3	SSOM grade coal dust Binder No. 3	74 26	SS-BM

Granules were extruded from the obtained CTC. In order to specify the temperature regimes of granules heat treatment, thermo-gravimetric analysis of the samples of the raw granules was made with the use of a simultaneous thermal analysis device from the NETZSCH company, with the results being shown in Table 5 [22].

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Table 5: Results of raw granules samples thermogravimetric analysis for the following activated carbon grades: SS-KA, SS-ATGC, SS-BM

Sample			SS-KA	SS-ATGC	SS-BM
Stages of thermal decomposition	1	Temperature, °C	203	154	205
		Loss of weight, %	5.33	1.45	1.68
	2	Temperature, °C	402	361	541
		Loss of weight, %	16.87	12.70	32.70
	3	Temperature, °C	636	555	825
		Loss of weight, %	13.84	22.67	5.96
	4	Temperature, °C	864	784	1000
		Loss of weight, %	4.13	5.33	1.43
	5	Temperature, °C	1000	1000	—
		Loss of weight, %	0.63	1.36	—
Total loss of weight, %			40.85	43.51	41.77

The analysis of the obtained data showed that withdrawal of volatile matter for all samples was within 40.85 to 43.51%. The temperature of the maximum volatiles yield is in the range between 400 and 550°C.°

Thermal treatment of raw granules with stage-wise analysis

Table 6: Characteristics of samples of carbon sorbents at various stages of heat treatment

No.	Characteristics	Activated carbon grade		
		SS-KA	SS-ATGC	SS-BM
1	2	3	4	5
Carbonization stage				
1	Mass fraction of ash, %	6.9	7.3	7.2
2	Mass fraction of volatile substances, %	8.9	9.8	10.2
3	Bulk density, kg/m^3	604	588	581
4	Abrasion resistance, %	87	83	81
5	Water total pore volume, cm^3/g	0.30	0.33	0.34
6	True density, kg/m^3	1,495	1,487	1,486
7	Apparent density, kg/m^3	888	855	847
8	Coefficient of volume shrinkage	1.617	0.950	1.056
Devolatilization stage				
1	Mass fraction of ash, %	7.7	8.7	—
2	Mass fraction of volatile substances, %	—	2.4	2.4
3	Bulk density, kg/m^3	693	691	658
4	Abrasion resistance, %	93	92	88
5	Water total pore volume, cm^3/g	0.30	0.35	—
6	Adsorption activity in terms of iodine (powdered), %	12.7	—	8.0
7	True density, kg/m^3	1,859	1,861	1,859
8	Apparent density, kg/m^3	1,086	976	962
9	Coefficient of volume shrinkage	1.345	1.253	1.259
Activation stage				
1	Number of activations	6	5	6
2	Mass fraction of ash, %	15.7	17.7	16.0
3	Bulk density, kg/m^3	485	491	482
4	Abrasion resistance, %	85	85	85
5	Water total pore volume, cm^3/g	0.73	0.75	0.81
6	Equilibrium activity in terms of toluene, kg/m^3	153	163	143
7	Adsorption activity in terms of iodine (powdered), %	95	89	94
8	True density, kg/m^3	2,119	2,134	2.132
9	Apparent density, kg/m^3	804	756	765
10	Coefficient of volume shrinkage	1.469	1.750	1.759

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Figure 2 shows a histogram of the changes in the coefficient of volume shrinkage of granules at various stages of heat treatment.

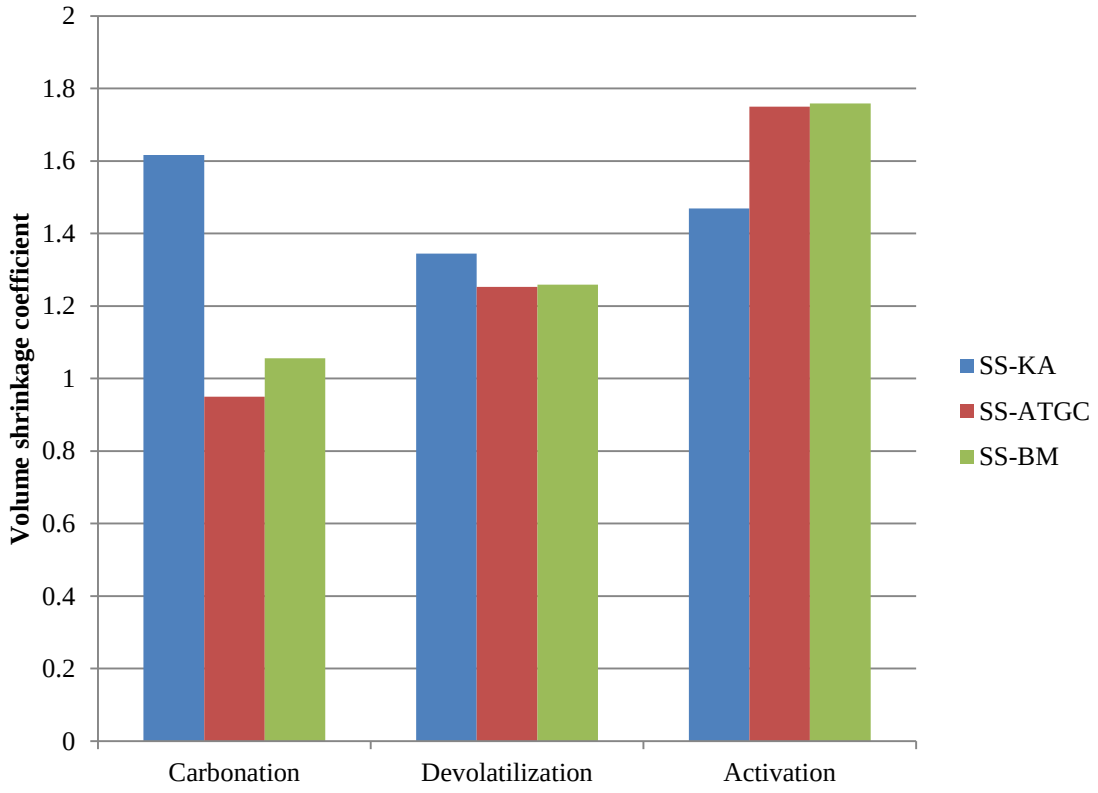

Figure 2: Dependence of the granules volume shrinkage coefficient on the stage of heat treatment

The obtained granules were further subjected to heat treatment: carbonization in inert atmosphere at a temperature of (500±50)°C, devolatilization in an inert atmosphere at (800±50)°C, and activation in an atmosphere of superheated steam at (900±20)°C till the volatiles yield of 45-50 wt. % [23]. The characteristics of granules samples at various stages of obtaining extruded activated carbons are shown in Table 6.

The coefficient of volume shrinkage of the granules obtained with the use of binders No. 2 and 3 at the stages of carbonization and devolatilization is considerably lower than that of the reference sample (SS-KA). However, in case of activation of devolatilized granules, the opposite phenomenon is observed: the coefficient of volume shrinkage of granules in samples SS-ATGC and the SS-BM is 1.2 times higher than that for the SS-KA sample.

As shown in Table 6, the samples of activated carbons obtained with the use of compounds No. 2 and 3 feature the mechanical strength (abrasion resistance) that is comparable to that of the extruded activated carbons based on traditional binders.

Analysis of the microporous structure of finished extruded activated carbons

Surface properties are extremely important characteristics of the sorbents, and much attention is paid to studying them [24]. For the purpose of a detailed study of the surface properties of granular activated carbons, analysis has been made with the use of automatic high-speed analyzer of porous structures NOVA–1200e. The study of the porous structure (Table 7) showed that by the nature of the porous structure, all obtained carbons were microporous, but the size of micropores was large (0.759 to 0.839 nm), which is also manifested by low characteristic energy of adsorption (15.488 to 17.130 kJ/mol). The volume of mesopores is very small (0.0637 to 0.0780 cm^3/g).

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Table 7: Characteristics of the porous structure of EAC samples

No.	Surface area	Coal grade		
		SS-KA	SS-ATGC	SS-BM
1	Specific BET surface area, m^2/g	1,074.2	933.2	1,064.0
2	Micropores DR surface area, m^2/g	1,230	1,076	1,232
3	Total DR pore volume, cm^3/g	0.5039	0.4460	0.5158
4	Micropores DR volume, cm^3/g	0.4372	0.3823	0.4378
5	Mesopores DR volume, cm^3/g	0.0667	0.0637	0.0780
6	Pores DR half-width, nm	0.759	0.804	0.839
7	Adsorption energy, kJ/mol	17.130	16.174	15.488

Based on the obtained data, the dependence of forming porous structure on the characteristics of binders used for obtaining extruded activated carbons has been established.

Figure 3 shows changing the pore volume in samples of activated carbons, depending on the viscosity of the binder used.

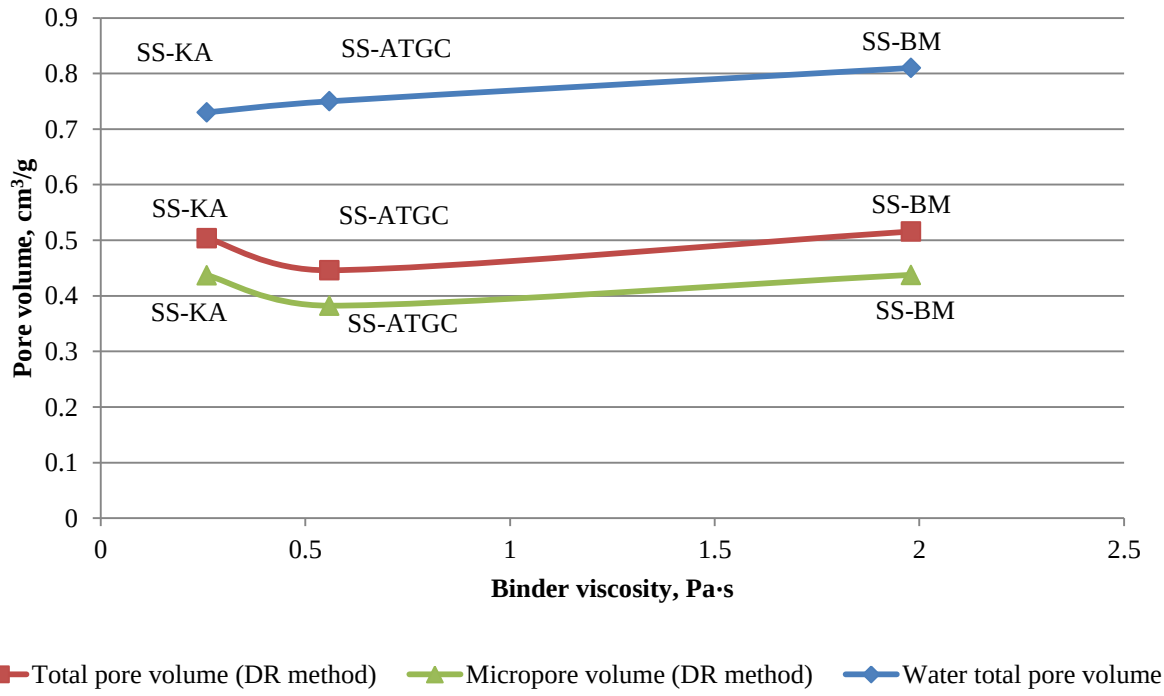

Figure 3: Dependence of EAC pore volume on the viscosity of the binder

As can be seen in Figure 3, binder viscosity does not considerably affect formation of micro- and mesoporous structures in extruded activated carbons.

One of the main indicators of extruded activated carbons quality is their sorption capacity, which is assessed by the value of the equilibrium activity in terms of toluene (kg/m^3). Sorption properties of activated carbons largely depend on the nature of their porous structure. As one can see in Table 6 and Figure 4, the highest sorption capacity is observed in the sample of extruded activated carbon obtained with binder No. 2 (SS-ATGC).

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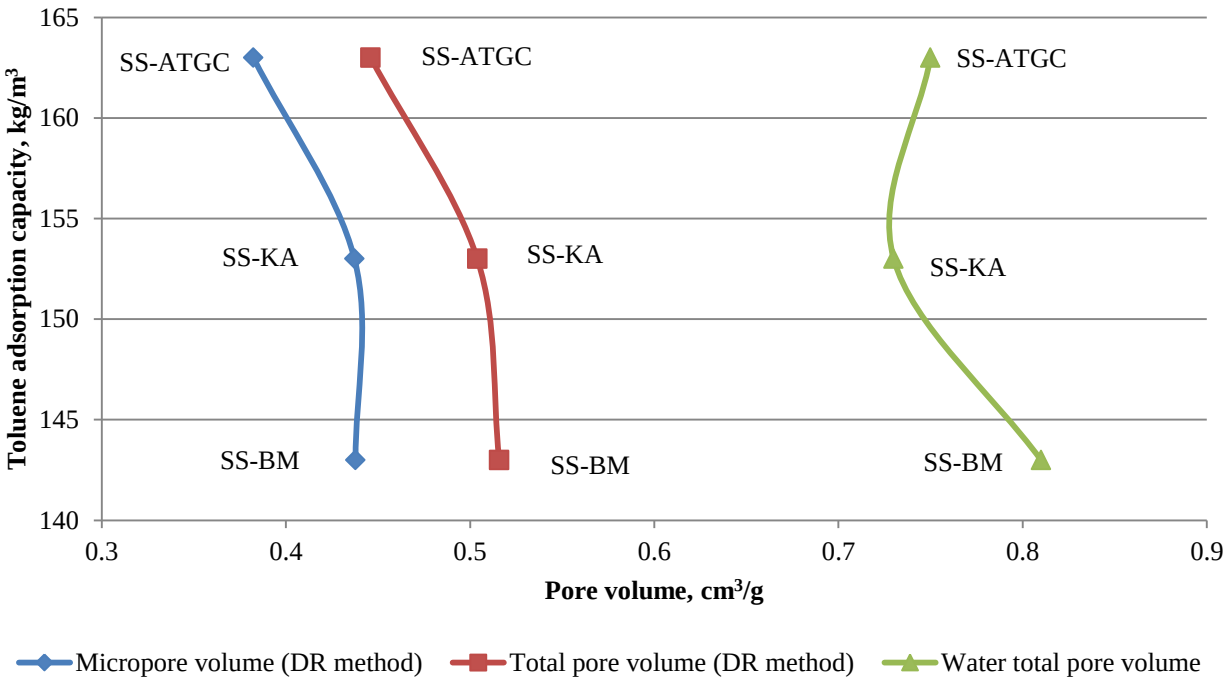

Figure 4: Dependence of sorption properties of extruded activated carbons on the volume of pores

CONCLUSION

Based on present study data, the following conclusions can be made:

- If petroleum processing products are used individually, the binder features either excessively high viscosity, or insufficient value of the carbon residue.
- The optimum values of viscosity and carbon residue of the binder may be achieved by the use of compositions of low-viscosity products with low content of carbon residue, and high viscosity products with high carbon residue value.
- When activated carbon is obtained using a binder based on compositions of petroleum processing products, sorbents may be obtained, whose characteristics are not inferior to those of activated carbons based on conventional coal and wood tars.
- Beside petroleum processing products, assessment of the usability of heavy petrochemical products and natural highly viscous mixtures of hydrocarbons (heavy oils and bituminous sands) as binder for extruded activated carbon production is also of interest.

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