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Physicochemical and Adsorption Properties of Thermochemically Activated Carbon Materials

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ABSTRACT: In this study, the thermal activation times of coal within the temperature range of 400-850°C were determined, along with the optimal activation conditions. The physical and chemical property alterations of the coal samples, activated using CO2 and H2O steam, were systematically analyzed. Additionally, the textural properties of the activated coal samples were investigated through low-temperature nitrogen adsorption studies.

KEYWORDS: Activated carbon, adsorbent, thermal activation, adsorption, surface area, total pore volume, pore diameter.

I.INTRODUCTION

In 2020, coal production volumes in Uzbekistan reached 402.1 million tons (in 2021 - 439 million tons, and in 2022 - 442 million tons) [1]. The majority of Russian coal is extracted using cost-effective open-pit mining methods, with underground mining contributing only 21-25% of total production. Approximately 77% of the produced coal is thermal coal, which includes hard coal, lignite, and anthracite; the remainder is coking coal.

Uzbekistan's coal reserves are estimated at 1,900 million tons, consisting of 1,853 million tons of brown coal and 47 million tons of hard coal. The projected resources exceed 5.7 billion tons. Significant coal reserves are concentrated in the southern regions, particularly in the Surkhandarya and Kashkadarya areas. Currently, coal mining operations are conducted in three deposits: the Angren brown coal deposit, as well as the Shargun and Baysun hard coal deposits [2].

Structurally, coal is comprised of complex organic macromolecules that form a solid matrix filled with pores and cracks. During coalification, processes such as graphitization and coking of organic components influence the structural characteristics of the coal material. The microstructural properties of coal, including crystal size and shape, pore content and distribution, density, and particle size distribution, play crucial roles in its adsorption and mechanical strength properties [3-5].

Adsorbents must possess sufficient mechanical strength to maintain their structural integrity under high pressure, mechanical agitation, and aggressive environments. Analyzing the influence of coal's physicochemical properties, such as structure, porosity, and microstructure, on the strength properties of coal adsorbents is essential [6].

Recently, coal has been increasingly utilized as an adsorbent for various industrial applications due to its high carbon content and porous structure, which allow it to effectively adsorb a range of substances, including water, gases, and pollutants. To optimize coal's use as an adsorbent, it is necessary to consider its properties, composition, structure, and the impact of activation conditions on its strength and adsorption capabilities.

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The primary chemical and structural characteristics of coal, including carbon and aromatic hydrocarbon content, are the main factors determining its adsorption properties. Microstructural parameters such as pore size and distribution also significantly affect the adsorption capacity of the carbon material. The mechanical strength of carbon adsorbents is a critical parameter that dictates their stability and resistance to degradation during operation. Evaluating the influence of coal's physicochemical characteristics, including its structure, porosity, and microstructure, on the mechanical strength properties of coal adsorbents remains a significant research focus [6].

II. SIGNIFICANCE OF THE SYSTEM

Particular attention is paid to the physico-chemical properties, elemental composition, thermal activation and adsorption properties of coal. Research methodology is explained in Section III, Section IV includes experimental results of the study and Section V discusses future research and conclusions.

III. METHODOLOGY

The selected coal samples were obtained by thermal activation at a temperature of 400-850°C in a pyrolysis device designed for laboratory conditions. The coal heating process was carried out for 2 hours in an inert environment - in the presence of argon gas. The temperature-dependent heating rate was modified as follows:

The heating rate up to 200°C was 5°C/min, and the heating up to 200–700°C was carried out at a rate of 10°C/min, and the subsequent heating was reduced to the previous level. During the procedure, argon gas was supplied at a rate of 100 ml/min.

The adsorption activity of activated carbon samples towards nitrogen at a temperature of 77K was studied.

Moisture content of the obtained coal adsorbents GOST 11014-2001 and non-volatile substances; The amount of minerals was determined by weighing according to GOST 12596-67 [7]

The distribution of pore sizes and structure characteristics of solid materials with gas adsorption according to GOST ISO 15901-2:2022 and ISO 9277:2022 (comparative surface area – Ssurface area, total pore volume - Vs, pore diameter - d) Autasorb IQ was determined by the method of low-temperature nitrogen adsorption at a temperature of 77.35 K on a Quantachrome Nova 1000e type static adsorption device.

IV. EXPERIMENTAL RESULTS

The physicochemical characteristics of coal were determined according to the requirements of GOST R 56357-2015, GOST 8302-87, GOST 8298-89, and TSh12-18:2001. The carbon and ash content in the samples was determined by absolute combustion of the material in a tubular furnace using the accelerated method according to GOST 2408.1-95. The qualitative characteristics of the hard coals are presented in Table 1.

Table 1.

Qualitative Characteristics of Hard Coals from Deposits

Indicator	Grade (Group)		
	1SSKOM *	1SSSH **	1TR ***
Standard Document	TSh12-18:1998	TSh12-18:1998	TSh12-20:2003
Lump Size, mm	18-90	≤13	20-120
Ash Content, % (not more than)	25,0	30,0	32,0
Total Moisture Content, % (not more than)	10,0	10,0	14,0
Lower Heating Value, kcal/kg	6200	5400	4600

*1SSKOM: Specific coal grade 1 **1SSSH: Specific coal grade 2 ***1TR: Specific coal grade 3

The subsequent analysis of the structure is related to the thermal behavior of the samples. The analysis of sample 1SSKOM indicates that within the temperature range up to 600°C, these samples lose up to 26% of their mass. For the 1SSSH hard coal, the temperature range with the maximum mass loss is broader, spanning 500-800°C, with a mass loss

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of over 18% at these temperatures, and a total mass loss not exceeding 30%. In the temperature range of approximately 610-850°C, the third coal sample, 1TR, exhibits a mass loss of 15-16%, with the total mass loss not exceeding 20%.

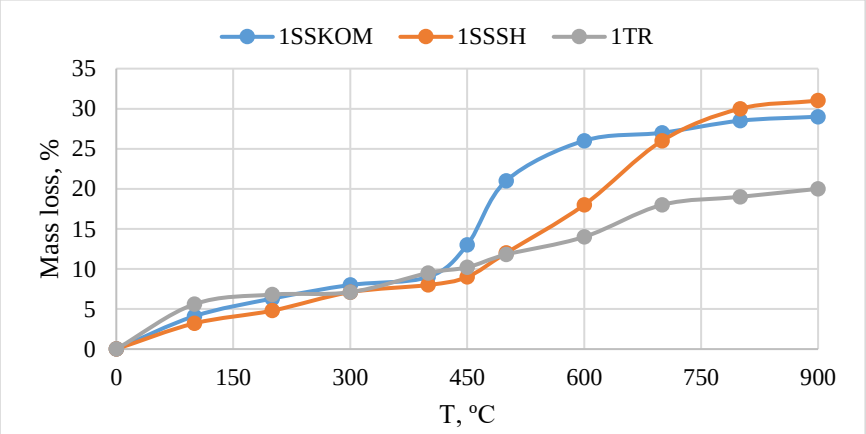

Figure 1. Change in the mass of coal samples during thermal treatment.

To obtain activated coals, physical activation was conducted in an inert atmosphere. Various coal fractions were subjected to carbonization in a fixed-bed laboratory reactor under identical experimental conditions. The reactor was heated to 450°C at a heating rate of 8 K/min, and thermal activation was performed at 850°C using a nitrogen flow of 100 ml/min, maintained for 2 hours.

Investigating the chemical composition of the coal samples is crucial, as it was found that these hard coal samples contain a significant amount of ash-forming substances. It is known that the presence of the mineral fraction in coal reduces the adsorption properties of the final coal adsorbents. Therefore, it is essential to conduct studies aimed at understanding the processes of thermal, physical, and chemical activation of the raw hard coal.

To obtain activated coals, they were physically activated in an inert atmosphere. Various coal fractions were subjected to carbonization in a fixed-bed laboratory reactor under identical experimental conditions. The reactor was heated to 450°C at a heating rate of 10 K/min up to 200°C, and thermal activation was performed at 850°C using a nitrogen flow of 100 ml/min, maintained for 2 hours.

The activated coals were designated by adding the letter "A" before the name of the original coal, indicating activation (e.g., A1SSKOM, A1SSSH, and A1TR) [8]. Subsequently, these coals were separately activated with carbon dioxide or steam at various burn-off levels to study the influence of the activating agent and ash content on the development of the porous structure. Activation with CO_2 was conducted at 850°C with a flow rate of 80 ml/min for different time intervals in the same reactor used for carbonization. Steam activation was also performed in the same reactor at 850°C, using a total H_2O/N_2 mixture flow of 100 ml/min for various time intervals. For coals activated with CO_2, the nomenclature included the original coal name followed by the number 1 (e.g., A1SSKOM1, etc.), and for coals activated with steam, the original coal name was followed by the number 2 (e.g., A1SSKOM2, etc.).

The coal samples thermally treated at 450ºC for 1 hour are characterized by the following properties (Table 2).

Table 2.

Indicator	Sample		
	1SSKOM	1SSSH	1TR
Mass Loss, %	13,1	9,3	10,3
Ash Content, %	26,47	30,87	33,44
Carbon Content, %	68,01	59,32	49,72
Moisture, %	4,10	3,80	4,60

Analyzing the changes in ash content and coal yield during the carbonization of 1SSKOM, 1SSSH, and 1TR coal grades, it can be inferred that the ash content of the coal samples increases with thermal treatment and the duration

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of the process. The 1SSKOM sample has the lowest ash content (26.47%), whereas the 1TR sample has the highest ash content (33.44%). This difference may be attributed to the varying compositions of the initial coals and their reactions to the carbonization process at the specified temperature. [9].

The coal yield (from the mass of the original coal) also decreases with thermal treatment and with prolonged exposure to the treatment. The 1SSKOM sample exhibits the highest coal yield (68.01%), while the 1TR sample shows the lowest yield (49.72%). This can be explained by factors such as mass loss due to the burning of part of the coal and the removal of water during thermal treatment.

The initial moisture content of the coals also influences changes in ash content and coal yield. Generally, higher moisture content in coals correlates with higher ash content. The moisture content of the coals is up to 10%, 10%, and 14% for the 1SSKOM, 1SSSH, and 1TR grades, respectively. Consequently, the 1TR sample with the highest moisture content also exhibits the highest ash content.

Therefore, the carbonization process at 450ºC results in increased ash content and reduced coal yield. This is due to mass loss from the burning of part of the coal, the removal of physically and chemically bound water, and differences in the initial moisture content and composition of the coals. These results are valuable for further studies on the carbonization processes and the optimization of coal production.

Tables 3 and 4 present the results reflecting activation time, total product yield, burn-off degree, ash content, and specific surface area of the thermally activated and steam-activated coal obtained in this study. As anticipated, the carbonization process leads to an increase in ash content in the samples. For each series of activated coals, a linear relationship is observed between burn-off degree and activation time. Simultaneously, the reaction rate during steam activation is comparable for all three coal samples, including those activated with CO_2. [10].

Table 3.
Characteristics of Coals Depending on the Duration of Thermal Activation (T) with CO2

Indicator	Sample											
	A1SSKOM1				A1SSSH1				A1TR1			
T, h	-	1	2	3	-	1	2	3	-	1	2	3
Mass Loss, %	0	8,1	16,7	21,7	0	14	22,1	27,2	0	8,5	11,9	14,8
Ash Content, %	26,5	23,2	22,9	21,8	30,9	28,7	27,2	26,9	33,4	31,2	30,9	30,1
Carbon Content, %	68,0	64,5	65,2	65,8	59,3	55,5	56,8	57,1	49,7	45,2	47,3	47,9
Moisture, %	4,1	3,6	3,3	2,9	3,8	2,9	2,5	2,4	4,6	2,8	2,7	2,6

**- duration of carbonization - 1 hour.*

Table 4.
Characteristics of Coals Depending on the Duration of Thermal Activation with water Steam

Indicator	Sample											
	A1SSKOM2				A1SSSH2				A1TR2			
T, h	-	1	2	3	-	1	2	3	-	1	2	3
Mass Loss, %	0	13,2	21,8	26,8	0	20,3	28,4	33,5	0	16,1	19,5	22,4
Ash Content, %	26,5	14,7	14,4	13,3	30,9	17,2	14,8	14	33,4	21,9	19,3	17,7
Carbon Content, %	68,0	72,4	72,7	72,8	59,3	67,2	69,2	69,7	49,7	59,8	63,8	65,1
Moisture, %	4,1	4,8	5,1	5,1	3,8	4,6	4,7	4,9	4,6	5,1	5,2	5,4

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Thus, the study results indicate that increasing the KOH content in the initial mixture reduces the ash content of coals across all types of activation. This confirms the effectiveness of chemical activation using KOH in reducing the ash content of coals and enhancing their potential as adsorbents.

The most significant factor in the activation process is the flow rate of the activating gas (CO2) and water vapor. Figure 3.9 shows the nitrogen (N_2) adsorption-desorption isotherms obtained at 77 K for coal samples produced with CO_2 flow rates ranging from 100 to 400 cm^3/min. The coal/KOH ratio was 1:4, and the carbonization temperature was 850°C (1 hour) for all samples. The study results demonstrated that different CO_2 flow rates significantly influence the porous structure of the samples.

Increasing the CO2 flow rate can facilitate more efficient transport of gaseous products to the surface of the solid during the activation process, thereby reducing mass transfer resistance. It was noted that the activated coal samples produced at a CO_2 flow rate of 200-250 cm^3/min exhibited higher adsorption capacity and greater micropore volume.

Therefore, these results confirm that the selection of the optimal CO_2 flow rate plays a crucial role in forming the porous texture of activated coals and can impact their adsorption properties.

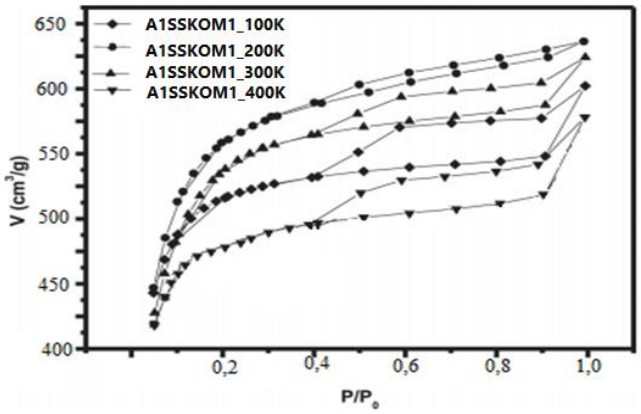

Figure 2. Nitrogen adsorption isotherms at 77 K on A1SSKOM coal samples.

Processing the obtained isotherms with corresponding adsorption equations facilitated the derivation of values for the textural characteristics of coals, which are presented in Tables 5 and 6.

Table 5.
Textural characteristics of coal samples (activation temperature 850°C)

Sample	BET Surface Area, m^2/g*	BET Surface Area, m^2/g**	t-Plot (external surface), m^2/g	V_a, cm^3/g	V_b, cm^3/g	Pore Size, Å
1SSKOM	251.21	422.54	53.17	0.107	0.020	28.320
1SSSH	209.34	352.12	44.31	0.089	0.017	42.480
1TR	174.45	293.43	36.92	0.074	0.014	46.728
A1SSKOM	376.81	633.81	79.75	0.160	0.030	23.600
A1SSSH	314.01	528.18	66.46	0.133	0.025	28.320
A1TR	261.67	440.15	55.38	0.111	0.021	31.152
A1SSKOM1	565.22	950.72	119.63	0.240	0.045	19.667
A1SSSH1	471.01	792.26	99.69	0.200	0.038	25.745
A1TR1	366.34	616.20	77.53	0.156	0.029	23.963
A1SSKOM2	734.78	1235.93	155.51	0.312	0.059	16.389
A1SSSH2	588.77	990.33	124.61	0.250	0.047	17.879
1SSKOM	251.21	422.54	53.17	0.107	0.020	28.320

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Table 6.
Textural characteristics of coal samples (activation temperature 850°C, coal/KOH ratio = 4/1)

Sample	BET Surface Area, m^2/g*	BET Surface Area, m^2/g**	t-Plot (external surface), m^2/g	V_a, cm^3/g	V_b, cm^3/g	Pore Size, Å
A1SSKOMK	546.37	919.02	115.64	0.168	0.032	22.476
A1SSSHK	458.45	771.14	97.03	0.140	0.026	26.971
A1TRK	379.43	638.21	80.30	0.117	0.022	29.669
A1SSKOM1K	898.69	1511.64	190.20	0.252	0.047	18.730
A1SSSH1K	753.62	1267.62	159.50	0.210	0.039	24.519
A1TR1K	586.15	985.93	124.06	0.165	0.031	22.822
A1SSKOM2K	988.56	1662.80	209.22	0.277	0.052	17.838
A1SSSH2K	791.30	1331.00	167.48	0.221	0.041	23.352
A1TR2K	644.76	1084.52	136.46	0.181	0.034	21.735

*- Specific surface area by BET;
**- Specific surface area by Langmuir.

From the data presented in tables 5 and 6, it can be observed that the specific surface area by BET (m^2/g) of coal samples subjected solely to thermal activation is significantly lower compared to samples activated using KOH. This indicates that KOH activation contributes to the formation of a greater number of active surface sites on coal, leading to an increase in its specific surface area.

Samples activated solely by thermal means exhibit higher values of pore volume (V_a and V_b) and pore sizes compared to samples activated with KOH. This may be attributed to the formation of larger and more open pores during thermal activation, resulting in an increase in both pore volume and size. [11].

V. CONCLUSION AND FUTURE WORK

Chemical analysis of the raw coals and elemental analysis of the ash component allow for the identification of differences in the content of chemical components and minerals depending on the coal grade. Coal of grade 1TR is characterized by a higher content of silicon oxide and lower content of CaO compared to samples of 1SSKOM and 1SSSH.

Increasing the activation temperature enhances the specific surface area of the coal for all samples, but after reaching a certain temperature (above 800°C), the increase in specific surface area slows down or ceases.

Sample 1SSKOM exhibits the highest specific surface area compared to other samples at all concentrations of KOH.

The addition of anhydrous carbonate or water vapor during the coal activation process improves the textural characteristics of the coal, and the optimal values of activation temperature and KOH concentration to achieve the highest specific surface area depend on the type of coal and its characteristics.

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