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RADIATION-INITIATED PROCESSES OF ACTIVATION OF CHARCOAL

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Abstract: The regularities of the formation of carbon adsorbent from charcoal coke under the influences of ionizing radiation and heat have been studied. In both stages of obtaining active adsorbent, i.e. in coking and activation processes, the stimulating effect of radiation is observed. Thus, a temperature decline by 200-450°C compared with thermal processes, and an increase in sorption capacity and mechanical strength of the obtained product were observed. The sorption capacity of the activated carbon by radiation-thermal methods 2,3 times more the adsorbent produced by thermal methods. As a result of polycondensation processes occurring under the effect of radiation on the carbon material, the mechanical strength of the product increases by 11.3%. The mechanism of the investigated processes is discussed, and it is shown that the occurring processes are due to the high penetrating ability and chemical effects of ionizing radiation. The technico-economical evaluation has been conducted and it has been found that using the electron accelerator having the beam power of 5,0 kW, allows producing 28,800 tons' high-quality carbon adsorbents per year.

Keywords: charcoal, gamma rays, micropores, sorption volume, adsorbents, mechanical strength

1. Introduction

Active charcoals are multifunctional according to their purpose and properties [1]. Purification of water and air from various contaminants, widespread use in hemodialysis, gas masks, and other areas also impose selective requirements on their properties. Considering these requirements, raw materials and methods to obtain active charcoal are selected. To increase the sorption capacity of active charcoal, it is necessary to achieve a high purity of micropores by cleaning resins from their structure. However, the possibilities of influence on micropores are very limited in traditional thermal methods. Because the heat-mass exchange at micropores of 1.0-1.5 nm is very weak which makes it difficult to decompose the resins in these pores. At the temperature of 800-900°C and pressure of 1–2 MPa, during the activation process by water vapor, the carbonic residues prevent a significant increase in sorption volume. Under more extreme conditions, partitions between the created micropores interact and unite with pores, resulting in the creation of transition pores greater than 10 nm and macropores greater than 100 nm. This leads to a decrease in the sorption volume and mechanical strength of active charcoal. Various literature data present variants of radiation usage to enhance the adsorption capacity of adsorbents [2]. As a result of the irradiation of carbon adsorbents with γ-rays and accelerated electrons, at room temperature, their adsorption capacity in concerning zinc acetate increases by 60% [3]. I.B. Krichko [4] investigated the effect of high-frequency discharge on adsorption kinetics of O_2 and CO_2 on the surface of charcoal and graphite. It was found that the adsorption of gases on the surface of carbon adsorbents accelerated by the effect of slow electrons, which energy was E = 2.5-9.5 eV. The authors [3] found that as a result of two-stage processing, the adsorption capacity of carbon adsorbents "Pittsburq"," AST"," Dreaer E-900 " for gases under optimal conditions increases to 69%.

In our investigation, based on the high penetrating ability and chemical effects of ionizing radiation, we obtained active charcoal under mild conditions (under relatively low temperatures and pressures.)

Producing carbon adsorbent was carried out in two stages: In the first stage, the substance containing carbon was coked in an oxygen-free environment, and in the second phase, the coke was activated in a water vapor medium. The results of the first stage are given in [5]. At the second stage, the resulting semi-coke was subjected to radiation-thermal gasification with water vapor and the final product was obtained-activated carbon. These results are presented in this paper.

2. Materials and Methods

From a methodological point of view, the gasification setting (Fig. 1) differs from semi-coking in that in this case a unit for supplying water vapor (7) is used and there is no receiver of liquid products since such products are not formed. In both phases, the substance was exposed to gamma radiation of the Co-60 isotope. A dose rate determined by ferrous sulfate dosimetry ranged within the interval P = 0,14-0,18 Gy/s.

The sample is exposed to ionizing radiation and temperature throughout the experiment in reactor 3 under stationary conditions. To take the products out of the reaction zone, a gas was given from inert gas balloon (1) through communication pipes (2)with a speed of 1 ml/sec. The sample (5) temperature was maintained constant in the reactor by heating spirals (4) and thermoregulator (6), water vapor is fed to the system through the water volume by a metering device (7), gas products are collected in the Gasometer (8), and solid products remain in the reactor (3). The reactor part of the device is located in the zone of maximum exposure to gamma radiation.

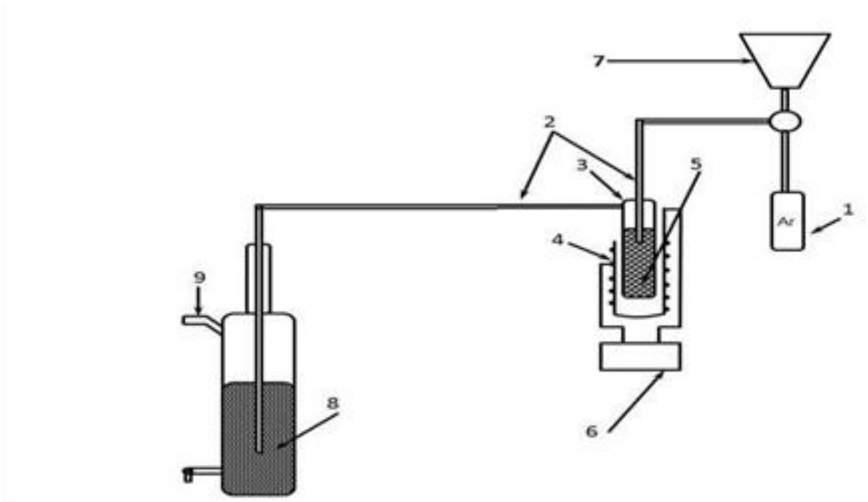

Fig. 1. Scheme of an experimental device for producing activated carbon from semi-coke: 1 - gas cylinder; 2 - communication pipes; 3-reactor; 4 - spirals for heating the reactor; 5 - sample; 6 - temperature regulator; 7 - volume for water with a dispenser, 8 - gas meter; 9 - exit to the chromatograph.

After the experiment, the benzene sorption capacity and mechanical strength of the activated charcoal in the reactor were determined. The benzene sorption capacity was measured in the vacuum unit and the MIS-60-8 the method was used to determine mechanical strength.

3. Results and discussion

As we showed in [5] at 500°C, the yield of semi-coke from coal was 66%. In this work, this semi-coke was gasified with water vapor under the influence of radiation and heat. Then the properties and yield of gas and solid products of the process were measured.

The coke obtained in the second stage was activated at 500 ° C in a water vapor medium. The relationship between the benzene sorption capacity and the absorbed radiation dose is shown in Fig. 2.

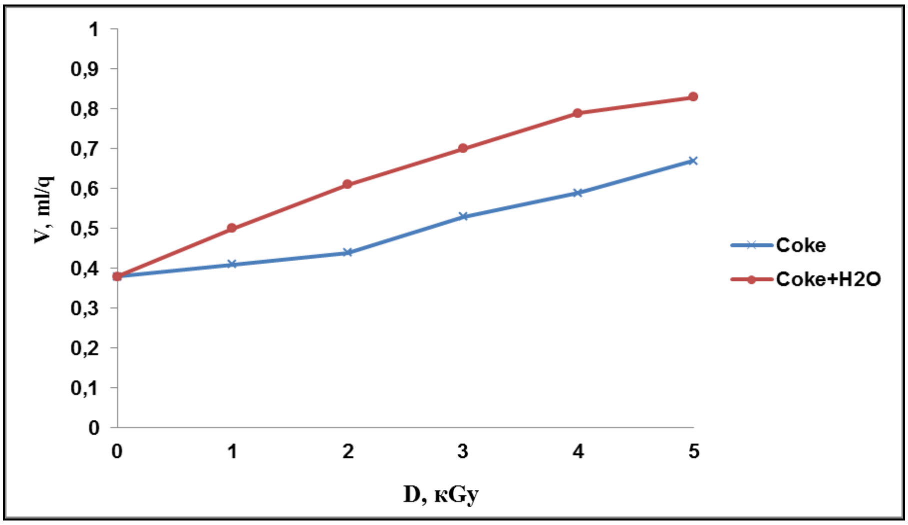

Fig. 2. Dependence of the sorption capacity of activated coke on the absorbed dose.
T = 450°C

Thus, the sorption volume after radiation-thermal activation of coal-coal coke in the presence of water vapor increases by 2.3 times. In the absence of water vapor, this growth does not exceed 1.7 times. The difference in the radiation effect is due to the reactions of resinous substances with water vapor. In the absence of a gasifying agent (H_2O), micropores are difficult to open, and therefore a significant increase in the sorption volume is not observed.

It should be noted that although there is an increase in the volume of micropores to the absorbed dose of 5.0 kGy, at subsequent dose values, there is a tendency to saturation, and this dose can be considered as the optimal dose.

Since the study of the features of the radiation-thermal process is a relatively new field, there is a limited amount of research and design work in the literature. Under the influence of radiation, ionizing radiation is inhibited and secondary electrons are formed with high chemical effects in the entire volume. As a result of this, the decomposition of tar in micropores and paths leading to them occur at a high speed.

The formation of hydrogen, carbon monoxide and methane in the pores occurs in the following radiation-stimulated reactions

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$

$$RH(tar) \rightarrow CH_4 + M \quad (2)$$

Even though these reactions occur at a significant rate at a temperature of more than 700°C, ionizing radiation, which causes activation and dissociation of gases, significantly accelerates the process

$$H_2O^* \rightarrow H + OH \tag{3}$$

Since carbon atoms are relatively more active in micropores and the pathways leading to them, they even actively participate in chain reactions:

$$C + OH \rightarrow CO + H \tag{4}$$
$$H + H_2O \rightarrow H_2 + OH \tag{5}$$
$$RH^* + H \rightarrow H_2 + R \tag{6}$$

The kinetics of the formation of H2, CO, and CH4 upon radiation-thermal activation of coke in a water vapor medium are shown in Fig. 3

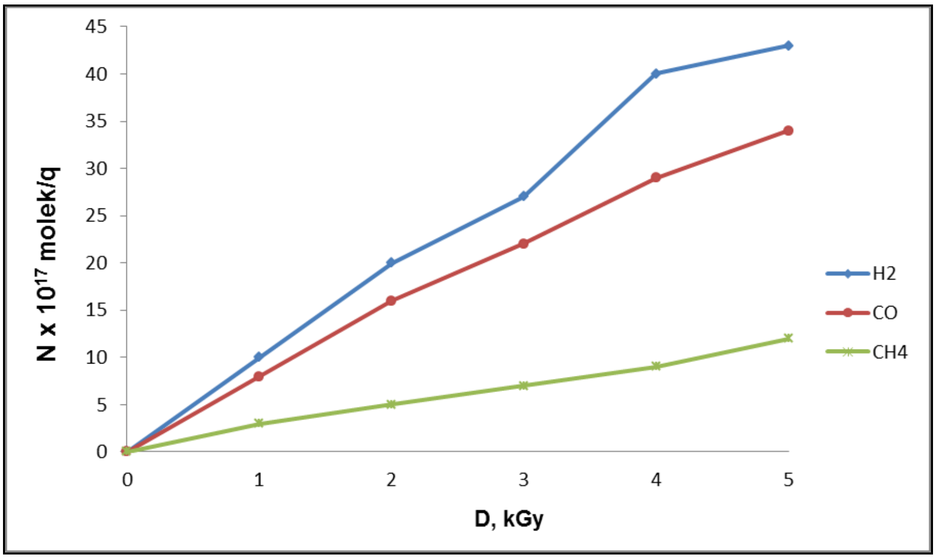

Fig. 3. Kinetics of H_2, CO and CH_4 formation during radiation-thermal activation of coke in a water vapor medium, T=450°C

It should be noted that in reaction scheme (4-6) the rate of the process is determined by the rate of reaction (5), since its activation energy is about 1 eV. Other reactions have significantly less activation energy.

The OH radicals formed in the last reaction react again with C atoms and tar in micropores at a high rate, producing H_2, CH_4, and CO gases. In similar experiments, it was found that the radiation-chemical yield of these gases is G (H2) = 50-60 molecules/100 eV. The same can be said about the formation of carbon monoxide. The same results were obtained when measuring the formation of carbon monoxide. In addition to the C + OH reaction, depending on the process conditions, it is also possible to recombine OH radicals

$$OH + OH \rightarrow H_2O_2 \tag{7}$$

In these processes, the radiation-chemical yield of the target reaction is determined by rates of reactions (3-6). The rate of reaction 3 depends on the intensity of the ionizing radiation, whereas the rates of reactions (4-6) depend mainly on temperature. Thus, by changing the rate of the adsorbed dose and temperature it is possible to control the rate and direction of the radiation-thermal process.

It is known that radiation effects on high-molecular compounds stimulate the build-up event at certain doses and increases their mechanical strength. In these studies, the dependence between the mechanical strength of the active charcoal obtained from the petroleum coke and the adsorbed dose was determined. Figure 4 shows the effect of adsorbed radiation dose on mechanical strength.

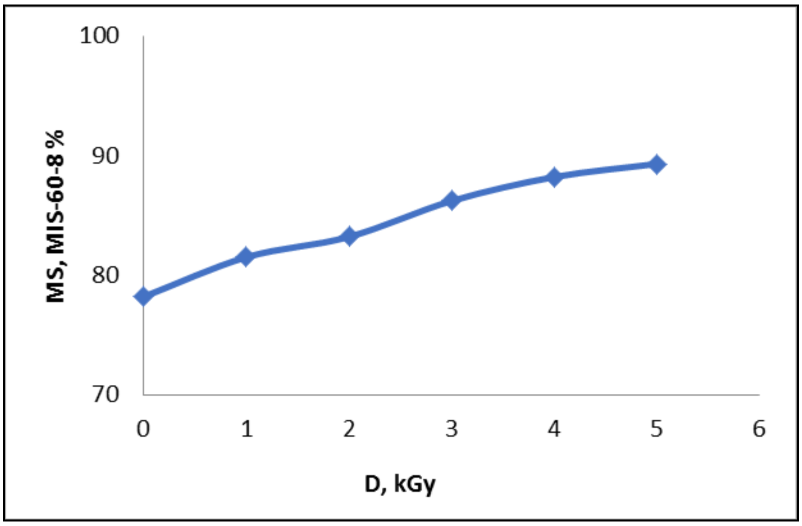

Fig. 4. Dependence of mechanical strength on absorbed radiation dose, T=450°C

Based on the MIS-60-8 method, the adsorbed dose up to 5 kGy results in the increase in mechanical strength from 78.2 % to 89.3% and this leads to the decrease in active charcoal consumption by 11.1% or increases exploitation time.

When a heterogeneous C + H_2O system is irradiated, in addition to the gas medium, radiation-induced chemical defects also appear in the carbon matrix. The concentration of these defects is calculated using the following formula:

$$N_a = G_a \cdot P \cdot 10^{-2} \tau \quad (8)$$

Where G_a- radiation-induced chemical yield of active particles, 1/100 eV

P- rate of the adsorbed radiation dose, eV/g s

τ – irradiation time

Radiation effects on macromolecular compounds in certain doses stimulate the crosslinking process and increase their mechanical strength. In these experiments, the dependence of the mechanical strength of active coal obtained from coal coke on the absorbed dose was determined.

It is known that [6] charcoal contains a lot of multifunctional polyaromatic compounds with a polyconjugated chemical bond system. Similar to polymeric materials having polyconjugated bonds, destruction, and build-up processes are possible during charcoal irradiation. The course of these processes depends on the characteristics of the irradiated object and the value of absorbed dose [7].

During γ-irradiation of charcoal and their semicokes [4,8], conjugated bonds in their organic masses are disturbed, and formation of the lattice structure is observed. This leads to a decrease in charcoal paramagnetism and an increase in the thermal stability of charcoal. An analysis of existing data in the literature allowed us to assume that if the conditions for processing coal with ionizing radiation are correctly determined, in addition to increasing the adsorption capacity, their mechanical strength can also be increased.

Technical and economic indicators of charcoal modification under the radiation-induced chemical effect are also of interest. Increasing the speed of processes under the influence of radiation, lowering the temperature, and increasing the sorption volume affect economic indicators of charcoal.

The productivity of the radiation-induced chemical process is determined by the following formula:

$$\Pi = \frac{kP_e}{D_0} \tag{9}$$

Where:
k –adsorption coefficient of the substances containing carbon ~ 0.80.
P_e – power of the radiation source, kW
D_0 – dose necessary for implementing the process. In our experiment Do= 4.0 kJ/kg.
When using an electron accelerator with a beam power of 5.0 kW:

$$\Pi = \frac{5kVt \cdot 0{,}8}{4kJ / kq} = 1kq / s$$

The efficiency of the device is 3.6 t/h that meets the existing requirements for the production or modification of active charcoal.

The conditional economic effect (Eef) was calculated using the following formula

$$Eef = \Delta M\kappa\ Ck - \Delta Dr\ Mr \tag{10}$$

$\Delta M\kappa$ -the amount of additional conditional adsorbent obtained by increasing the sorption volume due to irradiation, kg
Ck - the cost of the active charcoal, \$/kg
ΔDr - the cost of the radiation energy used for the modification, \$
Mr - the quantity of the radiation energy, kWh
If we consider the increase in sorption as the acquirement of the additional sorbent (i.e., consider the doubling of sorption volume as using 1 kg of charcoal instead of 2 kg) and use the following literature data :
Market prices for active charcoal: 1.0- 40.0 \$/kg
Radiation energy prices: 0.05- 4.0 \$/kW h

Considering these prices, the conditional economic effect can be achieved by thousands of dollars per hour. The economic effect is higher when charcoal prices increase and the cost of radiation energy decreases.

The effect of radiation on the obtaining and modification of active charcoal may be explained by the fundamental principles of radiation chemistry [9,10].

The use of radiation in obtaining carbon adsorbents has the following features:

- Absorption and high chemical effects of ionizing radiation,
- Ensuring high speed of energy-consuming chain processes at relatively low temperatures;
- Substances which are ecologically pure and do not form radioactivity when irradiating at relatively low energies (<5 MeV);

- Simple, few-stage radiation-induced chemical process, high economical efficiency when using low-tonnage and expensive substances.

4. Conclusions

The mechanism for increasing the sorption volume of coal coke under radiation-thermal effects consists in the volume absorption of ionizing radiation and the initiation of chemical reactions of the decomposition of resinous substances in micropores with the participation of reactive radiolytic particles and water vapor.

Due to the occurrence of radiation-stimulated polycondensation processes in the carbon material, the formation of a mesh structure occurs, which leads to an increase in its mechanical strength.

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РАДИАЦИОННО-ИНИЦИИРОВАННЫЕ ПРОЦЕССЫ АКТИВАЦИИ УГЛЯ

Р.Г. Ахундов, И.И. Мустафаев

Резюме: Исследованы закономерности образования активного угля из каменноугольного кокса под действием гамма-лучей и высокой температуры. Было выявлено стимулирующее воздействие радиации на этапах получения активированного угля, то есть в процессах коксования каменного угля и активации. По сравнению с термическими процессами наблюдалось снижение температуры процессов на 200-450°С, увеличение скорости реакции углеродистых веществ газифицирующим агентом, повышение сорбционной емкости и механической прочности полученного продукта. Сорбционная способность активных углей, модифицированных радиационным методом больше в 2,3 раза, чем у адсорбентов, полученных термическим методом. Под воздействием радиации в углеродном материале в результате процессов поликонденсации механическая прочность изделия увеличивается на 11,3%. Обсужден механизм изучаемых процессов и показано, что происходящие процессы связаны с высокой проницаемостью и химическим воздействием ионизирующего излучения. Проведены технико-экономические оценки и показано, что на электронном ускорителе мощностью 5,0 кВт можно производить 28800 тонн высококачественного углеродного адсорбента в год.

Ключевые слова: каменный уголь, гамма лучи, микропоры, адсорбция, адсорбенты, механическая прочность.

KÖMÜRÜN RADİASİYA TƏSİRİ ALTINDA AKTİVLƏŞDİRİLMƏSİ

R.Q. Axundov, İ.İ. Mustafayev

Xülasə: İonlaşdırıcı şüaların və istiliyin təsiri altında karbonlu maddələrdən aktiv kömür alınmasının kinetik qanunauyğunluqları tədqiq olunmuşdur. Aktiv kömür alınmasınının hər iki mərhələsində, yəni kokslaşma və aktivasiya proseslərində radiasiyanın stimullaşdırıcı təsiri aşkar olunmuşdur. Belə ki, termik proseslərə nisbətən proseslərin baş vermə temperaturunun 200-450°C azalması, reaksiya sürətlərinin artması və alınan məhsulun sorbsiya qabiliyyətinin və mexaniki möhkəmliyinin artması müşahidə olunmuşdur. Radiasiya üsulu ilə modifikasiya olunmuş aktiv kömürlərin sorbsiya qabiliyyəti termik üsulu ilə əldə edilən adsorbentlərdən 2,3 dəfə çoxdur. Karbon materialında radiasiyanın təsiri altında baş verən polikondensasiya prosesləri nəticəsində məhsulun mexaniki möhkəmliyi 11,3 % yüksəlir. Tədqiq olunan proseslərin mexanizmi müzakirə olunur və göstərilir ki, baş verən proseslər ionlaşdırıcı şüaların yüksək keçicilik və kimyəvi təsiri ilə bağlıdır. Texniki-iqtisadi qiymətləndirmələr aparılmış və göstərilmişdir ki, gücü 5,0 kVt elektron sürətləndiricisində ildə 28800 ton yüksək keyfiyyətli karbon adsorbenti istehsal etmək mümkündür.

Açar sözlər: daş kömür, neft koksu, polimer, qamma şüalar, sorbsiya həcmi, mikroporlar, hemodializ, mexaniki möhkəmlik