

ХИМИЧЕСКИЕ НАУКИ

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THE FORMATION OF CARBON ADSORBENT AT THE INFLUENCE OF RADIATION TO THE CARBONEOUS SUBSTANCES

Abstract. Kinetic regularities of the formation of carbon adsorbent from carboneous- substances under the influences of ionizing radiation and heat have been studied. In both stages of obtaining active charcoal, i.e. in coking and activation processes, the stimulating effect of radiation is observed. Thus, a temperature decline by 200°C-400°C compared with thermal processes, an increase in the reaction rate and increases in sorption capacity and mechanical strength of the obtained product were observed. The obtained carbon adsorbents were tested in the process of sorption of phosgen sorption from air medium. Sorption capacity of active charcoal obtained by the radiation method was found to be 30-40% higher compared with that obtained by the thermal method. As a result of polycondensation processes occurring under the effect of radiation on the carbon material, the mechanical strength of the product increases by 11.1%. 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 power of 5,0 kW, allows producing 28,800 tons' high-quality carbon adsorbents per year.

Keywords: coal, petroleum coke, polymer, gamma rays, sorption volume, micropores, hemodialysis, mechanical strength

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. In order to increase the sorption capacity of active charcoal, it is necessary to achieve 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 relation to zinc acetate increases by 60% [3]. I.B. Krichko [4] investigated the effect of high-frequency discharge on adsorption kinetics of O₂ and CO₂ 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.

There are reports on increasing [3] the chemisorption ability of carbon adsorbents in relation

to gasses using radiation. The authors of this work studied a two-stage process of the sorption capacity increase of active charcoals of “Pittsburg”, “AST”, “Dreaer E-900” types. In the first phase of the process, copper carbonate, silver nitrate, and chromium oxide were adsorbed on the surface of carbon adsorbents up to 2.0-7.8% concentrations. In the second phase, these samples were irradiated at room temperature, with γ -rays at a dose rate of 7 kGy/s, in the nitrogen, oxygen, helium and air environments up to 1000 kGy doses. As a result of these two-step processing, the gas adsorption capacity of carbon adsorbents under optimal conditions increases by 69%.

Based on the high penetrating ability and chemical effects of ionizing radiation we obtained active charcoal under mild conditions (under low temperature and pressure).

Materials and Methods

Producing of 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. 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 $P = 0,14-0,30$ Gy / s. The experiments for each phase were conducted using a laboratory device, schematically described in Figure 1.

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). Liquid products formed in the reactor are collected in the receiver (7), while gases are

collected in the gasometer (8). The reactor part of the device is located in the maximum impact zone of gamma radiation. During the coke activation phase in the aqueous medium, water vapor entered into the

reactor by the dispenser. The total amount of the formed liquid and gaseous products is measured in the graded gasometer, and the composition is determined by chromatographic and spectroscopic methods.

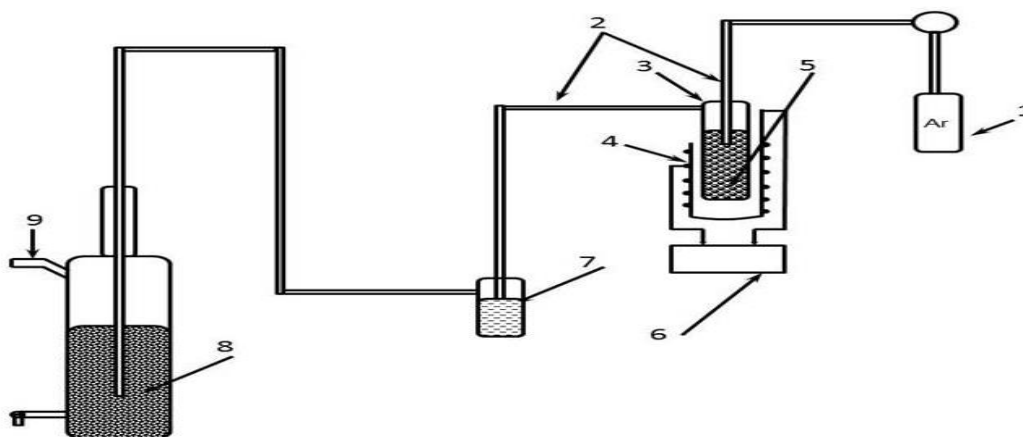
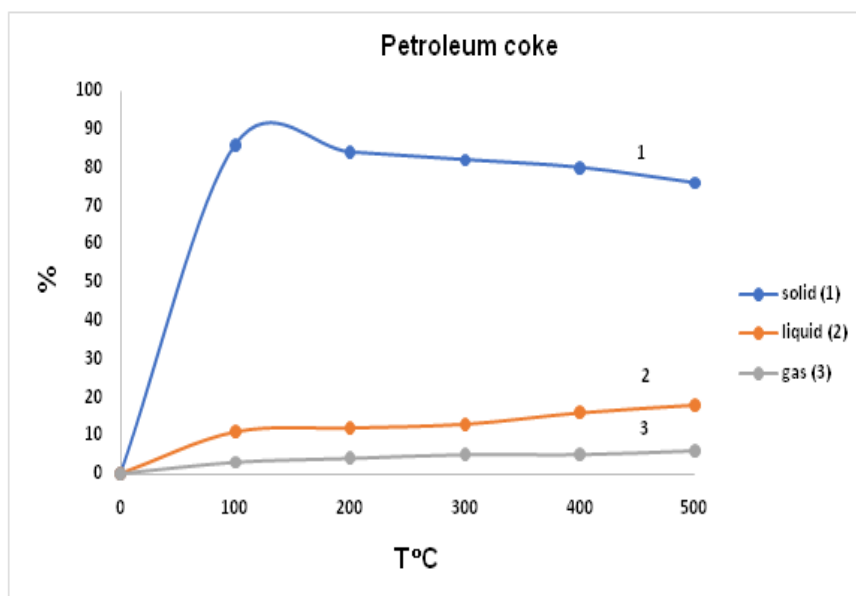


Figure 1. Schematic diagram of the experimental device for the study of the effect of radiation on the radiation-thermal decomposition of carbon-containing substances.

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 method was used to determine mechanical strength. The sorption of phosgene in the activated charcoal is determined by the dynamic sorption device.

Due to thermal effects, radiation isolates volatile compounds from petroleum coke, coal, and polymeric material. Depending on the chemical stability of the compound, the rate and direction of the occurring radiation and chemical processes are different. Temperature-related changes in solid, liquid and gaseous product yield under 1.0 kGy radiation are presented in Figure 2.

Results and discussion



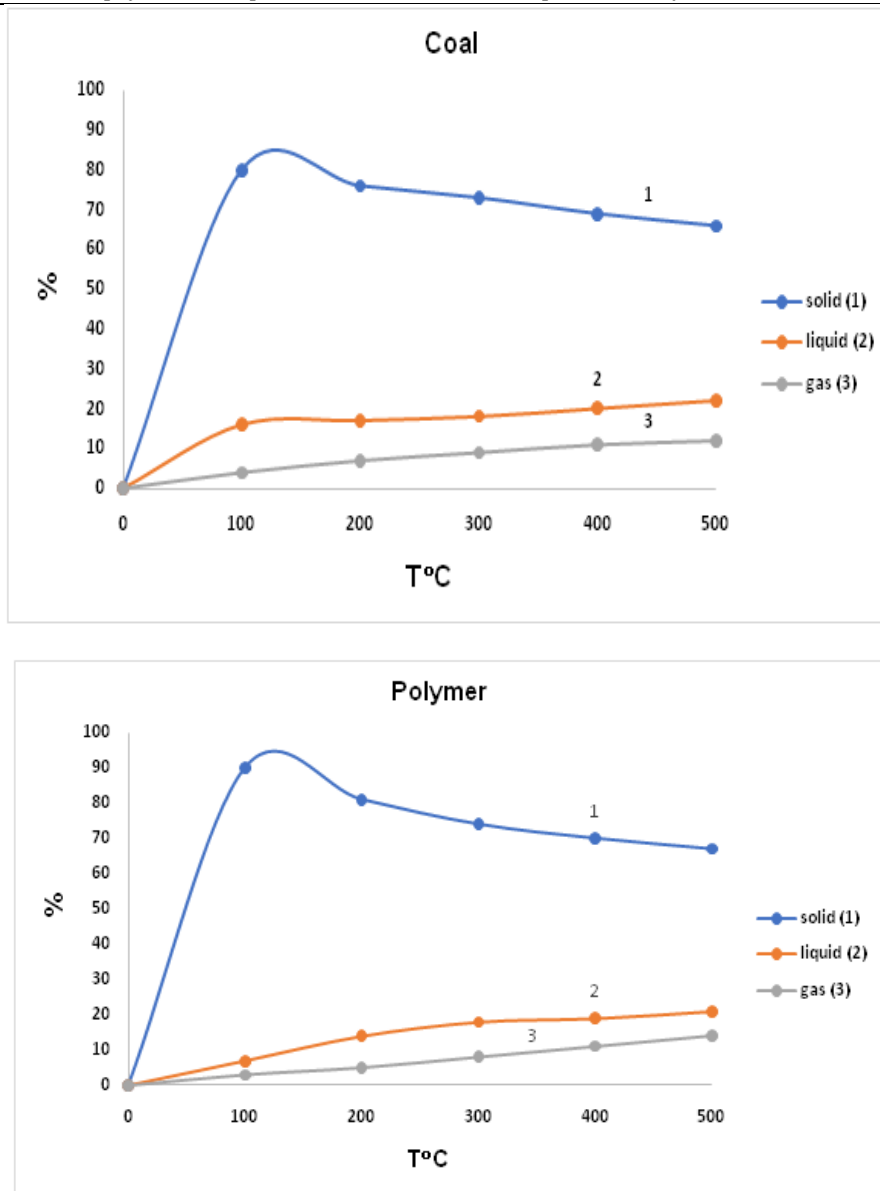


Figure 2. Dependence between temperature and yield (mass %) of products in various phases, formed from carbon-containing substances under radiation-thermal effects ($D=1.0$ kGy).

As seen in the figure, the maximum yield of compounds in the solid phase is detected for petroleum coke, and at 500°C, the yield of coke, coal and polymer is, respectively, 76%, 66% and 67%. Liquids formed during the coking process are mainly polycyclic aromatic compounds. In gas products, the total yield of H_2 , CO , CH_4 is more than 70%. When the temperature

rises, amounts of hydrogen-containing gases decrease, while amounts of heavy gases increase. It should be noted that similar reactions occur without exposure to radiation, but the rate of thermal reactions (Wt) is at least 2 times lower than that of the radiation-thermal process (Wrt). As seen in Figure 3, the Wt/Wrt ratio increases exponentially with increasing temperature.

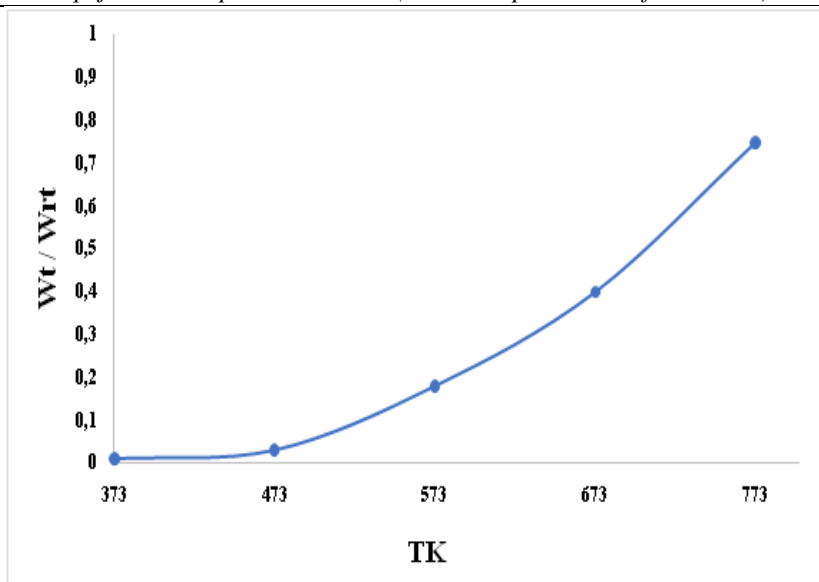


Figure 3. Temperature dependence of Wt / Wrt ratio (Burada 673 T uyun ordinat 0.40 olmalidir)

Considering the fact that, in thermal reactions, the dependence between the reaction rate and the absolute temperature is expressed as $k = A k_0 e^{-E/RT}$ and at constant dose rate the initial rate of radiation-induced chemical processes is not dependent on temperature,

the results presented in Table 1 can be explained kinetically.

Cokes obtained in the second stage was subjected to activation at 500°C in a water vapor medium. The dependence between benzene sorption capacity and the dose is given in Figure 4.

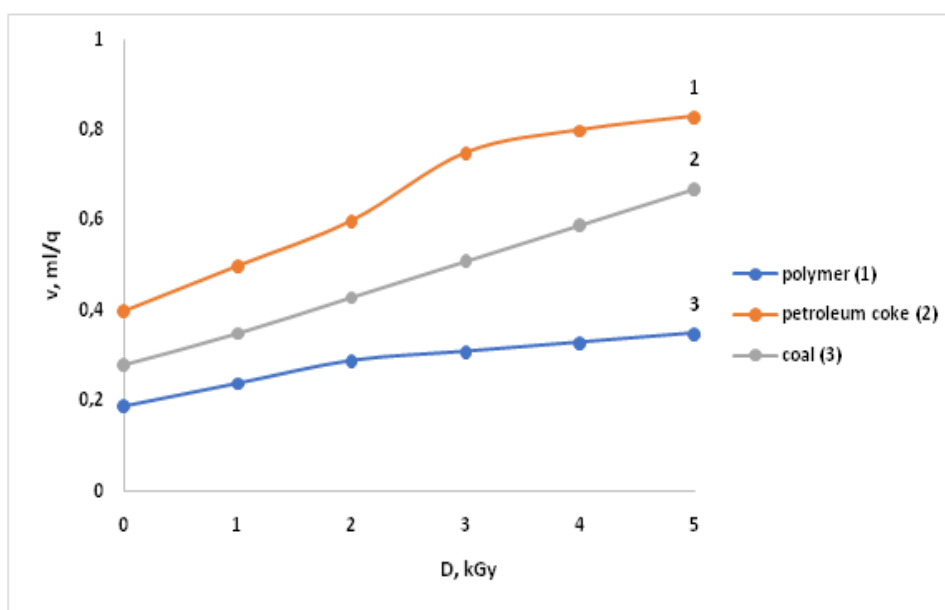


Figure 4. Dosage dependence of sorption capacity due to benzene

Thus, the sorption volume of radiation-thermally activated polymer-based coal increased 1.8 times, that of obtained from petroleum coke 2.1 times, and sorption volume of coal-based active charcoal 2.3 times. The difference in radiation effect is due to the amount of resins in the primary raw material and their radiation resistance. In the absence of a gasifying agent (H₂O), micropores are difficult to open and therefore, 30% reduction in the sorption volume occurs. The role of the radiation and gasifying agent in the cleaning of micropores and the leading paths has been discussed in detail in our work [5]. Although there has been an

increase in the volumes of micropores up to the dose of 4.0 kGy, there are almost no changes in the further increase of dose rates and therefore, this dose can be considered as optimal.

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 5 shows the effect of adsorbed radiation dose on mechanical strength.

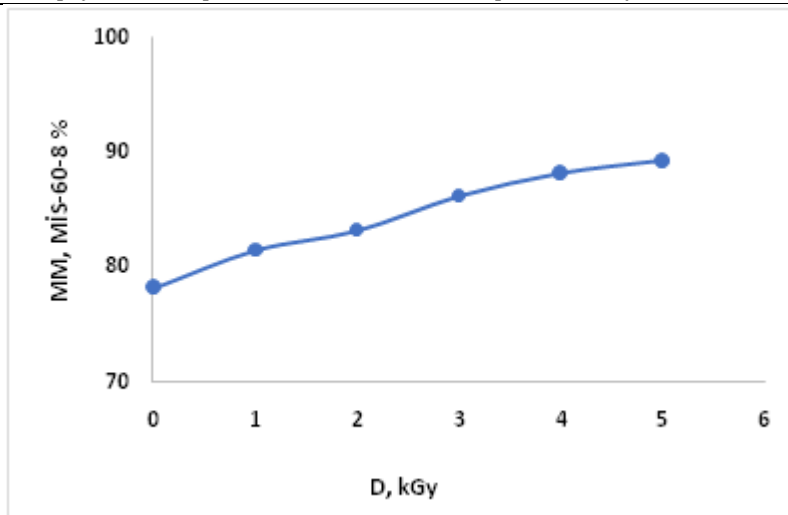


Figure 5. Dependence of mechanical strength on absorbed radiation dosage

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.

Ionizing radiation can confer mechanical strength to charcoal [6]. It is known that [7, 8] 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 [9,15].

During γ -irradiation of charcoal and their semicokes [4,10], 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. This situation assumes that the correct choice of the radiation treatment conditions of charcoal can increase the adsorption capacity along with mechanical strength.

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:

$$\Pi = \frac{kP_e}{D_0} \quad (I)$$

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 $D_0 = 4.0$ kJ/kg.

When using an electron accelerator with a beam power of 5.0 kW:

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

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 (E_{ef}) was calculated using the following formula

$$E_{ef} = \Delta M_{\kappa} C_{\kappa} - \Delta D_r M_r \quad (II)$$

ΔM_{κ} - the amount of additional conditional adsorbent obtained by increasing the sorption volume due to irradiation, kg

C_{κ} – cost of the active charcoal, \$/kg

ΔD_r – cost of the radiation energy used for the modification, \$

M_r - 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 \$/kWh

Considering these prices, the conditional economic effect can be achieved by thousands of dollars per hour. Apparently, 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 [11,12].

A developed porous mass confers unique properties to carbon materials. The common characteristic of such materials is the presence of gaps or pores described in Figure 6, which have a decisive effect on their functional properties [13].

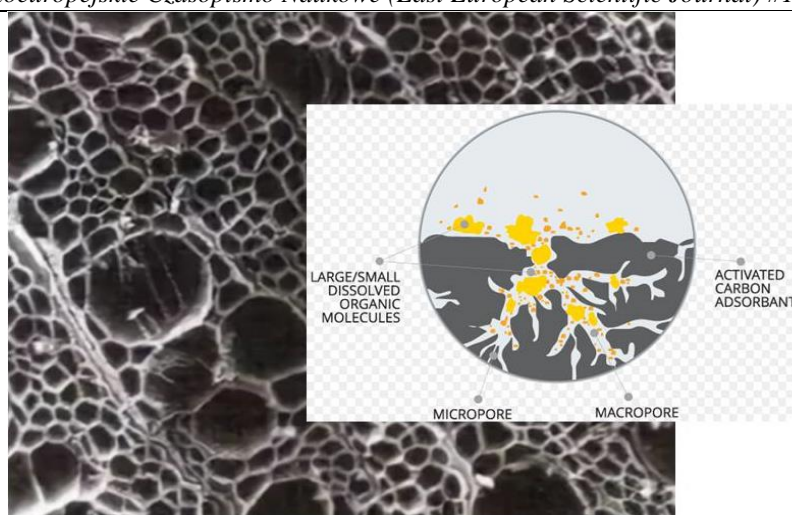


Figure 6. Schematic description of the carbon adsorbent network[1].

Despite the total volume of macro- and micropores in active charcoal is in the range of 0.34-0.61 cm³/g, more than 60% of this volume is attributed to macromolecules, and these pores are not actively involved in the adsorption of many toxins.

In classical methods, the process of the activation of carbon materials is generally as follows: during $T \geq 1$ hours, under the effects of high temperatures $T > 800^\circ\text{C}$ and active gases (He, Ar, N₂, H₂O, CO₂, etc.), an organic part of the carbon materials are decomposed, pores are opened in the charcoal mass, thus the sorption volume increases. The sorption volume, pore volumes and size-based distribution of pores, special surface, mechanical strength are the main parameters that characterize the effectiveness of the mentioned adsorbents. These parameters, in turn, depend on the characteristics of the primary raw material (its structure, porosity, ash content, composition) and the mode of obtaining carbon adsorbents (temperature, rates of combustion and heating). However, the adsorption capacity determined by the distribution of pores in the carbon mass is a key feature of carbon adsorbents. In this process, micropores and paths leading to them are blocked by resinous substances. Therefore, they can be only partially decomposed by thermal effects and a large part of the sorption volume is lost. Under more extreme conditions, during the activation of the carbon material, all oxidizing carbons on the upper surface of granule are involved in the reaction due to the high oxidation rate. In this case, a considerable loss of the material is observed due to surface combustion, which does not lead to the development of the porous structure of coal masses.

There are reports on performing the radiation modification of carbon adsorbents at room temperature. At room temperature, the rate of decomposition of resinous substances, which block micropores of carbon adsorbents, is very low. In this case, the rate of formation of low molecular weight compounds does not exceed $G \sim 0.1$ molecules/100 eV. Under these conditions, the increase in the adsorption capacity of carbon adsorbents is probably due to the radiation generation of chemisorption centers on the adsorbent surface.

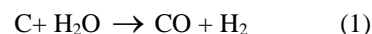
In these studies, we used high energy chemistry methods to solve the above problem. In the high energy chemistry, the kinetic energy of the atom and translational motion of the molecules varies from 0.1 parts of electrovolt (eV) to several electrovolts. These particles formed under the influence of ionizing radiation, light, plasma, and laser are called "heated" particles. With the use of these particles, it is possible to carry out endothermic reactions even at room temperature. On the other hand, depending on the energy of ionizing radiation, its ability to penetrate solid substances can be several centimeters or more, which means that ionizing radiation can stimulate chemical reactions in the organic matrix, pores, and pathways leading to pores of carbon materials.

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

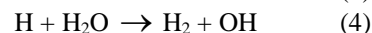
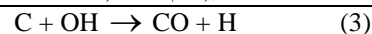
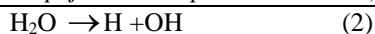
- Absorption and high chemical effects of ionizing radiation,
- Ensuring high speed of energy-consuming chain processes at relatively low temperatures;
- Substances which are ecologically pure and do not form radioactivity when irradiating at relatively low energies (<5 MeV);
- Simple, few-stage radiation-induced chemical process, high economical efficiency when using low-tonnage and expensive substances.

Since the study of these features is a relatively new field, there is a limited number of research, design and construction activities. Under the effect of radiation, inhibition of ionizing radiation and the formation of secondary electrons with high chemical effects occur in the whole volume. The decomposition of resin in micropores and pathways leading to them occur at a high speed under the influence of radiation.

The formation of hydrogen and carbon-monoxide in pores occurs with the following radiation-stimulated reaction



Despite this reaction occurs at more than 700°C temperature, radiation causing activation and dissociation of gasses, considerably accelerates the process



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

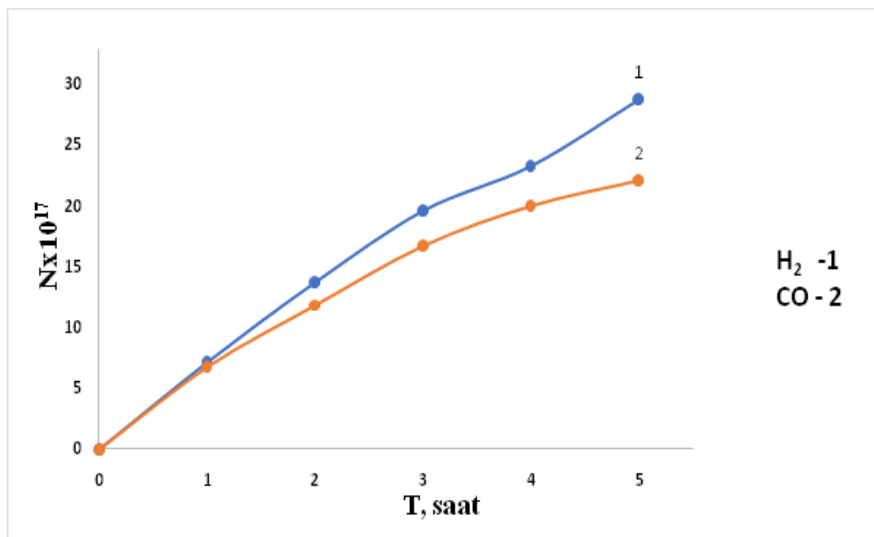
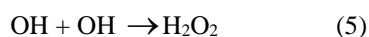


Figure 7. Kinetics of the formation of H₂ and CO in the radiation-thermal modification of active charcoal in the water vapor environment, 400°C

OH radicals formed in the last reaction react again with the C atoms in the micropores rapidly producing hydrogen and CO gases. In similar experiments, G (H₂) was found to be 50-60 molecules / 100 eV. The same results were obtained for the formation of carbon monoxide. In addition to the C + OH reaction [14,15], depending on the process conditions, recombination of OH radicals is also possible



In these processes, radiation-chemical yield of the target reaction is determined by rates of reactions 2, 3 and 4. The rate of reaction 2 depends on the intensity of the ionizing radiation, whereas the rates of reactions 3 and 4 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.

In addition to the gas phase, radiation-induced chemical defects also appear in the carbon matrix. The concentration of these defects is calculated by the following formula

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

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

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

τ – radiation duration

The role of these defects in increasing the mechanical strength of the carbon adsorbent has been explained above. Besides, after reaching a certain concentration, recombination of the defects occurs and

a stationary concentration of defects (N_s) is set up, which is calculated by the following formula:

$$N_s = G_a \cdot P \cdot 10^{-2} \cdot \tau - k_r [Na]^2 \quad (IV)$$

k_r – recombination constant of the defects

At the concentrations determined by this formula, the high mechanical strength of the carbon adsorbent is determined. The high sorption ability and mechanical strength can be attributed to the high penetrating power of radiation and the formation of highly active chemical particles in the whole volume.

Conclusions

It has been established that the rate of coking by radiation increases 1.2-3.0 times depending on the temperature, the sorption capacity of the coke is 30-40% higher than that of the coke obtained by the thermal method. This is attributed to the processes of destruction and polycondensation in the organic mass due to the high penetrating power and chemical impact of the ionizing radiation.

The mechanism of increasing the sorption rate of carbon-containing substances by the thermal radiation method is the decomposition of resinous substances in micropores by the absorption of ionizing radiation and the water vapor stimulation of the endothermic stages of radiation-induced chemical reactions. In contrast to thermal methods, ionizing radiation creates high-density and reactive particles in micropores, which result in the cleaning of micropores and the pathways leading to them.

Sorption ability of active charcoals modified under optimal conditions was tested in relation to carbon dioxide and phosgene. As a result of the development of the micropore structure due to

radiation-induced modification, the sorption ability of active charcoals increased in relation to toxins more than 40%.

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METHOD OF ELECTROCHEMICAL RECOVERY OF WASTE WATER AND ELECTROLESS COPPER PLATING ELECTROLYTE

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