Granulated activated carbon production based on petroleum coke

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Abstract. The current tendency of the world oil refining towards a decrease in the fuel oil production and raise petroleum refinery efficiency is expressed in a significant increase of the delayed coking units capacity. This approach leads to an increase in the production of low-quality sulphurous petroleum coke, which is difficult to use for the production of electrodes, which makes it necessary to search for new ways of using this product. Present study considers the production possibility of granulated activated carbon based on anode-grade petroleum coke and petroleum coke with an increased content of volatiles. The experimental part of the work included the study of the effect of petroleum coke carbonization and water vapor activation conditions on the properties of the obtained activated carbon, such as BET surface area, t-plot external area and micropore volume. It is shown that the optimal thermal treatment parameters of petroleum coke for granulated activated carbon production is carbonization at a temperature of 700°C, followed by subsequent activation in water vapor atmosphere at a temperature of 800°C. This approach makes possible to obtain sorbents with a BET surface area reaching 400 m²/g with an activated carbon yield of up to 30 wt.% of the feedstock. Results obtained in the study will expand the possibilities of qualified use of oil refinery delayed coker unit products.

1. Introduction

There is a strong tendency in the world oil refining to a systematic decrease of fuel oil production to raise petroleum refinery efficiency, which is reflected in a significant increase in the capacity of delayed coking units, since this process is the most common method for processing the heaviest part of oil – vacuum residue. This approach really makes it possible to obtain additional amounts of fuel fractions from the low-value oil vacuum distillation residue, but at the same time it leads to an increase in the production of low-quality sulphurous petroleum coke, which is difficult to use for the production of electrodes (the main consumer of petroleum coke of many enterprises in the Russian Federation).

At the same time, this petroleum coke can be used as a raw material for the production of activated carbons (AC), which are widely used in industry as sorbents. AC of various grades are used in the processes of adsorption purification (separation and concentration in gaseous and liquid media), in the recovery of solvents, as well as in solving environmental problems (purification of drinking water, waste water, waste gases etc.) [1-3]. However, due to the fact that the range and volume of production of industrial carbon adsorbents in the Russian Federation industry does not correspond to the needs, the share of imports in the market of activated carbons is about 75% [4].

Solving the problems of achieving waste-free oil processing at enterprises simultaneously with the production of sorption materials that can be used to reduce the environmental load from emissions of various industries is a very important goal in the development of northern (including the Arctic) regions, characterized by a very fragile ecological balance.
Currently, AC is mainly produced from carbon-containing mineral materials, such as coal and lignite, as well as from raw materials of organic and plant origin: peat, coconut and walnut shells, fruit seeds, etc.

A significant amount of research has been devoted to the study of the optimal approaches to the preparation and heat treatment of these raw materials for the carbon sorbents production. There are also studies that consider the production of AC on the basis of secondary raw materials, for example in [5], the results of a study on the thermal utilization of polymer parts based on polypropylene and polycarbonate with the production of activated carbons are presented. Described method allows to obtain product with similar sorption characteristics to AC used in the practice of wastewater treatment.

Despite the wide range of types of raw materials that are potentially applicable for the production of activated carbons on an industrial scale, the task of finding cheap and affordable alternative raw materials remains to be very important.

In this regard, researchers are actively working on the possibility of obtaining AC from heavy oil feedstock. An example of such feedstock is heavy oil residues and products of their processing, for example, oil pitches and petroleum cookes. Compared to conventional types of raw materials (for example, of plant or mineral origin), oil derived feedstock has a certain advantage – the relatively high constancy of its properties at relatively large production volumes due to the ability to strictly control the production process [6].

The study [7] confirmed the possibility of using heavy oil refining residues and petrochemistry residues as binders for the production of extruded AC. It is shown that when using coal as a carbonaceous material, and mixtures of high-boiling point petroleum products as a binder, it is possible to obtain high-quality carbon sorbents while improving the stability of their production.

The work [8] describes research on the production of activated carbons by means of physical and chemical activation from oil sands. Experimental results show that this feedstock is highly promising and can be considered as an industrial raw material.

In study [9], the production of AC using petroleum coke is considered, while it is noted that the maximum quantitative yield of carbon material with a specific surface area of 270 to 460 m²/g is achieved with a mass loss of the carbon material of the order of 30-45%. The source [10] reports on the production of activated carbon by physical activation of the delayed coking unit petroleum coke with a surface area of up to 494 m²/g.

In accordance with the aforementioned reasons, research in the field of production of activated carbon material based on petroleum coke is currently very relevant and will expand the possibilities of qualified use of this oil refinery product.

Thus, the purpose of this work was to study the possibility of obtaining activated carbon sorbents based on petroleum coke of various grades, obtained from refinery delayed coking units.

2. Materials and methods

Present study considers the production of AC on the basis of various grades of petroleum coke from delayed coking units – anode-grade coke (AGC-1 and AGC-2, produced with different feedstocks) and coke with an increased content of volatiles (CV). The properties of the initial coke samples are presented in table. 1. To analyze the porous structure, Quantachrome NOVA-1200e gas sorption analyzer was used (with the method of nitrogen adsorption at its condensation temperature).

The ways of using cokes are largely determined by their properties [11]. In 1985, Fischer and Perruci [12] put forward a hypothesis formalizing the influence of coke quality on the properties of anodes by three main features: the amount and composition of impurities in the coke, perfection of the crystal structure and porosity. These three factors are decisive not only for the use of cokes for the production of anodes, but also for their use for the synthesis of other carbon materials, including activated carbons.
Table 1. Properties of the initial samples of petroleum cokes

| Properties                  | AGC-1  | AGC-2  | CV     |
|-----------------------------|--------|--------|--------|
| Water content, wt. %        | 0.49   | 0.47   | 0.34   |
| Ash content, wt. %          | 0.17   | 0.20   | 0.22   |
| Sulphur content, wt. %      | 3.67   | 3.30   | 3.46   |
| Crystallinity, %            | 12.52  | 14.07  | 12.27  |
| Real density, kg/m³         | 1386.5 | 1386.4 | 1374.8 |
| Bulk density, kg/m³         | 1163.2 | 1101.0 | 1108.9 |
| Porosity, %                 | 16.08  | 22.52  | 19.34  |
| Total pore volume, cm³/g    | 0.1379 | 0.2096 | 0.1743 |
| Micropore volume, cm³/g     | 0.0097 | 0.0080 | 0.0119 |
| Surface area, m²/g          | 1.64   | 2.85   | 4.62   |
| Volatiles, wt. %            | 8.17   | 7.67   | 10.03  |

The original petroleum coke was crushed and sieved. A fraction with a grain size of 1.0-2.0 mm was used for further experiments in order to obtain granulated AC on its basis.

The activation of carbon-containing materials with such low volatiles yields can be carried out both directly for the initial coke and after preliminary thermal treatment (carbonization) of the raw coke. During the carbonization stage, endothermic decomposition of non-carbon impurities occurs with their removal in the form of volatile compounds (so-called "volatiles"), the process usually takes place in an inert atmosphere in a stationary or rotary kiln, or in a fluidized bed by blowing nitrogen gas [13].

Carbonization provides the formation of the initial porosity, which develops further at the main stage of activation. The influencing factors in AC production at this stage are determined by the nature of the carbonaceous material and consisted of the final heating temperature, heating rate, heating time, and the surrounding atmosphere. Among these factors, temperature plays a key role. Slow heating rates result in less volatiles removal and shrinkage, which affects the formation of micropores. A high heating rate causes damage to micropores and increases the proportion of mesopores and even larger macropores [14, 15].

In this work, carbonization was carried out by keeping the sample at a high temperature (from 500 to 900 °C) in the electrical oven in a closed container without air access for 3 hours.

To determine the efficiency of carbonization, the mass of the coke sample and the sulphur content were measured before and after carbonization (using a LECO CS-230 sulphur and carbon analyzer).

The activation process of carbon materials was carried out on a laboratory unit that included tubular electrical furnace, which provides heating to the required temperature. The sample was placed inside the tube in crucible. The process temperature was controlled using a thermocouple. To ensure that the sample is in a water vapor environment without air access, distilled water from the tank was constantly pumped by a dosing pump into an evaporation tank, the temperature of which was maintained above 100°C. The water vapour formed in the evaporation tank was fed through a heated tube to the activation zone. Typical weights of samples for activation were about 1.5 g. The consumption of liquid water was 1.5 ml/min. The temperature in the reaction zone was about 800 °C.

3. Results and discussion
The coke mass loss and sulphur content change during carbonization under various conditions are shown in table 2.
Table 2. Coke mass loss and sulphur content change during carbonization at different temperatures

| Coke sample | Carbonization temperature, °C | Mass loss, % | Sulphur content, wt. % |
|-------------|-------------------------------|--------------|-----------------------|
| Initial coke | - | 3.67 | |
| AGC-1 | 500 | 9.5 | 3.35 |
| 600 | 13.2 | 3.59 |
| 700 | 18.8 | 3.52 |
| 900 | 22.1 | 3.71 |
| Initial coke | - | 3.30 | |
| AGC-2 | 500 | 12.8 | 3.28 |
| 600 | 17.0 | 3.17 |
| 700 | 19.2 | 3.32 |
| Initial coke | - | 3.46 | |
| CV | 500 | 13.8 | 3.43 |
| 600 | 15.8 | 3.38 |
| 700 | 18.1 | 3.30 |

With an increase in the carbonization temperature in the specified range, the mass loss in the form of volatiles increased from 9.5 to 22.0%. At the same time, it is important to note that these indicators are quite close for the studied cokes of different grades.

The sulphur content during the carbonization changed insignificantly, which indicates that the sulphur compounds removal with volatiles occurs in a proportion corresponding to their average concentration in the coke.

The results of the activation of the coke samples in study and their characteristics - the BET surface area, the t-plot external surface area and the t-plot micropore volume are presented in table. 3.

Table 3. Carbonization and activation conditions of sorbent samples based on various petroleum cokes

| Sample number | Carbonization temperature, °C | Activation time, min | Activation mass loss, % | Recovery of AC, wt.% | BET surface area, m²/g | t-plot external area, m²/g | t-plot micropore volume, cm³/g |
|---------------|-------------------------------|----------------------|------------------------|----------------------|------------------------|---------------------------|-------------------------------|
| AC samples based on AGC-1 coke | | | | | | | |
| 1 | - | 45 | 42.3 | 57.7 | 164.6 | - | - |
| 2 | - | 70 | 52.1 | 47.9 | 175.4 | 42.9 | 0.0542 |
| 3 | 600 | 45 | 53.2 | 40.6 | 203.0 | 46.9 | 0.0639 |
| 4 | 700 | 45 | 55.3 | 36.3 | 347.8 | 79.8 | 0.1088 |
| 5 | 700 | 80 | 67.9 | 26.1 | 352.0 | 73.6 | 0.1134 |
| 6 | 700 | 90 | 84.1 | 12.9 | 446.0 | - | - |
| 7 | 900 | 45 | 36.9 | 49.2 | 176.9 | 68.9 | 0.0435 |
| AC samples based on AGC-2 coke | | | | | | | |
| 8 | - | 70 | 42.9 | 57.1 | 161.4 | 54.2 | 0.0402 |
| 9 | - | 100 | 46.4 | 53.6 | 177.3 | 66.1 | 0.0427 |
| 10 | - | 130 | 68.3 | 31.7 | 241.7 | - | - |
| 11 | 500 | 70 | 60.7 | 34.3 | 185.9 | 46.9 | 0.0551 |
| 12 | 700 | 60 | 61.2 | 30.9 | 409.2 | 117.0 | 0.1074 |
| AC samples based on CV coke | | | | | | | |
| 13 | - | 45 | 22.5 | 77.5 | 122.7 | 31.2 | 0.0376 |
| 14 | - | 90 | 26.8 | 73.2 | 171.4 | 35.0 | 0.0558 |
| 15 | - | 150 | 60.3 | 39.7 | 190.3 | - | - |
| 16 | 700 | 60 | 43.0 | 46.7 | 267.4 | 74.3 | 0.0759 |
| 17 | 700 | 80 | 74.8 | 20.7 | 299.0 | - | - |
Table. 3 data shows that, on the one hand, an increase in the activation time leads to the development of AC porosity, but on the other hand, the yield of the active carbon (AC recovery) decreases. Therefore it is important to determine optimum duration of the process.

AC samples with a preliminary carbonization stage have a significantly higher BET specific surface area relative to samples without preliminary heat treatment at close or even higher product yields (for example, samples No. 10 and No. 12, as well as No. 15 and No. 16). Thus, it is obvious that the activation of the initial petroleum coke without the carbonization stage will not be able to provide high quality sorbents. In this work, 700°C was taken as the optimum temperature for carbonization of petroleum cokes, since at a lower temperature (samples No. 3 and No. 11) and at a higher temperature (sample No. 7), a decrease in the specific surface area is observed.

Some of the AC samples obtained (in particular, No. 6 and No. 12) are already approaching the specific surface area of typical activated carbons (for which it is usually in the range of 400-1500 m²/g). However, more intensive carbonization and activation conditions are accompanied by significant product losses due to its gasification (for example, for sample No. 6 with the highest specific surface area in study, the AC recovery was only at 12.9 wt.%).

AC obtained on the basis of AGC cokes have relatively higher porosity, than based on CV coke with comparable AC recovery.

Thus, the preliminary results of the carried out studies indicate the possibility of obtaining granulated activated carbons on the basis of petroleum cokes of different grades.

It has been shown that the optimal thermal treatment parameters of petroleum coke for the production of granulated activated carbon is preliminary carbonization at a temperature of 700°C, followed by activation in water vapor atmosphere at a temperature of 800°C. This approach makes possible to obtain sorbents with a BET surface area reaching 400 m²/g with an AC yield of up to 30 wt.% of the feedstock.

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