Influence of thermochemical activation of hydrolytic lignin by hydroxide of potassium on properties of carbon adsorbents

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Abstract: It was found that increasing the temperature of thermochemical activation of up to 750 °C and increasing the dosage of potassium hydroxide to 2.1 g / g of activated carbon (AC) synthesis of hydrolytic lignin has a positive influence on the formation of adsorption and structural properties of the AC.
Keywords: thermochemical activation .potassium hydroxide , activated carbon, synthesis, hydrolytic lignin, formation, adsorption and structural properties.

Introduction

Russia, as one or the other country, has a rich source of raw materials for the production of adsorption material, which makes it possible to obtain a wide range of carbon adsorbents for various purposes with the best consumer value, namely combination of price and quality. It should be noted that in a continuous rise in environmental pollution, and rapidly increasing consumption of different filter materials. The most common and effective filters are filters based on activated carbon (AC).

The one of the main determining factors in the production of various types of activated carbon is the primary products and conditions of activation. The raw material for activated carbon are a wide variety of carbon-containing natural resources and their by-products: wood and wood waste processing products, peat, peat coke, some bituminous coals and lignite, waste hydrolysis industry in particular, lignin, which is a secondary resource for the chemical processing of wood and annual plants and many others [1 - 5].

Currently, trend of using thermochemical methods of activation of raw materials was observed in the synthesis of active carbon, because these methods allow to obtain adsorbents with predetermined adsorption properties and pore structure parameters [6]. When thermochemical processing of vegetable raw material molecular weight lignin is reduced by several times, and its reactivity increases.

Determining factors in the synthesis of activated carbons (AC) with the use of thermo-chemical activation methods are the choice and dosage of an activating agent, and the process temperature. As activating agent it was offered to using orthophosphoric acid, alkali metal hydroxides, alkali and alkaline earth metals, calcium oxide, chlorides. There is a large amount of evidence on the application NaOH as an activating agent and its effectiveness in the synthesis of adsorbents methods thermochemical activation of various carbonaceous materials [7, 8].

Given the urgency of utilization of secondary resources of chemical processing of wood, the volume of which is now in Russia amount to tens of millions of tons per year, is very timely search and learning opportunities for active coals from hydrolytic lignin with using various activating agents.

The purpose of this work is the synthesis and study of properties of carbon adsorbents obtained thermochemical activation of hydrolytic lignin with potassium hydroxide at varying conditions of the process. We determined the effect of predpyrolysis and pyrolysis temperature, and dosage of an activating agent - potassium hydroxide to form the adsorption properties of adsorbents and porous structure.

Materials and methods of research

One of the methods of mathematical modeling is used to study the effect of active carbon synthesis conditions of the hydrolytic lignin formation and adsorption properties and the porous structure of adsorbents, in particular, a central composite rotatable uniforms - second-order plan for the three factors [9]. The most significant variables of active coal synthesis factors are the temperature of the pre-carbonization ($T_{P/P}$), consumption of an activating agent (D) and the pyrolysis temperature (T_{TCA}). The values and intervals varying factors are presented in Table 1.

According to plan of experiment it was attained twenty samples ACfrom hydrolysis lignin and potassium hydroxide, which is used as an activating agent. The first phase was carried out predpyrolysishydrolytic lignin, which was formed as a result of the primary pore structure of coal-raw, the next - pyrolysis - activation of coal-raw.

The adsorption properties of active carbon was evaluated by the adsorption aqueous solutions of iodine (J_2) and methylene blue (MB)[10]. Important characteristics of adsorbents, ceramics, nanotubes and other porous nanostructured material are highly specific surface (S sp.), pore size and volume.

Specific surface area is a measure of strength of solid body interaction with the environment, whether it is gas, liquid or another solid. Therefore, the definition of the specific surface area is one of the most common methods for studying nanomaterials indicators developed porous structure.

Determination of specific surface area based on the quantity of adsorbate gas which is adsorbed on the surface of the adsorbent at different relative partial pressures P/P_0 at the boiling temperature of liquid nitrogen T = 77 K [11]. For the practical implementation of this technique most widely used adsorption volumetric (volume measurement) analyzers based on the method of low-temperature nitrogen adsorption.

In this case it was studied the structure of the porous adsorbents, data of the specific surface area were obtained onthe analyzer ASAP 2020 MP. The gas - adsorbate is nitrogen.

The data is obtained by adsorption isotherms, which are used to determine the specific surface area and pore structure of the synthesized carbon adsorbents. Calculation was conducted on the specific surface polymolecular adsorption BET equation [12]:

$$\frac{1}{(a(P_0/P)-1)} = \frac{1}{a_m C} + \frac{C-1}{a_m C}(P/P_0),$$

where P - the gas pressure;

P_0 - the pressure of its saturated vapor;

a- the magnitude of adsorption;

a_m- limit adsorption;

C - a constant, which is characterizing the interaction of the adsorbent / adsorbate.

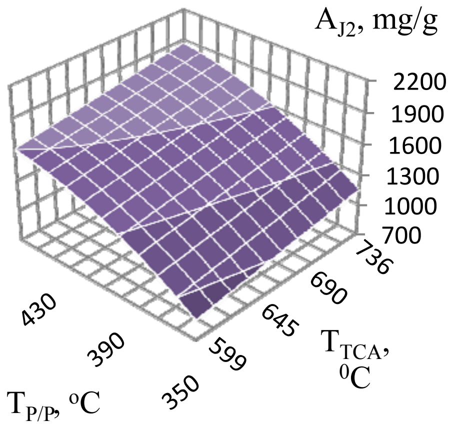
Table 1 - The levels and ranges of variation factors hydrolytic lignin thermochemical treatment in the presence of an activating agent

Variable factors	Plan Features					
	Step variation, λ	Factor levels				
		-1,682(-α)	-1	0	1	1,682(+α)
Temperatureofpredpyrolysis, °C	30	350	370	400	430	450
Temperatureofpyrolysis, °C	45	600	630	675	720	750
Dosage of KOH, г/г	0,24	1,00	1,16	1,40	1,64	1,80

The discussion of the results

According to the experimental data the coefficients of the regression equations were calculated and determined their significance. The equations of regression with the significant coefficients relating the values of output parameters with experimental conditions are mathematical models of the process. On this basis response surface was constructed, which is shown the effect of a two-step thermochemical processing parameters of hydrolytic lignin on the adsorption properties of the AC (Figure 1-2).

Adsorption activity on iodine (A_{J2}, Figure 1) describes mainly the development of microporous structure of activated carbon.



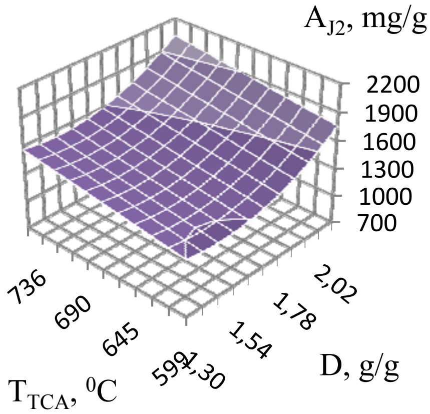


Fig. 1 - Effect of temperature thermochemical processing hydrolysis lignin and KOH dosage on the adsorption properties on iodine of the AC.

As seen from the graphic dependency, increasing temperature of lignin thermochemical treatment has a positive effect on the adsorption activity of AC for iodine. Influence temperature thermochemical treatment on the adsorption activity of AC for iodine increases with rise consumption of potassium hydroxide. Consequently, when the temperature rises in the considered thermochemical activation intervals and the variation in the presence of potassium hydroxide the adsorption properties of synthesized adsorbents are improved.

Adsorption of methylene blue (A_{MB}, Figure 2) gives an idea of the specific surface area of activated carbon, formed by pores with a half-width greater than 1.0 nm.

Temperatures preliminary carbonization and pyrolysis are interconnected, and the best properties with regard to adsorption of methylene blue are formed at the maximum temperature values of these factors in varying intervals. Increasing the dosage of potassium hydroxide has a positive effect on the output parameter. Note that the highest values are reached MB adsorption under the same conditions of heat treatment, and that on J2. Therefore, these conditions should be recognized as optimal for the synthesis of AC.

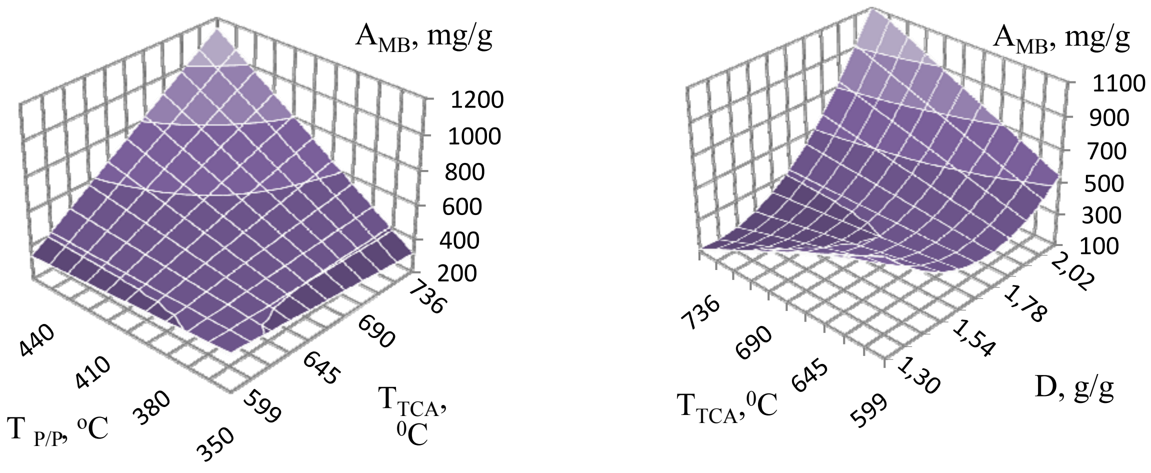


Fig. 2. Effect of temperature thermochemical processing of hydrolytic lignin and dosage of KOH on the adsorption properties by methylene blue of the AC.

Characteristics of activated carbon adsorption properties only does not give a complete picture of the formation of its structure. However, it shows that the choice of the activating agent plays a key role in the formation of the porous structure of carbon adsorbents, because it can significantly vary since its properties.

There are many types of porous systems. Thus in various samples, and in the same sample, individual pores of the porous body may vary considerably in shape and size. Table 2 shows the results of a study of the porous structure of the experimental samples CA. Analysis AC porous structure showed that it is presented mainly micropores. The mean half width of micropores ranges from 1.11 nm to 1.16 nm. According to the classification of IUPAC this range of pore size relates to supermicropores. Supermicropores represent an intermediate region of porous bodies between micropores and mesopores.

Table 2. The pore volume and specific surface area of activated carbon samples from the thermochemically treated with hydrolytic lignin in the presence of potassium hydroxide.

Sample	V $_{micropore}$, sm^3/g	V $_{mesopore}$, sm^3/g	$V_{\sum pores}$, sm^3/g	S, m^2/g
	Dubinin-Radushkevich	BJHdes, Broekhoff-deBoer	BET	BET
Л-1	0,28	0,03	0,31	553
Л-2	0,47	0,02	0,51	903
Л-3	0,32	0,04	0,37	612
Л-4	0,41	0,02	0,43	755
Л -5	0,29	0,02	0,32	563
Л -6	0,41	0,13	0,56	809
Л -7	0,37	0,04	0,42	717
Л -8	0,70	0,03	0,81	1446
Л -9	0,29	0,06	0,36	600
Л -10	0,57	0,03	0,62	1147
Л -11	0,44	0,03	0,49	885
Л -12	0,49	0,03	0,54	941
Л -13	0,35	0,03	0,38	731
Л -14	0,77	0,10	1,07	2024
Л -15	0,35	0,02	0,39	685
Л -16	0,39	0,04	0,44	775
Л -17	0,43	0,04	0,49	868
Л -18	0,42	0,03	0,47	816
Л -19	0,43	0,03	0,57	831
Л -20	0,45	0,03	0,60	795

The obtained experimental data are calculated regression equation, that used for the construction of plots - response surface (fig.3-4), showing the dependence of the output parameters of the technological parameters of obtaining AC.

Thus, it should be noted that the nature of changes in both adsorption and structural properties AC samples, represented as response surfaces, the same character indicates the dependency on the conditions of the thermochemical treatment of hydrolytic lignin (Fig. 1-4).

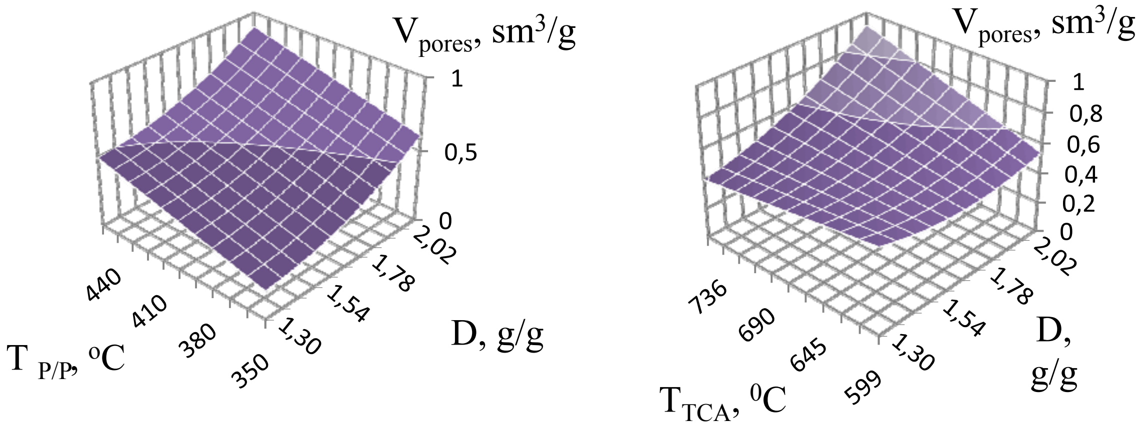


Fig. 3 Effect of thermochemical processing temperature hydrolysis lignin and KOH consumption per volume of micropores formed AC.

As seen from the results is shown in the graphs, an increase in dosage KOH and thermochemical treatment temperature of hydrolytic lignin gives positive effect on the formation of micropores. There is a mutual positive impact of these factors on the output parameter. With increasing temperature predpirolisys, the volume of micropores definitely increases. However, it is expedient to raise the activation temperature only at high doses of potassium hydroxide.

It is known that activated carbons with a high micropore volume are characterized by the specific surface. The micropores have a high ratio of surface area to volume ratio and, consequently, make the largest contribution to the value of this parameter of activated carbons. Size of micropore is comparable to the size of molecules and it plays an important role in adsorption selectivity as limited diffusion and provides the effect of molecular sieves.

Based on the experimental data one can conclude that the consumption of potassium hydroxide, and the temperature of the thermochemical treatment of hydrolytic lignin has a positively influence on the surface area of synthesized activated carbons (Figure 4).

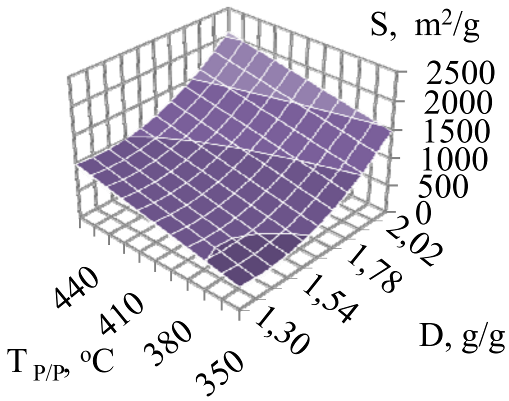


Fig. 4 Effect of lignin thermochemical treatment temperature and KOH consumption per surface area of active carbon.

When the temperature of thermochemical processing of hydrolytic lignin and the dosage of an activating agent are increase, adsorption and structural properties of the AC are improved. The research hold a great promise in the directed synthesis of carbon sorbents with the set of properties and structural characteristics.

Conclusions

1. Carbon adsorbents are obtained with high specific surface area and high adsorption properties by thermochemical activation of hydrolytic lignin with potassium hydroxide by varying the conditions of the process using the method of the planned experiment.

2. It was determined the positive impact predpyrolysis and pyrolysis temperature, and dosage of an activating agent - potassium hydroxide to form the adsorption properties of adsorbents and their porous structure.

3. It was found that increasing the temperature of thermochemical activation of up to 750 ° C and increasing the dosage of potassium hydroxide of up to 2.1 g / g have a positive influence on the formation of adsorption and structural properties of the ACfrom hydrolytic lignin.

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