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ПОЛУЧЕНИЕ АКТИВИРОВАННЫХ УГЛЕЙ ИЗ ОТХОДОВ ДЕРЕВООБРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ

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Эффективное использование отходов является актуальной задачей деревообрабатывающей промышленности. Термохимические методы переработки древесной биомассы позволяют обеспечить комплексную переработку невостребованного древесного ресурса. В работе рассмотрена возможность получения углеродных сорбентов из отходов деревообрабатывающих производств, относящихся к V классу опасности. В качестве исходного сырья использовались мелкие отходы деревообработки - опилки и щепа мягких пород древесины. В работе показано влияние введения в исходное сырье малых количеств неорганических добавок (серной, фосфорной кислоты и смеси кислот) на пористую структуру и адсорбционные свойства полученных активированных углей. Исследована кинетика карбонизации модифицированной и немодифицированной углеродной основы, кинетика активации карбонизатов водяным паром. Показано, что введение неорганических кислот заметно интенсифицирует реакции синтеза органической массы угля, что приводит к снижению начальной температуры терморазложения, увеличению температурного интервала потери массы и выхода углеродного остатка при пиролизе. Использование фосфорной кислоты и смеси неорганических кислот, в качестве модификатора отходов мягких пород древесины, замедляет процесс активации водяным паром, что связано с преобладанием реакции поликонденсации. Модифицирование серной кислотой существенно не влияет на скорость активации, но способствует более равномерному ее протеканию. Оценены технологические характеристики и параметры пористой и микропористой структуры активированных углей на основе отходов деревообрабатывающих производств, определено влияние на них степени обгара. Существенное изменение макропористой структуры в процессе прогрессирующей активации наблюдается для образцов из щепы, что связано с размером и плотностью материала. Наиболее интенсивное развитие сорбирующей пористости происходит при увеличении степени обгара с 30 до 45%. Модифицирование неорганическими кислотами приводит к повышению осветляющей способности по сравнению с промышленно выпускаемыми углями. На основе проведенных исследований предложена принципиальная схема получения порошкообразных осветляющих углей из отходов мягких пород древесины.

Ключевые слова: древесина, отходы, активированный уголь, пористая структура, сорбция, пиролиз, активация, кинетика

PRODUCTION OF ACTIVATED CARBONS FROM THE WOODWORKING INDUSTRY WASTE

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Effective waste management is an urgent task of the woodworking industry. Thermochemical methods of wood biomass processing allow to secure comprehensive processing of untapped wood resources. This work considers the possibility of obtaining carbon adsorbents from the woodworking industry waste of hazard class V. Small waste from wood processing such as sawdust and chips of different breeds of softwood were used as raw materials. The paper shows the effect of introducing small amounts of inorganic additives (sulfuric acid, phosphoric acid, and a mixture of acids) on the porous structure and adsorption properties of the resulting activated carbons. The kinetics of carbonization of modified and unmodified carbon base as well as the kinetics of activation of carbonisates by water vapor are investigated. It is shown that the introduction of inorganic acids noticeably intensifies reactions of the synthesis of the organic mass of carbon, which leads to a decrease in the initial temperature of thermal decomposition, an increase in the temperature range of mass loss, and the yield of carbon residue during pyrolysis. The use of phosphoric acid and a mixture of inorganic acids as softwood waste modifiers slows the process of activation by water vapor, which results from the predominance of the polycondensation reaction. While modification with sulfuric acid does not significantly affect the activation rate, it contributes to a more uniform course of the process. The technological characteristics and parameters of the porous and microporous structures of activated carbons based on woodworking industry waste are evaluated. The influence of the degree of burn-off on activated carbons is determined. A significant change in the macroporous structure during the activation process is observed for chip samples, which is associated with the size and density of the material. The most intensive development of adsorbing porosity occurs due to an increase in the degree of burn-off from 30 to 45%. Modification with inorganic acids leads to an increase in the clarification capacity compared to commercially produced carbons. Based on the conducted research, a schematic diagram of obtaining clarified powdered carbons from softwood waste is proposed.

Key words: wood, waste, activated carbon, porous structure, adsorption, pyrolysis, activation, kinetics

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INTRODUCTION

In order to solve the problem of environmental protection, the use of industrial waste as secondary raw material is of great importance. According to some researchers [1, 2] around 35.5 million m^3 of secondary wood waste is generated annually in the Russian Federation. That includes 41.8% of wood lump waste, 13.47% of bast, 13.88% of bark, 5.77% of wood chips, 19.95% of sawdust and wood shavings, as well as 5.13% of veneer trimmings. No more than 30% of the total volume of sawdust is used. The largest part is disposed in landfills to rot or burned in dumps. Wood waste belongs to hazard class V [3], which denotes a practically non-hazardous waste, but its utilization is costly and has an adverse effect on the environment. "The Strategy for the Development of the Forest Complex of the Russian Federation until 2030" approved by the Decree of the Government of the Russian Federation (No. 312-r) dated February 11, 2021, noted that one of the problems of the development of the forest complex is the insufficient utilization of wood waste. Therefore, special attention should be paid to the development of deep (waste-free) wood processing accompanied by its complete utilization, in order to prevent the abandonment of non-exportable small-scale timber and waste in logging areas as well as to improve sanitary and fire safety in forests [4].

One of the main raw materials used in Russia for the production of activated carbon is charcoal [5,6]. At the same time, dispersed waste such as sawdust, bark, and wood chips can be used as raw material in the production of charcoal [7-9].

The yield of wood charcoal during the pyrolysis of wood is (25-45)% and depends on wood type, moisture level in the raw materials, and the process conditions [10-12]. Based on the information about the chemistry of thermal decomposition of isolated components as well as the entire wood complex, it can be concluded that by changing the physical parameters of wood pyrolysis, it is difficult to achieve a significant increase in the yield of charcoal. The components of wood–hemicellulose, cellulose and lignin–decompose in similar temperature ranges. Changing the parameters of the process does not allow to interfere with the primary mechanisms of the formation of valuable products, nor does it allow to carry out a directed thermal decomposition of wood. The problem can be radically solved only by applying chemical reagents [12, 13]. The use of chemical reagents is of great interest for solving the most important task of pyrolysis which is increasing the yield of charcoal.

In [14], it was determined that inorganic catalysts (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, and HZSM-5 (acid catalyst based on pentasil zeolite ZSM-5), H_3PO_4, and $Fe_2(SO_4)_3$) increase the yield of carbon.

The study of the kinetics of wood pyrolysis in the presence of inorganic salts, different classes of alkaline halides, alkaline earth metal halides (NaCl, KCl, KBr, $CaCl_2$, $BaCl_2 \cdot 2H_2O$), and Lewis acids ($AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $CuCl_2$, $CuBr_2$, $ZnCl_2 \cdot 1.5H_2O$, $NiCl_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$) using TG-DSC (thermal gravimetric analysis and differential scanning calorimetry), showed in [15, 16] that the use of Lewis acids as pyrolysis catalysts leads to a decrease in the starting temperature and activation energy of the process. In the presence of other catalysts, the activation energy does not change significantly. The increase in the apparent order of reactions in the presence of Lewis acids may be a consequence of the complication of the mechanism of thermal degradation accompanied by the appearance of new parallel competing stages.

In [17], the authors showed the possibility of synthesis of microporous carbon adsorbents by thermochemical activation of spruce sawdust using potassium hydroxide as the activating agent. The technology allows to obtain activated carbons exceeding 3 times the sorption capacity of iodine and methylene blue of industrially produced carbons.

Since different types of wood differ significantly in structure, micro- and macrostructure [18], it is advisable to directly study a certain breed as a raw material for the production of activated carbons.

The purpose of this work is to develop a technological mode of obtaining active carbons based on softwood.

EXPERIMENT METHODOLOGY

Wood waste in the form of chips and sawdust of soft hardwoods, mainly aspen of the Volkhov Forestry of the Leningrad region, was used as the starting material.

Characteristics of the raw material:

- Carbon content – 40%;
- Volatile matter content – 60%;
- Ash content – 0.5%;
- Humidity – 35%.

The starting material is impregnated with solutions of orthophosphoric acid, sulfuric acid or a mixture of both in the ratio of 1:1. Additives were introduced in the amount of 1.25 wt. % in relation to absolutely dry wood. Modifiers are chosen in accordance with their capacity to catalyze polycondensation processes that occur during the pyrolysis of wood, which leads to an increase in the yield of carbon residue. The

introduction of additives with a more significant content is impractical, as it leads to the need to clean emissions from sulfur and phosphorus compounds released during heat treatment. It also has a negative impact on equipment, which increases the cost of production.

The amount of the impregnated solution was calculated based on the moisture capacity of the starting material. The ratio of the solid and liquid phases is approximately 1:2, so that the impregnation solution containing the required amount of additive fills the entire porous space of the source material without forming an excess of the liquid phase. The impregnated material was stored for 8 h with periodic stirring. Then, after drying at the temperature of (100 – 110) °C the starting material was exposed to carbonization. The main difficulty in using small waste consists in large losses due to the entrainment by gases as their mass decreases during pyrolysis [15]. Part of the impregnated and dried sawdust was ground on a vibrating mill to a dispersion of no more than 0.05 mm, pressed in a hydraulic press under the pressure of 20 MPa, and exposed to carbonization. Carbonization was carried out under stationary conditions in a retort furnace in an inert gas (nitrogen) current. The rate of temperature rise was 5 °C/min followed by exposure at the final temperature of 550 °C for the duration of 2 h. Carbonized charcoal was activated under stationary conditions in a retort furnace at a temperature of 850 °C. Water vapor was used as an activating agent. The water vapor consumption was 5 g/g. Charcoal was heated and cooled in an inert gas (nitrogen) current.

The quality of the sorbents obtained was evaluated according to the methods adopted for the certification of activated carbons (mechanical abrasion strength according to GOST 16188-70, total pore volume in water according to GOST 17219-71, and adsorption capacity in relation to methylene blue according to GOST 4453-74). The parameters of the microporous structure were calculated from the benzene adsorption isotherm determined by the adsorption-vacuum method. The kinetics of carbonization and activation were measured on a kinetic setup using McBain scales under conditions close to real processes. To study the kinetics of carbonization, the sample was placed on the scale and heated at a rate of 5 °C/min to a temperature of 550 °C in an inert gas (nitrogen) current and adjusted to a constant weight, while the temperature and mass of the sample changed over time. When determining the kinetics of activation, the sample was heated to the temperature of 850 °C in nitrogen current and adjusted to a constant weight. Next, water vapor was supplied to the system and the decrease in mass over time was recorded.

RESULTS AND DISCUSSION

The study of the parameters of technological processes that occur during the production of wood charcoal will allow to obtain raw materials at the lowest energy consumption and with a consistently high quality of product [19]. To assess the effect of the introduction of inorganic additives on the rate of thermal decomposition of the carbon base, the temperature of the maximum mass loss, and the yield of carbon residue, the kinetics of thermal decomposition was studied by using pressed samples.

The results of thermal decomposition studies presented in Fig. 1 indicate that the addition of sulfuric acid at the initial stage of thermal decomposition of wood, which is characterized mainly by the removal of structurally bound water, has a greater hydrolyzing ability.

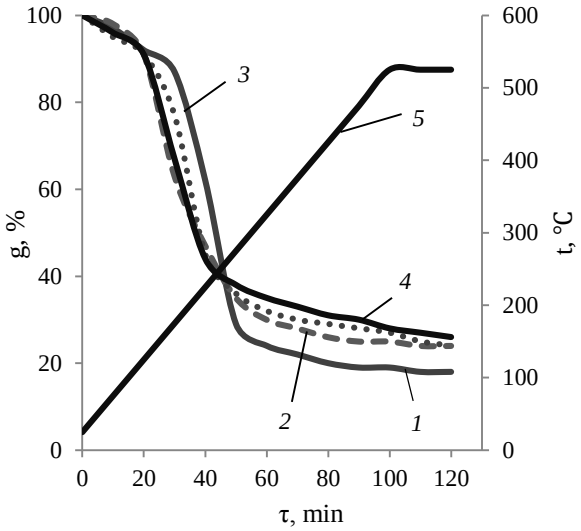

Fig. 1. Thermal decomposition curves 1 – no modifier, 2 – modified with sulfuric acid, 3 – modified with phosphoric acid, 4 – modified with a mixture of acids, 5 – temperature

Рис. 1. Кривые терморазложения 1 – без модификатора, 2 – модифицирован серной кислотой, 3 – модифицирован фосфорной кислотой, 4 – модифицирован смесью кислот, 5 – температура

At the stage of the main release of volatiles, additives cause the intensive release of volatiles to shift to a low-temperature region. Additionally, the temperature range of the main mass loss is noticeably expanding. The change in the rate of mass loss can be explained by the fact that the introduction of inorganic additives noticeably intensifies reactions of synthesis of the organic mass of charcoal, which further leads to an increase in the yield of carbon residue. The effect of additives can be explained by the fact that sulfuric acid can guide dehydration both through the intermediate

formation of carbonium ions and through the intermediate formation of complex esters. Sulfuric acid esters with cellulose are more mobile compared to phosphoric acid esters. The decomposition of sulfuric acid esters occurs already at the temperature of 100 °C, which explains the form of the mass loss curve (Fig. 1). It is likely that due to the high lability of sulfuric acid in cellulose, dehydration occurs at a lower temperature and at a higher rate than in the presence of phosphoric acid. In samples modified with phosphoric acid, dehydration begins at 150 °C, since it proceeds mainly through the intermediate formation of complex esters whose stability is relatively high. In the absence of catalyzing additives, dehydration in the samples begins at 200 °C. For samples modified with a mixture of acids, the rate of volatile release slows down, which is likely due to the predominance of condensation and cyclization reactions over the destruction of polymer molecules. The introduction of sulfuric or phosphoric acid additives into the composition increases the yield of carbonized charcoal compared to the starting wood material by 25%. For the sample modified with a mixture of sulfuric and phosphoric acids, during the initial stage of mass loss the additivity of the action of additives can be observed. At the stage of carbon residue formation (from 180 to 500 °C), some synergistic effect of their joint influence on the process of carbon residue formation may appear. In all likelihood, polycondensation and synthesis reactions prevail over destruction.

Process energies are calculated for steep sections of thermal decomposition curves (Table 1).

Table 1

Dependence of the characteristics of thermal decomposition of wood on the type of modifier

***Таблица 1.* Зависимость характеристик терморазложения древесины от вида модификатора**

Thermal decomposition parameters	Modifier			
	No modifier	H_2SO_4	H_3PO_4	Mixture
Starting temperature of decomposition, °C	200	150	100	130
Temperature range of maximum mass loss, °C	230-250	170-220	140–230	150–210
Decomposition rate, %/min	9.5	3.7	2.5	3.1
Carbon residue yield, %	19	24	24	27
Activation energy, kJ/mol	25	20	36	29

The study of the kinetics of activation of carbonized samples by water vapor shows that inorganic additives have a significant effect on the parameters of the process.

During the thermal decomposition of wood, a number of parallel and sequential reactions occur in the same temperature range. Therefore, the experimentally obtained activation energy values are apparent and not unambiguously related to the mechanisms of the carbonization process. Based on the kinetic curves (Fig. 2), the reaction rates of the activation process are calculated and presented in Table 2. The rate constants of the activation processes of materials (their effective values, regardless of the mechanism of the processes) were calculated by the tangent of the angle of inclination of the straight lines (Fig. 2) with respect to $\Delta g/\Delta\tau$ at the initial values of the exposure time.

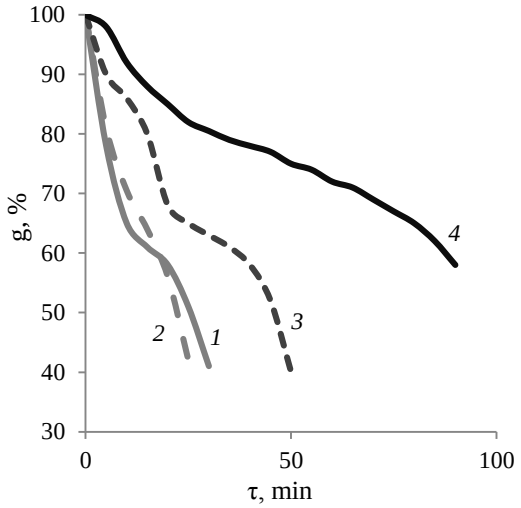

Fig. 2. Kinetic curves of the interaction between water vapor and carbon residue 1 – no modifier, 2 – modified with sulfuric acid, 3 – modified with phosphoric acid, 4 – modified with a mixture of acids

Рис. 2. Кинетические кривые взаимодействия водяного пара с углеродным остатком 1 – без модификатора, 2 – модифицирован серной кислотой, 3 – модифицирован фосфорной кислотой, 4 – модифицирован смесью кислот

Table 2

Reaction rate constants of the activation process

***Таблица 2*. Константы скорости реакции процесса активации**

Modifier	K, c^{-1}
No modifier	$4.83 \cdot 10^{-4}$
Sulfuric acid	$4.58 \cdot 10^{-4}$
Phosphoric acid	$2.62 \cdot 10^{-4}$
Sulfuric + Phosphoric acid	$1.25 \cdot 10^{-4}$

Studies show that the initial sample is characterized by a sharp drop in mass of up to 65% and a further slowdown follows. This may indicate that the initial stage of activation of a less condensed structure than in the case of samples with inorganic additives is characterized by the burning out of larger structural

fragments. The introduction of sulfuric acid does not significantly change the activation rate. However, as can be seen from Fig. 2, it contributes to a more uniform flow of the process of activation. For the sample with phosphoric acid, the activation process slows down; that is, the presence of phosphoric acid slows down the reaction between water vapor and charcoal. This process is especially noticeable for the sample with a mixture of acids. This can be explained by the predominance of synthesis and polycondensation reactions. The results of the study of the kinetics of carbonization and activation show the possibility of choosing optimal process modes. Based on the obtained results, the following parameters of the process of obtaining activated carbons from used wood waste were selected: carbonization at the temperature of 550 ℃ for 2 h and activation at 850 ℃.

In this work, the effect of progressive activation on the parameters of the porous structure of the activated carbons is investigated. As can be seen from the results presented in Table 3, the difference in the formation of the volume of macropores in the samples is laid at the carbonization stage due to the difference in shrinkage phenomena and the uneven release of volatiles. For chip wood samples, the dynamics of macroporosity development is more pronounced, which can be explained by the influence of the diffusion factor that makes it is difficult for the activating agent to penetrate deeper into the grains of larger sizes and with a more intense interaction between water vapor and carbon in the peripheral regions. In sawdust samples with a finer grain, the concentration gradient of the activating agent from the outer surface into the interior is less noticeable. Modification of wood waste with sulfuric acid has practically no effect on the macropore volume development, and the presence of phosphoric acid apparently slows down the reaction between water vapor and carbon.

Table 3

The effect of the degree of burn-off on the parameters of the porous structure of activated carbons from wood waste

***Таблица 3*. Влияние степени обгара на параметры пористой структуры активированных углей из древесных отходов**

Modified	Micropore volume, cm^3/g				Mesopore volume, cm^3/g				Macropore volume, cm^3/g			
	Burn-off, %				Burn-off, %				Burn-off, %			
	0	20±5	35±5	45±5	0	20±5	35±5	45±5	0	20±5	35±5	45±5
Wood chips-based												
No modifier	0.06	0.14	0.27	0.36	0.08	0.15	0.23	0.29	1.87	2.21	2.65	2.88
H_2SO_4	0.06	0.28	0.47	0.49	0.10	0.19	0.37	0.66	1.92	2.20	2.37	2.62
H_3PO_4	0.06	0.24	0.37	0.46	0.10	0.15	0.28	0.52	1.90	2.16	2.45	2.72
Sawdust-based												
No modifier	0.05	0.23	0.30	0.40	0.08	0.18	0.24	0.47	1.22	1.37	1.41	1.51
H_2SO_4	0.08	0.22	0.45	0.48	0.09	0.13	0.28	0.66	1.34	1.40	1.50	1.57
H_3PO_4	0.06	0.33	0.47	0.52	0.10	0.22	0.28	0.40	1.32	1.38	1.43	1.47
Pressed sawdust												
No modifier	0.05	0.23	0.32	0.36	0.09	0.16	0.30	0.44	0.67	0.73	0.81	0.84
H_2SO_4	0.06	0.17	0.43	0.48	0.10	0.13	0.27	0.58	0.98	1.01	1.07	1.11
H_3PO_4	0.06	0.28	0.39	0.41	0.09	0.17	0.28	0.48	0.92	1.03	1.1	1.16
Mixture	0.06	0.20	0.40	0.44	0.09	0.12	0.24	0.52	0.88	0.97	1.02	1.10

During progressive activation, the peak development of the mesopore volume for all samples is observed in the area from 30 to 50% of the degree of burn-off (Table 3). Burn-off is a quantitative measure of the interaction of an oxidizer with non-activated carbon and, in this work, it was defined as the amount of carbon burned off during activation.

The dynamics of the development of micropores during activation also differs depending on the type of the starting material (Table 3). In the development of microporosity, there is a maximum, which for most samples lies in the range of the burn-off (35-45)%, and for samples modified with phosphoric acid also in the range (20-35)%. For activated carbon obtained from wood chips at an optimal degree of burn-off, the volume of micropores is lower than for sawdust carbon. Thus, it is shown that the introduction of modifying additives has a positive effect on the increase of sorbing pores in the obtained samples.

Based on the conducted studies, a scheme for obtaining powdered clarified carbons based on wood waste can be proposed. The block diagram and technological parameters of the process are shown in Fig. 3.

To obtain low-ash carbons, a washing stage can be introduced into the technological scheme.

According to the proposed method, experimental samples of activated carbons were obtained. Their parameters are given in Table 4. As can be seen from the presented table, activated carbons obtained from various types of woodworking waste and modified with additives of inorganic acids have a more developed porous structure than BAU-A carbons and, as a result, a greater clarification ability with respect to methylene blue, which is comparable to OU-A carbons. Impregnation of the wood base with inorganic acids allows to obtain crushed activated carbons that are not inferior in mechanical strength to BAU-A carbons. In terms of clarification ability, the modified samples are close to foreign analogues.

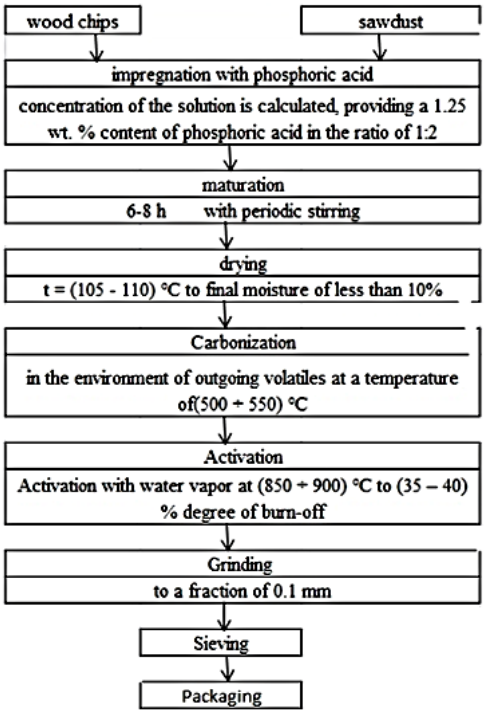

Fig. 3. Block diagram of obtaining powdered clarified activated carbons from wood waste

Рис. 3. Блок-схема получения порошкообразных осветляющих

The study of the porous structure and sorption properties of the obtained activated carbons did not reveal any clear advantage in any of the modifiers. Therefore, considering the corrosive activity of sulfuric acid, phosphoric acid should be recommended as the main modifier.

CONCLUSIONS

On the basis of various types of wood waste (wood chips, sawdust) from soft hardwoods by the method of steam-gas activation and mixed activation using sulfuric and phosphoric acids as chemical modifiers, activated carbons were obtained, and their properties were investigated.

The thermogravimetric method was used to investigate the kinetics of carbonization of the carbon base. It is shown that the preliminary acid treatment of wood waste initiates the dehydration process at an early stage of thermal decomposition and extends the temperature range of the main removal of volatiles. As a result, the carbon residue yield increases by 25-40%. The influence of the synergistic effect of a mixture of additives on the process of thermal decomposition of wood has been established.

Table 4

Parameters of the porous structure and technical characteristics of activated carbons

***Таблица 4.* Параметры пористой структуры и технические характеристики активированных углей**

Modifier	Pore volume, cm^3/g			S*, %	MB*, mg/g
	V_{mi}	V_{me}	V_{ma}		
Wood chips-based					
No modifier	0.38	0.38	1.47	-	210
H_2SO_4	0.49	0.49	1.55	-	300
H_3PO_4	0.54	0.55	1.48	-	315
Sawdust-based					
No modifier	0.35	0.27	2.90	40	230
H_2SO_4	0.51	0.55	2.53	55	320
H_3PO_4	0.45	0.47	2.68	58	300
Pressed sawdust					
No modifier	0.38	0.37	0.84	55	200
H_2SO_4	0.43	0.41	1.13	65	280
H_3PO_4	0.51	0.53	1.12	63	305
Commercial carbons [20, 21]					
BAU-A	0.22-0.25	0.08-0.10	0.35-1.45	≥60	165
OU-A (Russia)	0.28-0.29	0.13-0.18	0.23-0.41	-	≥225
KB(USA)	0.37	1.1	00	-	340
4SC (France)	0.32	0.59	00	-	280

Note: *) S – mechanical abrasion strength, %; MB – sorption activity in relation to methylene blue, mg/g; V_{mi} – micropore volume, cm^3/g; V_{me} – mesopore volume, cm^3/g; V_{ma} – macropore volume, cm^3/g

Примечание: *) S – механическая прочность на истирание, %; MB – сорбционная активность по метиленовому синему, мг/г; Vmi – объем микропор, $см^3/г$; Vme – объем мезопор, $см^3/г$; Vma – объем макропор, $см^3/г$

The kinetics of activation of the carbonized samples by water vapor in an inert medium has been studied. It was found that modification of wood with phosphoric acid and a mixture of sulfuric and phosphoric acids reduces the activation rate constant by 2.0-2.5 times.

The dynamics of the formation of a porous structure in the process of progressive activation was

investigated. It was found that modification with acid additives contributes to a more significant development of sorbing pores (mainly micropores). The optimal value of the degree of burn-off (35-40)% has been established.

The parameters of the porous structure and the clarification ability with respect to methylene blue of the obtained activated carbons were studied. It was shown that carbons obtained from unmodified waste are close in their properties to the industrial carbon OU-A, while carbons obtained by modification with inorganic acids have a clarification capacity in relation to methylene blue that is 1.5 times higher, which makes them close in that respect to foreign analogues.

Based on the conducted research, a scheme for the production of activated carbons of a clarifying type from wood waste (chips and sawdust) of soft hardwoods is proposed.

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