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Study of Thermochemical Transformations of Hydrolytic Lignin and the Properties of the Produced Active Carbons

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There has been studied the influence of the conditions of heat treatment of hydrolytic lignin and its mixtures with oil slime on the yield, structure and adsorption properties of active carbons (AC). With the increase in the temperature of lignin processing from 400 to 900 °C, the yield of active carbon decreases, and its specific surface area and sorption activity reach the maximum values at 800 °C. The mutual influence of the components of the mixture of hydrolytic lignin and oil slime during the thermochemical transformations, becomes apparent in the variation of the yield and the porous structure of AC. As for the oil slime, it acts as a binding and structure forming component.

Keywords: hydrolytic lignin, oil slime, thermal transformations, active carbon, structure, adsorption properties.

The technical lignin which is formed during the chemical processing of wood at the paper and pulp and hydrolytic plants, is the waste which is the most difficult to utilize. The amount of unutilized lignins in the Ukraine (that is the waste of the yeast, forage and paper and pulp industries) makes up, according to different data, from 5 to 15 million tons, whereas in Russia and Belarus their number is greater [1]. At present there are no exhaustive technical solutions on utilizing lignins, although the survey of the scientific literature for

the past years is evidence of the great interest that the researchers show in this raw material.

Lignin is a polymer of aromatic nature. Its structural unit is presented mainly by phenylpropane units [2]. The variety of connections between the latter determines the irregular molecule lignin structure [3]. Lignin is a polyfunctional substance, containing phenolic, alcoholic, carbonyl, acidic and methoxyl groups. The number of these groups varies greatly depending on the industrial hydrolysis conditions,

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which has a noteworthy effect on the lignin reactivity [4].

Lignin in itself is used as an effective sorbent of various organic and inorganic substances including those used in medicine (like, for example, an enterosorbent – polyphepane) [5]. It is also a precursor of activated carbons (AC), made by combining thermolysis and steam activation. The conditions of heat treatment to a great extent determine the AC structure based on the hydrolytic lignin [6, 7]. The survey of the scientific literature on the thermochemical conversion of lignin into AC, shows, that describing technological aspects predominates over the information about the physical and chemical regularities of transforming the organic substance lignin, as well as forming the porous structure and changing the adsorption properties.

There is some information about getting AC by means of combined carbonization of mixtures of different kinds of the carbon containing raw material [8 – 12]. The interaction of the mixture components in the processes of co-carbonization develops in the non-additive yield change and structural characteristics of the obtained carbonic materials. During the co-carbonization of the hydrolytic lignin with oil slimes, the latter can act as a binding and pore forming reagent [10].

The aims of the given work are as follows: 1) the studies of the regularities of transforming the lignin structure into the structure of activated carbons depending on the temperature and the time of steam activation; 2) the estimation of the influence of structural changes on the adsorption characteristics of AC obtained during the thermolysis and the lignin steam activation; 3) the studies of the peculiarities of thermotransformations of mixtures of hydrolytic lignin with oil slimes based on water emulsions of oil heavy fractions.

Experimental

To obtain AC, there was used the hydrolytic lignin of the Krasnoyarsk biochemical plant (Russia) having the following characteristics (%):

$W^a - 3,6$; $A^d - 1,8$; $V^{daf} - 63,4$; $C^{daf} - 60,2$; $H^{daf} - 6,0$; $O^{daf} - 33,0$; $(S+N)^{daf} \leq 0,8$.

The example of the oil slime (OS) is the waste products formed during the cleaning of the tanks at the washing and steaming station of Luzanovka (Odessa, the Ukraine). These are the aqueous emulsion of oil heavy fractions (the water content is $- 50 \pm 10$ %) including the admixtures of the surface active substances. The organic mass of OS is presented by alkanes (80 %) and arenes (18 %), the average molecular mass is 750 – 1100 a.e.m. [10]. The emulsified oil slime was dehydrated by settling the preheated (80 °C, for 3 hours) waste products [11].

The mixtures of lignin and oil slime were made by mechanical mixing at a temperature of 20 ± 2 °C for 5 minutes without the subsequent forming. The content of the oil slime in the mixture was 20 – 50 % mass, which corresponds with the most efficient interaction of the oil slime with the solid carbon containing material [12].

The activated carbons (AC) were obtained in the vertical tubular reaction vessel having the volume of 50 cm³, which is put into the electrical furnace providing the heating to the activation temperature (t_a) at a speed of 50 ± 5 degrees/min. and providing the thermostatic control of the reaction vessel with the accuracy of ± 5 °C. The sample of the dried lignin (5 g) was loaded into the reaction vessel. Then the system was blown by argon at a speed of 2 dm³/hr during 10 min. And the reaction vessel was heated to 200 °C. After that the flow of the argon was switched over to the steam generator (the productivity relative to water was 60 cm³/hr). The heating was continued to the activation temperature. On the expiry of

the given activation time (τ_a), there was carried out the cooling of AC in the atmosphere of the argon. There was determined the yield (Y , %) of the activation product (the determination error was $\pm 0,4$ %).

The value of the specific surface area S_{BET} (m^2/g) was estimated by two methods: the low temperature argon desorption [13] and from the isotherm of nitrogen adsorption – desorption using the installation “Sorpomatic – 1900”. The determination error S_{BET} made up ± 7 %.

The studying of the supramolecular AC structure was carried out with the the diffractometer DRON – 1 UM (the emission of CuK_α , 40 kV, 20 mA). There was determined the interlayer distance d_{002} (the measurement error was $\pm 0,002$ nm). There was also determined the height L_c ($\pm 0,02$ nm), the average diameter L_a ($\pm 0,2$ nm) and the number of the layers $n = L_c / d_{002} + 1$ in the crystallite. The degree of the crystallite space ordering was estimated as h / l , which is the relation of the height (h) of the reflex 002 to its half width (l) [14].

The values of the adsorption activity relative to methylene blue (A_{mb}) and iodine (A_{iodine}) were determined based on GOST 4453-74 and GOST 6217-74. There was also calculated the surface unit adsorption activity $A_{\text{mb}}/S_{\text{BET}}$ and $A_{\text{iodine}}/S_{\text{BET}}$.

The thermogravimetric studies were carried out with the help of the derivatographer Q – 1500 D of the Paulic – Paulic – Erdei with the linear temperature rise (10 °C/min.) from 20 °C to 950 °C, the sample is 300 mg, a ceramic crucible. The processing of the derivatograms was carried out according to the method [15].

The IR spectra of the diffuse reflection were recorded on the spectrometer of the type BIORAD FTS – 185 having the attachment GRASEBY SPACAC “Selector”. The spectra were obtained for the mixtures of the carbon sample (5 %) with the powdery KBr (95 %) by the addition

of 256 scans in the range of the wave numbers $4000 - 400$ cm^{-1} .

Results and discussion

The transformation of the lignin structure with the rise in temperature

The lignin thermolysis conducted in the range of $20 - 950$ °C, is characterized by the presence of the three maximums of the speed of emitting volatile substances at 115 , 240 and 370 °C. The first one is caused by the removal of the adsorbed gases and moisture from the lignin. The maximum at 240 °C is caused by the decarboxylizing of COOH groups and, perhaps, by the decomposition of the alkyl – alkyl ethers. The maximum at 370 °C is caused by the destruction of $\text{C}_{\text{alk}}-\text{C}_{\text{alk}}$, $\text{C}_{\text{alk}}-\text{O}$ and other bonds between the aromatic rings with the formation of active radicals and low-molecular products.

By means of using the methods of IR spectroscopy, there were studied the transformations of lignin into the AC structure during its heat treatment. The spectrum of the initial lignin is characterized by a set of absorption bands [16]: 3385 cm^{-1} is the hydrogen bond, 2930 , 2850 cm^{-1} are the valence vibrations of the bonds C–H in methyl and methylene groups, 1710 , 1667 cm^{-1} are the vibrations of the bonds C=O in β - and α -carboxylic acids respectively, 1603 and 1512 cm^{-1} are the vibrations of the bonds in the benzene ring, 1470 , 1420 cm^{-1} are the deformation vibrations of the bonds C–H in groups CH_2 and CH_3 in the methoxyls, 1365 cm^{-1} are the vibrations of the bonds C–O in the phenol –OH group, 1220 cm^{-1} are the vibrations of the bonds C–O–C and C–OH of the ethers and phenols, 1132 and 1072 cm^{-1} are the vibrations of C–O-bonds in methoxyl groups.

The heating of lignin to 370 °C leads to the appearance of the absorption bands at 3630 and 3510 cm^{-1} , since as result of removing the

moisture, there increases the content of free hydroxyl groups. One can also observe the appearance of the absorption band 3050 cm^{-1} and the strengthening of the intensity of the band at 1600 cm^{-1} corresponding to the vibrations of the bonds in the aromatic ring. The strengthening of the intensity of the band 1700 cm^{-1} takes place apparently because of the oxidation of aliphatic chains to forming carboxyls. The intensity of the band 1370 cm^{-1} increases, possibly, due to the formation of phenols. The intensity of the absorption bands $1030, 1125\text{ cm}^{-1}$ decreases. The band 1060 cm^{-1} disappears. This may be connected with removing the methoxy groups and breaking the ether bonds. In the solid thermolysis products, produced at $800\text{--}900\text{ }^{\circ}\text{C}$, there partially maintain oxygen and aliphatic fragments. And in the IR spectrums, one can see the absorption bands corresponding to these fragments. These are included into the polyaromatic AC skeleton.

Thus, in the solid thermolysis product, relatively speaking, one can point out two types of structures. The type I structures (S_I) – are the lignin fragments which were not fully subjected to aromatization during the heating. They contain aliphatic chains and oxygen in the form of phenol, carbonyl and hydroxyl groups. The type II structures (S_{II}) are polyarene carbonic clusters (graphenic blocks, that is crystallites). It is quite evident that their reactivity when interacting with steam, will be different.

The lignin steam activation

There were obtained the experimental data about the influence of the conditions of heat treatment of hydrolytic lignin by steam, on the yield as well as on the structural characteristics and the adsorption properties of the active carbons.

With the increase in the temperature from 400 to $900\text{ }^{\circ}\text{C}$, the AC yield decreases from $46,7$ to $10,3\%$ (Table 1). The value S_{BET} rises reaching the maximum value of $650\text{ m}^2/\text{g}$ at $800\text{ }^{\circ}\text{C}$ and

then it drops. The adsorption activity relative to MB and iodine, also increases reaching the maximum value at $800\text{ }^{\circ}\text{C}$ ($A_{\text{mb}} = 199\text{ mg/g}$ and $A_{\text{iodine}} = 1001\text{ mg/g}$). And with the further increase in temperature, it decreases. The lignin which was subjected to heat treatment at $800\text{ }^{\circ}\text{C}$, has the best porous system in the three-dimensional framework, presented by polyarene clusters (structures S_{II}), which are connected by aliphatic and oxygen – containing fragments (structures S_I).

There was calculated the number of the layers formed by the molecules of iodine or methylene blue on the surface of the lignin, which was activated in the temperature range $400\text{--}900\text{ }^{\circ}\text{C}$, as following from the adsorption activity values (Table 1), and the areas of setting their molecules [17, 18]. With the rise in the activation temperature, the calculated number of the iodine layers on the AC surface, decreases from $2,2$ to $1,0$ which corresponds to the monolayer (Fig. 1).

The absorption of iodine in the amount greater than it is necessary to form a monolayer, is caused, in our opinion, by reducing the iodine molecules as a result of the transfer of electrons from the lignin fragments, or by other chemical interactions with the structural fragments of organic macromolecules. These fragments are rather reactive and they correspond to type I structures.

As regards the second adsorbate – MB (methylene blue) – the situation is quite the opposite (Fig. 1): with the rise in the activation temperature, the number of MB layers, set on the surface of the produced AC, increases from $0,5$ to the monolayer. The obstacle to forming the MB monolayer may be a great part of micropores, whose surface is inaccessible for a large MB molecule. There are also possible steric hindrances during setting a molecule, which may be caused by the fact that various functional groups and heteroatoms are present on the surface.

Table 1. The temperature dependences of the yields, specific surface values and adsorption characteristics of activated carbons ($\tau_a = 30$ min)

$t_a, ^\circ\text{C}$	Y, %	$S_{\text{BET}}, \text{m}^2/\text{g}$	Adsorption activity			
			$A_{\text{mb}}, \text{mg/g}$	$A_{\text{iodine}}, \text{mg/g}$	$A_{\text{mb}}/S_{\text{BET}}, \text{mg/m}^2$	$A_{\text{iodine}}/S_{\text{BET}}, \text{mg/m}^2$
400	46,7	< 10	7	112	$\approx 0,7$	$\approx 11,2$
500	34,9	90	17	248	0,20	2,88
600	34,0	280	38	691	0,14	2,48
650	30,1	360	86	744	0,24	2,06
700	25,7	430	107	873	0,25	2,01
750	18,2	550	154	949	0,28	1,73
800	15,2	650	199	1001	0,30	1,53
850	12,4	610	183	907	0,30	1,50
900	10,3	540	161	824	0,30	1,52

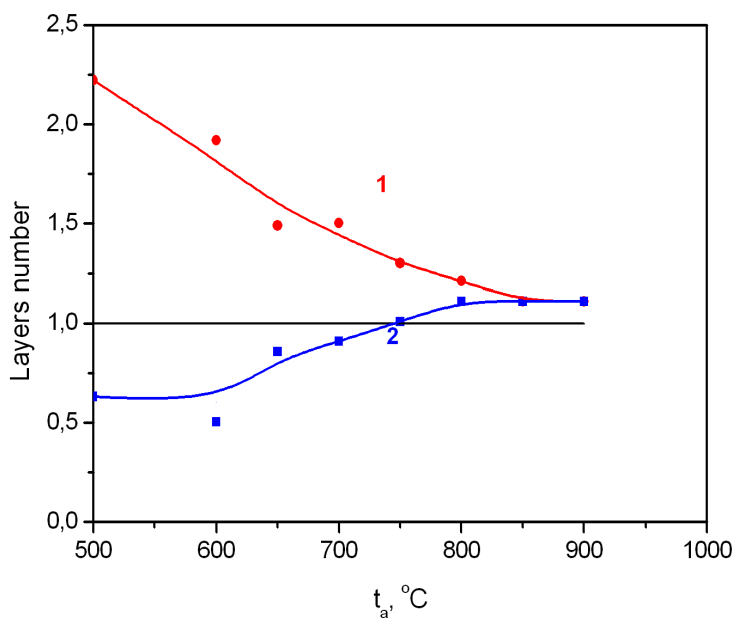


Fig 1. The number of adsorbed iodine layers (1) and methylene blue (2) on the surface of lignin adsorbents, obtained at different activation temperatures

As it was suggested earlier, during the heating to 800 °C, in the solid product of lignin thermolysis, there are formed two types of structural fragments (S_I and S_{II}) which differ considerably in their chemical activity with respect to steam. The change of the AC yield depending on the activation time at 800 °C, is characterized by the two areas with quite different gasification speeds. This allowed to kinetically distinguish between the interactions with the steam of the structures of types I and II [19]. The change of the contents of S_{II} structural fragments corresponds to the change of the activated carbons yield obtained in the range of $\tau_a = 30 - 120$ min and it is described by the equation of the kinetics of I order $Y_{II} = 16,3 \exp(-0,0023 \tau_a)$, (the correlation ratio $r^2 = 0,99$). Based on this equation, one can calculate the contents of the S_{II} fragments in the range $\tau_a = 0 - 30$ min. It is also possible to calculate the contents of the structural fragments of S_I in this area. The decrease of the contents of these fragments is also described by the equation of the kinetics of the first order $Y_I = 13,5 \exp(-0,0752 \tau_a)$, ($r^2 = 0,97$). Judging by the correlation of the effective constants of the gasification speed k_1 / k_2 , the reactivity structural fragments of S_I is 33 times higher than S_{II} [19].

Probably, the burning out of the structural fragments of S_I leads to the increase in the part of the structures of S_{II} , characterized by the lower reactivity and more perfect space construction. The decrease in the part of the structural fragments of type I is apparently accompanied by the considerable growth of the specific surface area whereas the reaction of the structural fragments of S_{II} with the steam, leads to the decrease in the surface area of AC. The purposeful creation of the structures of the type S_I in the thermolysis products and their subsequent interaction with the steam,

are the effective methods of forming a porous structure of AC having the given properties.

The thermal transformation of lignin and oil slime mixtures

The general shape of the lignin IR spectrum practically does not change after adding oil slime (OS). Only the intensity of the absorption bands increases in the area 2930, 2850 cm^{-1} , because in the oil slime, containing a great number of aliphatic hydrocarbons, their intensity is very great.

According to the functional analysis data (Table 2), the addition of oil slime to lignin, leads to a considerable decrease in the content of phenol and carbonyl groups in the mixture. This is, probably, due to the fact that the OS components decrease the accessibility of the lignin surface for interacting with the reagents used in the functional analysis. The contents of the lactone groups increase, maybe, owing to the oil components, that these groups contain. On the TGA curve of oil slime (Table 3), there are three maximums of the mass losses – at 120, 320 and 430 °C. The first maximum corresponds to removing the moisture and low-boiling hydrocarbons. The second maximum corresponds to the decomposition of oxygen-containing groups and the evaporation of the more high-boiling hydrocarbons. The third one corresponds to removing and the thermal decomposition of the high-boiling aromatic and aliphatic hydrocarbons.

According to thermogravimetric data, the addition of OS to lignin (1:1), leads to the following changes in the properties of the mixture thermal destruction: there increases the temperature of the beginning (T_b), and there decreases the temperature of the end (T_e) of the thermal decomposition area (TDA) and, accordingly, there narrows the TDA maximum from 210 to 148 °C. There also considerably increases the average decomposition speed (V_{avg}) in the TDA maximum. It is noteworthy that

Table 2. The information about the functional analysis of lignin, oil slime and their mixtures

Sample	Functional groups			
	COOH	Lactones	OH _{phenol}	H-C = O
	mg-eq/g			
Lignin (L)	2,45	0,50	1,2	1,10
Oil slime (OS)	0,20	0,27	0,23	0,36
L-OS	1,91	0,80	0,19	0,27

Table 3. The parameters of the thermal destruction of lignin, oil slime and their mixtures based on thermogravimetric analysis

Sample	Parameters								
	T _{H2O} ^o , °C	T _b ^o , °C	T _e ^o , °C	T _{max1} ^o , °C	T _{max2} ^o , °C	T _{max3} ^o , °C	V _{avg} ^o , mg/g·c	V ₂ ^{max} , mg/g·c	V ₃ ^{max} , mg/g·c
L	120	195	480	-	240	370	0,19	0,18	0,29
OS	115	345	500	-	320	430	0,40	-	0,77
L-OS	115	208	450	-	280	385	0,28	0,29	0,41

the maximum at 430 °C characteristic for OS, disappears on the derivatogram of mixture. At 280 °C, there appears the maximum which gives evidence of the interaction of the two components (L and OS) during their joint thermal destruction.

According to the IR spectroscopy, the heating of the L-OS mixture (4:1) to 240 °C (the temperature of the first maximum of the mass loss on the TGA curve) is accompanied by the disappearance of the absorption bands of -OH groups connected by hydrogen bonds (3350 cm⁻¹) and the appearance of uncombined hydrogen bonds and the -OH groups combined by one bridge (3630, 3530 cm⁻¹), which is caused by removing the moisture. Besides, there appears the absorption band at 3050 cm⁻¹ and the bands 866, 815 and 760 cm⁻¹ are strengthened which testifies to the increase of the content of aromatic structures in the thermally treated mixture. There is also observed a drastic drop in the intensity of the absorption bands in the area 2960, 2870 cm⁻¹, corresponding to the vibrations of the bonds in the methyl and methylene groups which is caused by the removal of low-molecular hydrocarbon gases. The band 1370 cm⁻¹ is strengthened, perhaps, due

to the increase in the contents of the phenol -OH groups. The absorption bands 1170, 1120, 1060 cm⁻¹ disappear, which may be connected with removing the methoxy groups and destroying the ether bonds.

The heating of the mixture to 370 °C (the temperature of the second maximum of mass loss on speed on the TGA curve) leads to increasing the intensity of the band 3630 cm⁻¹ (it corresponds to the free hydroxyl groups) and to strengthening the absorption bands intensity corresponding to the vibrations in the aromatic ring (3055, 1600, 866, 815, 760 cm⁻¹), which is the result of increasing the contents of the aromatic structures in the mixture. It also leads to the considerable strengthening of the intensity of the band 1720 cm⁻¹, which may be connected with oxidizing the aliphatic chains to form carboxyl groups. The disappearance of the band 1370 cm⁻¹, may indicate the destroying the phenols. And finally, there appearance of the band 1170 cm⁻¹ may serve as evidence of new ether bonds formations

The thermolysis of the L-OS mixture at 400 °C carried out for 3 hours, leads to the substantial increase in the intensity of the absorption bands

relating to the vibrations of the bonds in the aromatic ring (3055, 1600, 866, 815, 760 cm^{-1}). It also leads to the decrease in the intensity of the absorption bands relating to the vibrations of the bonds in the aliphatic CH_2 , CH_3 groups (2960, 2870 cm^{-1}), as well as in carboxyls and carbonyls (1700 cm^{-1}), in phenol and ether groups (1200, 1420, 1070 cm^{-1}). These data which testify to the fact that there occur the reactions of the thermal destruction of aliphatic hydrocarbon and oxygen-containing fragments with the subsequent carbonization of the material.

The mixing of the lignin with the oil slime leads to the following changes of the supramolecular structure (Table 4). The value of the interlayer distance d_{002} remains the same as with the lignin. The extent of the crystallites in the longitudinal direction L_a decreases considerably as compared to lignin. And the crystallite size in the cross-sectional direction L_c and the degree of the ordering h/l increase not so substantially.

The number of γ -bands does not change. The activation of the L–OS mixture leads to the formation of active carbons having the yields, whose value decreases with the rise in the activation temperature. The oil slime alone in the temperature range of 400 – 900 °C, forms a non-porous product with the yield of $\leq 0,5$ % mas. So, the yield of AC from OS in the range of measurement errors, may be neglected.

The character of the temperature dependence S_{BET} for the activated carbon made from the lignin

(AC_L) and that of the activated carbon made from the L–OS mixture (AC_M) are approximately the same. Till the activation temperature of 800 °C is reached, there is observed the increase in the specific surface of AC (to 650 and 760 m^2/g for AC_L and AC_M , respectively). And in the range 800 – 900 °C one can see its insignificant decrease. At the activation temperatures over 700 °C, the value S_{BET} of the product AC_M is substantially higher than AC_L . In agreement with the value S_{BET} , the adsorption properties of AC change (Fig. 2 and 3). The sorption activities based on MG (A_{mb}) and iodine (A_{iodine}) increase reaching the maximum value at 800 °C: $A_{\text{mb}} = 200$ mg/g and $A_{\text{iodine}} = 1000$ mg/g for AC_L and $A_{\text{mb}} = 220$ mg/g and $A_{\text{iodine}} = 950$ mg/g for AC_M . Under these conditions, there is formed the AC supramolecular structure which has the same sizes of the polyarene layers in the crystallite both of AC_L and of AC_M . It should be noted that the interlayer distance between the layers in the crystallite AC_M , is considerably greater, and the crystallite height and the ordering degree are smaller as compared to AC_L (Table 4).

The character of activating the L–OS mixture and the properties AC_M differ greatly from the lignin activation. The yield of the activated carbon from the L–OS mixture is lower than from the lignin. Since the AC yield from OS is very low, it may be assumed that the precursor of the activated carbon in the L–OS mixture is only lignin. As following from this, the calculated

Table 4. The X-ray diffraction characteristics of the initial and activated samples

Sample	Parameters					
	D_{002} , nm	L_a , nm	L_c , nm	h/l	n	The number of γ -bands
Lignin (L)	0,446	4,7	1,50	2,69	4,4	2
Oil slime (OS)	0,477	5,8	2,40	2,65	9,2	0
L – OS	0,446	1,8	1,71	2,85	4,8	2
L, 800 °C, 30 min	0,340	6,6	3,27	1,04	10,6	2
L – OS, 800 °C, 30 min	0,384	6,8	1,95	0,73	6,1	2

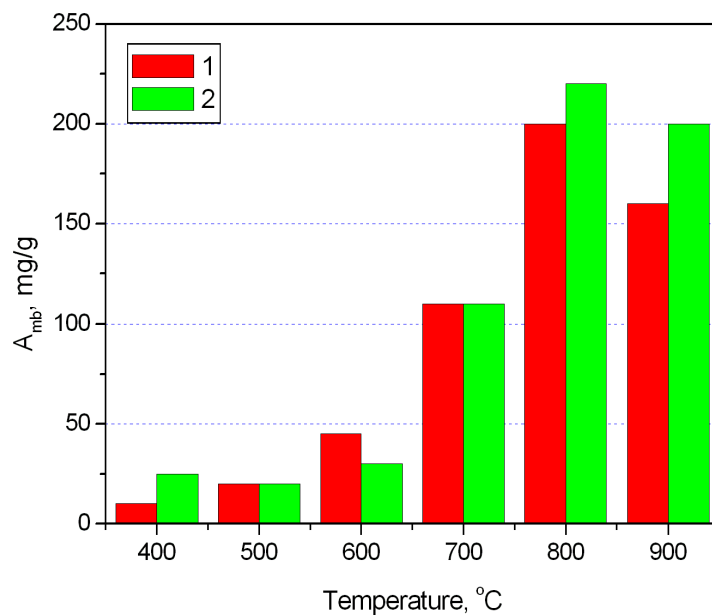


Fig. 2. The influence of activation temperature on the adsorption activity relative to methylene blue of the activated carbons from lignin (1) and the lignin – oil slime mixture (2) ($t_a = 30$ min)

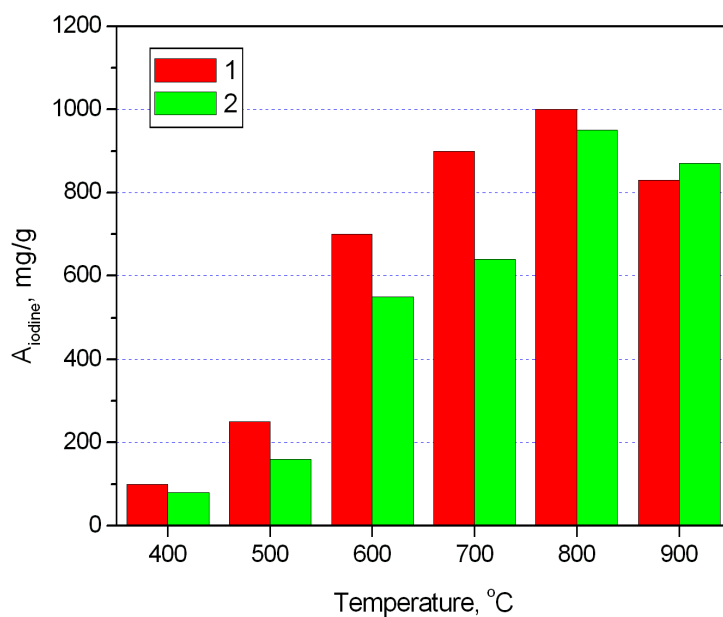


Fig. 3. The influence of activation temperature on the adsorption activity relative to iodine of the activated carbons from lignin (1) and the mixture lignin – oil slime (2) ($t_a = 30$ min)

yield of AC_M , makes up half of the yield of the activated carbon from lignin at the selected ratio of the mixture components. The real yield of AC_M is higher than the calculated one owing to the chemical interaction of the lignin components and the oil slime. The similar non-additivity effect was discovered earlier [20] for the system brown coal–OS. The value of the effect depends on the activation temperature and it is the most significant in the range of 800 – 900 °C, when the AC yield from the mixture is approximately equal to the yield of AC from lignin.

Under these conditions, the OS components are involved at a maximum degree in forming the AC porous structure. And the specific surface of the activated carbon from the mixture is substantially higher than AC from the lignin.

Thus, the interaction of the lignin components and the oil slime develops in the non-additive change of the functional groups composition, as well as in the shift of the temperature range of the thermal decomposition and in increasing the speeds of thermal transformations as compared to the initial lignin and oil slime.

One can also observe the changes of the supramolecular structure already at the stage of

mixing the hydrolytic lignin with the oil slime which progress during the heat treatment of the mixture.

The effect of the mutual influence of the mixture components during the thermochemical transformations develops in the non-additive change of the yield of the carbonized material and its textural characteristics. The value of the effect depends on the activation temperature and it is the most significant in the range 800 – 900 °C, when the yield of the active carbon from the mixture is approximately equal to the AC yield from the lignin.

On the basis of the established regularities, there have been worked out the methods of obtaining cheap carbon sorbents having a rather great specific surface area (to 750 m²/g), and having the high adsorption activity relative to iodine and methylene blue (to 1060 and 230 mg/g respectively).

The obtained porous carbon materials may be used in various technological processes of cleaning and separation in gaseous and liquid mediums, and also for the purpose of environmental protection.

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