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Influence of Copper Acetate on the Thermochemical Transformations of Hydrolytic Lignin and its Mixtures with Oil Slimes

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By using various physical and chemical methods there were studied the thermochemical transformations of hydrolytic lignin modified with copper and its mixtures with oil slimes. As a result at the accomplished study there was carried out the selection of the conditions for modifying and thermal activation this industrial waste providing the production the active carbons with the yield 18-19 wt% and specific surface area of 620 m²/g.

Keywords: hydrolytic lignin, modification, copper acetate, oil-slime, thermal transformation, active carbon, structure, properties.

Introduction

The traditional vegetable raw material for production porous carbon-based materials (PCM) is birch wood [1]. The low yield of the carbonic product (not more than 12 % of the initial raw material mass) encourages the studies aimed at broadening the raw material sources of production PCM at the expense of using wood waste. These are also aimed at developing more perfect ways of carrying out the pyrolysis and raw material activation.

To regulate the structure and properties of carbonic sorbents, there is widely used the

chemical modification of vegetable polymers.

In particular, the processing of lignocellulose materials by using various chemical reagents, such as the acids (H₃PO₄, H₃BO₃, H₂SO₄) [2-4], the alkalis (KOH and others) [5], the salts (ZnCl₂, AlCl₃ and others) [6, 7], allows to increase the yield and the specific surface of the formed PCM.

The perspective direction in production porous carbonic materials is modifying the vegetable polymers with the compounds of transition metals [8-10]. During the pyrolysis of the modified vegetable materials, at the same time,

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there take place the processes of carbonation and chemical activation.

The large-capacity waste of the wood chemical processing is hydrolytic lignin (HL) [11]. The most perspective directions of the hydrolytic lignin processing is production of enterosorbents [12] and active carbons [13, 14]. By way of the combined thermal activating HL and oil slimes (OS), there were obtained the mechanically strong active carbons (AC) having a higher specific surface as compared to the powder AC of hydrolytic lignin [15].

In the given work, by using various physical and chemical methods, there were studied the thermochemical transformations of hydrolytic lignin modified with copper and its mixtures with oil slime.

Experimental

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

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

As the oil slime (OS), there was used the waste formed during the cleaning of the tanks at the washing and steaming station (Odessa, Ukraine). It is a water emulsion of heavy oil fractions (the water content is 50 ± 10 %) with the additions of surface-active substances. The organic mass of OS is presented by alkanes (80 %) and arenes (18 %). The average molecular mass is 750-1100 [16]. The emulsified oil slime was dehydrated by means of settling for 3 hours at a temperature of 80 °C [17].

There were prepared the mixtures of lignin and OS in the ratios 1:1 and 4:1 as calculated by mass. Part of the samples obtained in this way, was mixed with the $Cu(AcO)_2$ solutions in amounts of 2,5 and 10 wt%. The samples were dried out till the air – dry state.

The AC were obtained in the vertical tubular reactor having the volume of 50 cm³, which was placed into the electric furnace providing the heating till reaching the activation temperature (t_a) at a speed of 50 ± 5 °C/min. and the thermostatic control of the reactor at t_a with an accuracy of ± 5 °C. The weighed portion of the dried sample (5 g) was charged into the reactor. The system was blown through with argon at a speed of 2 dm³/h for 10 min. Then the reactor was heated to the temperature of 200 °C and the argon flow was switched over to the steam generator (the efficiency by water was 60 cm³/h). The heating was continued till reaching the activation temperature. On expiring the given activation time τ_a , the AC were cooled in the argon atmosphere. There was determined the activation product yield (Y, %) (the determination error was $\pm 0,4$ %).

The value of the specific surface (S_{BET} , m²/g) was determined based on the low-temperature argon desorption [18] using the “Sorptomatic –1900”.

The study of the AC permolecular structure was carried out with the diffractometer DRON – 1UM (the emission CuK_{α} , 4 kV, 20 mA). There were determined the following parameters of the AC permolecular structure: the interlayer distance d_{002} (the measurement error is $\pm 0,002$ nm), the height L_c ($\pm 0,02$ nm) and the average diameter L_a ($\pm 0,2$ nm) of the crystallites. There was also determined the extent of their space ordering h/l which is the ratio of the reflex height 002 (h) to its half width (l) and the number of the layers in the crystallite $n = L_c/d_{002} + 1$ [19].

The values of the adsorption activity based on the methylene blue (MB) and iodine were determined according to GOST 4453 – 74 and GOST 6217-74.

The thermogravimetric studies were carried out with the derivatograph Q-1500D of the Paulic-Paulic-Erdei system having a linear temperature

rise (10 °C/min.) from 20 °C to 950 °C. The weighed portion of the sample is 300 mg, there is the ceramic crucible. The processing of the derivatograms was carried out according to the method [10].

The infrared spectra of the diffuse reflection were registered on the spectrometer BIORAD FTS – 185 having the attachment GRASEBY SPACAC “Selector”. The spectra were obtained for the mixtures of the carbon sample (5 %) with the powder-like KBr (95 %) by the addition of 256 scans in the range of the wave numbers 4000–400 cm⁻¹. The contents of the functional groups in the samples heated to 150 °C, were determined according to Boem [21].

Results and discussion

To understand the mechanism of the thermal destruction of lignin and its mixtures with oil slimes in the presence of copper acetate, there were studied the thermal transformations at various temperatures under the conditions of non-isothermic heating (DTA), pyrolysis and water-steam and gas activation. There were also studied the structural characteristics of the initial materials as well as the products of their thermolysis by using the methods

of IRC, XRD, the functional analysis and microscopy.

Lignin thermolysis and activation. By using the method of IR spectroscopy, there were studied the transformations of the lignin structure during its treatment with copper acetate and during the thermolysis (Table 1).

The lignin spectrum is characterized by a set of absorption bands which are identified in the following way [22]: 3385cm⁻¹ is the hydrogen bond, 2930, 2850 cm⁻¹ are the fluctuations of the C–H bond in the methyl and methylene groups, 1710, 1667 cm⁻¹ are the fluctuations of the C=O bond in β- and α- carbon-containing acids respectively, 1603 and 1512 cm⁻¹ are the fluctuations of the bonds in the benzene ring, 1470, 1420 cm⁻¹ are the fluctuations of the C–H bonds in the groups CH₂ and CH₃ in methoxyls, 1365 cm⁻¹ are the fluctuations of the C-O bond in the phenol OH-group, 1220 cm⁻¹ are the fluctuations of the C–O–C and C–OH bonds of the ethers and phenols, 1132 and 1072 cm⁻¹ are the fluctuations of the C–O bonds in methoxyls.

The addition of the 2 % copper acetate to lignin, leads to increasing the intensity of the absorption bands in the range of 1600 and 1420 cm⁻¹. As for the intensity of the rest of the bands,

Table 1. The relative intensity of the main absorption bands of the lignin IR spectra

Sample	The absorption band, cm ⁻¹									
	3630	3510	3350	3050	2950	2860	1700	1600	1510	1460
L	-	-	0,39	-	0,36	0,22	0,45	0,47	0,80	0,68
L+2 % Cu	-	-	0,65	-	0,46	0,29	0,54	0,67	0,95	0,79
L+5 % Cu	-	-	0,51	-	0,34	0,22	0,43	0,69	0,91	0,72
L+10 % Cu	-	-	0,33	-	0,28	0,16	0,38	1,08	0,93	1,04
L, 370 °C	0,07	0,16	0,15	0,14	0,19	0,11	0,59	0,76	0,70	0,76
L+2 % Cu, 230 °C	-	0,17	0,19	0,10	0,25	0,15	0,44	0,66	0,82	0,75
	1420	1370	1220	1155	1125	1060	1033	870	815	750
L	0,53	0,59	0,92	0,89	0,89	0,99	1,33	0,45	0,46	-
L+2 % Cu	0,71	0,67	0,91	0,83	0,84	0,92	0,96	0,36	0,39	-
L+5 % Cu	0,70	0,65	0,85	0,80	0,83	0,92	0,95	0,35	0,38	-
L+10 % Cu	1,00	0,66	0,87	0,86	0,88	1,00	1,11	0,43	0,49	-
L, 370°C	0,70	0,73	1,01	0,91	0,77	-	0,60	0,48	0,45	0,44
L+2 % Cu, 230 °C	0,68	0,67	0,94	0,90	0,86	0,83	0,90	0,48	0,49	0,46

it changes slightly. As the concentration of copper acetate in the lignin increases (5 and 10 %), there decreases the portion of the OH-groups, connected with the hydrogen bond (the intensity of the band 3340 cm^{-1} decreases). There are also reduced the contents of the free carboxylic groups (there decreases the intensity of the absorption band in the range of 1700 cm^{-1} , and there increase the intensities of the bands in the range of 1600 and 1420 cm^{-1} , corresponding to the fluctuations of the C=O bond in the ionized carboxyl group).

The changes observed in the IR-spectrum, are evidently the result of substituting a hydrogen ion of the carboxylic groups for a copper cation. The addition of the 2 % copper acetate to lignin, leads to appearing a new speed maximum of the decomposition on the DTG curve at $193\text{ }^{\circ}\text{C}$. Maybe this corresponds to the decomposition of the copper carboxylates. During this process, there decreases the temperature of the beginning of the main thermal decomposition from 195 to $174\text{ }^{\circ}\text{C}$. And there decreases the decomposition rate in the maxima corresponding to the main thermal decomposition of lignin at 230 and $370\text{ }^{\circ}\text{C}$.

In the IR spectrum of the sample heated to $230\text{ }^{\circ}\text{C}$ (Table 1), there appears the absorption band in the range of 3055 cm^{-1} . There are also strengthened the intensities of the bands 870 , 815 , and there appears the band of 760 cm^{-1} , which testifies that in the thermally treated mixture, there increases the portion of aromatic structures having various types of substitution in the ring. One can also observe the decrease of the absorption bands intensity in the ranges of 2950 , 2860 and 1700 cm^{-1} , corresponding to the fluctuations of the bonds in the methyl, methylene and carboxylic groups, which probably takes place due to removing the low-molecular hydrocarbon gases. There also decreases the absorption band intensity of 1060 cm^{-1} , which may indicate breaking the ether bonds.

The differences observed in the character of the lignin thermal decomposition in the presence of $\text{Cu}(\text{AcO})_2$, are connected first of all, with the influence of the copper on the composition of the functional groups both at the preparation stage, and during the process of thermodestruction. The data of the functional analysis, given in Table 2, to a certain degree confirm this supposition. It is established that adding copper acetate to lignin decreases the percentage of the carboxylic and phenol groups contained in the sample which is connected with the formation of copper carboxylates and phenolates.

By using the method of X-ray diffraction, there were studied the changes of the lignin permolecular structure, caused by introducing copper acetate into its structure (Table 3).

The addition of copper acetate to lignin leads to decreasing the interlayer distance value d_{002} , as well as to the substantial increase of the stack extent in the longitudinal and cross-sectional directions. And the degree of ordering in the stack decreases almost twice. Such changes of the permolecular structure are characteristic of the low-metamorphized coals in which a hydrogen ion of the carboxylic and phenolic hydroxyl groups is substituted for a transition metal cation, capable of forming the chelate structures [23].

One can also observe the decrease of the γ bands number, whereas the number of the layers in the stack increases by one unit.

The thermolysis and activation of the L-OS mixture. The general appearance of the lignin IR-spectrum when oil slime is added, practically does not change (Table 4). There increases only the intensity of the absorption bands in the range of 2930 , 2850 cm^{-1} , as the OS contain a great number of aliphatic hydrocarbons.

According to the functional analysis data (Table 2), the addition of OS to the lignin, leads to the decrease of the contents of the acidic phenolic and carbonyl groups.

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

Sample	Functional groups			
	COOH	Lactones	OH _{phen.}	H-C=O
	mg-equiv/g			
Lignin (L)	2,45	0,5	1,2	1,10
L + 2 % Cu	2,45	0,5	1,2	1,10
OS	0,20	0,27	0,23	0,36
L – OS	1,91	0,80	0,19	0,27
L – OS + Cu	1,83	0,53	0,19	3,48

Table 3. The X-ray diffraction characteristics of the initial and modified lignin

Sample	Parameters					
	d ₀₀₂ , HM	L _a , HM	L _c , HM	h/l	n	The number of γ -bands
Lignin (L)	0,446	4,7	1,50	2,69	4,4	2
L + 2 %Cu	0,419	11,1	1,86	1,40	5,4	1

The addition of copper acetate to the L+OS mixture, reduces the number of lactone groups and substantially increases the carbonyl groups contents. The decrease in the lactone groups concentration may be connected with the formation of hydroxyl acids salts. The significant increase in the carbonyl groups contents may be explained by oxidizing the alcoholic groups, which are present in the mixture components. It is known that the metallic copper, when heated, catalyses the oxidation of the alcoholic groups to aldehyde ones [24]. According to the X-ray diffraction data, during the thermolysis of the L-OS mixture in the presence of the copper acetate, there is observed the partial reduction of the copper to Cu⁰ [25].

Using the DTA method, it is established that adding copper acetate to the L+OS mixture, leads to broadening the temperature range of the main decomposition of the organic mass.

In the IR-spectrum of the copper-containing sample (Table 4), there is observed the decrease of the absorption band intensity in the range of 1700 cm⁻¹, and also in the frequency interval of 1460-1033 cm⁻¹ and 870-750 cm⁻¹, which testifies

about the decrease in the contents of the carboxyl, methoxyl, phenol and ether groups as well as the portion of aromatic structures having a different substitution type. This may be the result of the interaction of copper acetate with both the oil slime and the lignin components.

Adding the copper acetate to the lignin and the L-OS mixture has a substantial effect on the results of activating these samples with steam while varying the time and speed of heating (Table 5).

Activating the lignin with 2 % copper acetate at a heating speed of 40 °C/min. to the end temperature of 800 °C, is accomplished by decreasing the AC yield. It is also accompanied by the substantial decrease of its specific surface and the adsorption activity based on the methylene blue (MB) and iodine as compared to the AC from lignin. These results may be the consequence of increasing the rate of the interaction of the lignin organic mass with the steam in the presence of the copper cations, which leads to the intensive burning out of the material forming macropores.

The activation of the L+OS mixture (1:1) with the addition of 2 % Cu(AcO)₂ carried out at

Table 4. The relative intensity of the main absorption bands of IR-spectra of the initial and thermally treated samples

Sample	Absorption band, cm ⁻¹												
	3630	3510	3350	3050	2950	2860	1700	1600	1510	1460			
L+OS (1:1)	-	-	0,35	-	1,10	0,70	0,42	0,38	0,60	0,69			
->-+2 % Cu	-	0,23	0,36	-	1,16	0,67	0,36	0,35	0,45	0,55			
->- , 400°C, 3 h	0,16	-	-	0,17	0,18	0,16	0,37	0,58	-	-			
->-+2 %Cu, 400°C, 3 h	0,14	-	-	0,16	0,15	0,14	0,27	0,37	-	-			
L+OS, (4:1)	-	-	0,27	-	0,33	0,22	0,31	0,32	0,54	0,48			
->- , 240 °C	0,08	0,12	-	0,12	0,12	0,10	0,34	0,61	0,42	0,53			
->- , 370 °C	0,12	0,14	-	0,18	0,16	0,16	0,57	0,65	-	-			
L+OS (1:1)	-	0,49	0,59	0,56	0,54	0,63	0,54	0,18	0,20	-			
->-+2 % Cu	-	0,37	0,43	0,39	0,39	0,47	0,51	0,07	0,12	0,03			
->- , 400°C, 3 h	0,56	0,57	0,67	0,68	-	-	0,48	0,57	0,62	0,60			
->-+2 %Cu,400 °C, 3 h	0,36	0,37	0,41	0,41	-	-	0,31	0,36	0,38	0,36			
L+OS (4:1)	0,40	0,39	0,61	0,58	0,58	0,66	0,71	0,29	0,3	-			
->- , 240 °C	0,52	0,52	0,63	0,61	-	-	-	0,37	0,38	0,33			
->- , 370 °C	0,57	-	0,68	0,67	-	-	-	0,42	0,44	0,46			

Table 5. The characteristics of the active carbons from the lignin and the L-OS mixture (1:1), produced by steam activation at 800 °C

Sample	Parameters					
	Activation time, h	$V_{\text{heating}}^{\circ}$, °C/min	Yield, %	S_{BET}° , m ² /g	A_{mb}° , mg/g	$A_{\text{iodine}}^{\circ}$, mg/g
L	2	40	31,2	370	233	918
L + 2 %Cu	->-	->-	24,1	120	71	458
L – OS	->-	->-	27,6	250	137	529
L – OS +2 %Cu	->-	->-	13,9	341	134	798
L	0,5	90	15,1	631	232	1056
L + 2 %Cu	->-	->-	19,0	535	224	937
L + 5 %Cu	->-	->-	17,2	450	188	-
L + 10 %Cu	->-	->-	11,3	151	56	-
L – OS	->-	->-	14,1	739	137	727
L – OS +2 %Cu	->-	->-	18,6	620,5	126	951

the heating speed of 40 °C/min., is accompanied by reducing the AC yield almost twice. During this process, there increases the specific surface of the active carbon as well as its adsorption activity based on iodine as compared to the AC from the unmodified mixture. But the adsorption activity based on MB, practically does not change. As a result, the presence of the oil slime and copper acetate in the mixture makes for the primary formation of micropores in the active carbon.

The activation of the lignin containing 2 % copper acetate at 800 °C for 0,5 h at a heating speed of 90 °C/min., is accompanied by the increase in the AC yield, by the decrease of its specific surface value and its adsorption activity based on MB as compared to the activation of the unmodified lignin. The adsorption capacity of the AC samples from the initial and copper-containing lignin is comparable. Thus, due to the high heating speed, the lignin thermoreactivity in the presence of copper decreases, which leads to increasing the AC yield. During this process, there is formed PCM with a great number of micropores. With the increase in the copper acetate contents to 5, 10 % in the lignin, the AC yield sharply decreases. There substantially decreases its specific surface

and adsorption activity based on the methylene blue. The activation of the L+OS+2 %Cu(AcO)₂ mixture, carried out under the similar conditions, is accompanied by increasing the AC yield and the small decrease of the specific surface area. However, its adsorption activity based on MB and iodine, practically does not changed as compared to the AC from the L+OS mixture. So, the high heating speed of lignin as well as its mixture with the oil slime in the presence of 2 % copper acetate, leads a high yield of AC having good adsorption characteristics.

According to the XRD data (Table 6), the permolecular structure of AC, obtained by the high speed activation of the lignin containing 2 % of the copper at 800 °C for 0,5 h, differs from the AC structure, obtained from the unmodified lignin under the same conditions in the large interlayer distance, the smaller stack size in the longitudinal and cross-sectional directions, in the smaller number of the layers and the lower degree of ordering in the stack.

The structure of AC, obtained from the L+OS mixture in the presence of copper, is characterized by a higher interlayer distance, a smaller thickness and degree of ordering in the

Table 6. The influence of copper acetate on the parameters permolecular structure of the active carbons from lignin and the L+OS mixture obtained by the activation with steam at 800 °C for 0,5 h

Sample	Parameters				
	$d_{002, \text{HM}}$	L_a, HM	L_c, HM	h/l	n
L	0,340	6,6	3,27	1,04	10,6
L + 2 % Cu(Ac) ₂	0,374	5,0	2,83	0,89	8,6
L – OS	0,384	6,8	1,95	0,73	6,1
L – OS + 2 % Cu(Ac) ₂	0,407	5,5	1,99	0,57	5,9

stack as compared to the AC from the L+OS mixture. Still the stack diameter and the number of the layers in the stack for these AC samples, are the same.

Conclusion

There were determined the peculiarities of the thermochemical transformations of the hydrolytic lignin and its mixtures with oil slimes modified with copper acetate as well as the structure and properties of the active carbons produced by using the methods of IRS, DTA, XRD, BET and the functional analysis.

It was established that the interaction of copper acetate with the oxygen-containing lignin functional groups, leads to forming carboxylates and copper phenolates as well as to changing the permolecular structure and the lignin reactivity during the thermochemical transformations. The indicated changes develop in decreasing the values of the interlayer distance of d_{002} , increasing the crystallites size, the number of the layers in the crystallite and the substantial lowering of their ordering degree.

The AC yield from the lignin samples and its mixture with the oil slime, is determined by the speed of the temperature rise during their activation.

At the heating speed of 90 °C/min., there increases the AC yield from the lignin, containing 2 %Cu and its mixtures with the oil slime as compared to the AC yield from the unmodified lignin samples and the lignin-oil slime mixtures. During this process, there is formed the carbon material having a great number of micropores.

The further increase of the copper contents in the lignin is undesirable, since there is intensified the reaction of the burning out of the organic mass with the formation of macropores, which substantially decreases the active carbon yield, its specific surface and sorption activity.

As a result of the accomplished study, there was carried out the selection of the conditions for modifying and thermal activating the hydrolytic lignin and its mixtures with the oil slime providing the production from this industrial waste the active carbons with the yield of 18-19 wt% and the specific surface of 620 m²/g.

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