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Properties of Active Carbons Produced by Thermochemical Transformation of Lignin, Brown Coal and Oil Slime Mixtures

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The yield and properties of active carbons (AC) produced by combined pyrolysis and activation of the mixtures: hydrolytic lignin – oil slime, brown coal – oil slime and hydrolytic lignin – brown coal – oil slime have been compared. The yield of AC from a triple mixture is lower than that from brown coal – oil slime, but higher than that of lignin – oil slime mixtures. The reached yield (15-20 %) and surface area (about 400 m²/g) of AC from triple mixture hydrolytic lignin – oil slime – brown coal are enough for their industrial using.

Keywords: mixtures, hydrolytic lignin, brown coal, oil slime, pyrolysis, activation, active carbons, yield, surface area.

Introduction

Increasing scale of using carbon sorbents in technological processes and in environmental protection stimulates the research in the field of sorbents producing from cheap and available natural raw material.

Cheap carbon sorbents can be obtained by co-carbonization of different mixtures of carbon-containing waste materials [1, 2]. Interaction of the mixture components in co-carbonization processes is exhibited through non-additive changes in the product yield and structural characteristics of the produced active carbons.

In the process of hydrolytic lignin, and oil slime carbonization, the oil slime can play the role of binding and pore-forming agent. [3, 4].

The present paper compares the yield and properties of active carbons, produced by pyrolysis and activation of the mixtures: hydrolytic lignin – oil slime, brown coal – oil slime and hydrolytic lignin – brown coal – oil slime.

Experimental

To produce AC the hydrolytic lignin (L) from Krasnoyarsk Biochemical Plant (Russia) with the following composition (%): W^a – 3.6, A^d – 1.8,

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$V^{\text{daf}} - 63.4$, C – 60.2, H – 6.0, O – 33.0, (S+N) – 0.8; brown coal from Alexandryisky deposit (Ukraine) with the composition (%): $W^{\text{a}} - 12.4$, $A^{\text{d}} - 11.7$, $V^{\text{daf}} - 57.6$, C – 70.4, H – 6.0, O – 17.8, N – 2.0, S – 3.8 and oil slime (OS) i.e. waste of cleaning cisterns at wash-curing station (Odessa), being a aqueous emulsion of heavy oil fractions with surface-active substance admixtures were used .

The mixtures lignin – oil slime, lignin – brown coal, and lignin – brown coal – oil slime were produced by mechanical mixing at room temperature during 5 minutes without the consequent forming. The oil slime content was 20-50 wt. %, corresponding to the most effective interaction between carbon-containing components of the mixture [5].

Active carbons were produced in a vertical reactor with a fixed layer under simultaneous processes of pyrolysis and steam activation according to the method described in paper [4].

The value of specific surface area (S_{BET} , m^2/g) was estimated with the use of low-temperature argon desorption at “Sorptomatic-1900” [6]. The definition error S_{BET} was $\pm 7\%$ rel.

The study of AC permolecular structure was conducted by diffractometer DRON-IUM (radiation $\text{CuK}\alpha$, 4 kV , 20 mA).

Results and Discussion

Earlier the thermal destruction peculiarities of hydrolytic lignin (L) and oil slime (OS) mixtures under different temperatures have been studied under conditions of non-isothermic heating, pyrolysis and steam gaseous activation [4]. The interaction of lignin and oil slime components was exhibited in non-additive changes in the mixture functional composition, displacement of the temperature interval of thermal decomposition areas, increase in the rate of thermal transformations in the maximum points of thermal decomposition areas in comparison

with of the initial lignin and oil slime samples. The changes in permolecular structure are evident already on the stage of mixing hydrolytic lignin with oil slime with the following progress under thermal processing of the mixture.

In the present paper the yield and textural characteristics of active carbons, produced by pyrolysis and activation of lignin – oil slime mixtures, and hydrolytic lignin – brown coal – oil slime mixtures were compared.

The effect of the mutual influence of the components in lignin – oil slime mixture is exhibited in non-additive changes in the carbonaceous materials yield and there textural characteristics. The observed changes depend on the activation temperature, which is the most important in the interval of 800-900 °C, when the active carbon yield from the mixture is approximately equivalent to the active carbon yield from lignin (Fig. 1). Under these conditions oil slime components are involved in a maximum degree into the active carbon space lattice formation. The specific area of active carbons from the lignin – oil slime (1:1) mixture is higher than that of the active carbons produced from lignin (Fig. 2).

Oil slime components taking part in active carbon formation influence on the characteristics of AC porous structure. The amount of mesopores in AC from lignin – oil slime mixture is considerably (up to 3 times) higher than that of AC produced from lignin [4].

The differences in porous structure of AC from lignin and lignin – oil slime mixture correspond to their peculiarities in their permolecular structure, studied by X-ray technique. The higher degree of AC space lattice disorder in the presence of oil slime can be a possible reason for the increased mesoporosity of AC obtained from lignin – oil slime mixture.

The increased amount of mesopores in AC from lignin – oil slime mixture after activation

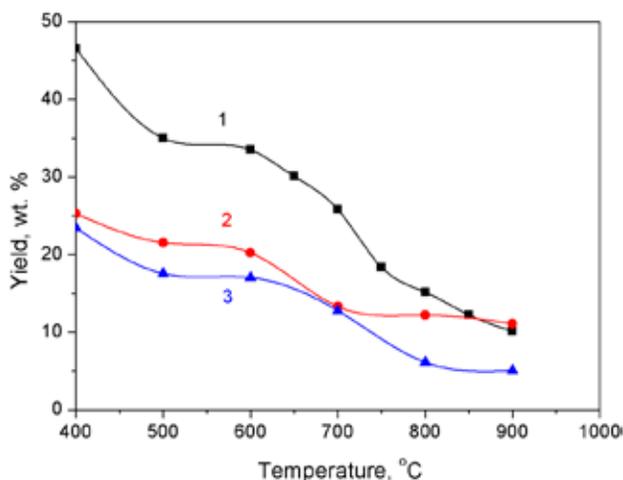


Fig. 1. The influence of activation temperature on yield of active carbons from lignin (1) and from lignin – oil slime mixture (2). Estimated yield of AC from lignin – oil slime mixture

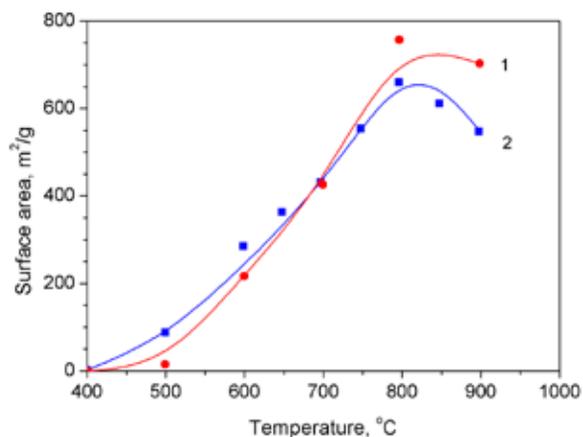


Fig. 2. The influence of activation temperature on the specific surface area of active carbons from lignin (1) and lignin – oil slime mixture (2)

under 800-900 °C results in the higher adsorption activity in methylene blue than that of AC produced from lignin.

Thus, the co-activation of lignin with oil slime makes it possible to produce AC with a well developed BET surface area ($\leq 800 \text{ m}^2/\text{g}$). Probably, the interaction of lignin with the oil slime components creates an additional number of reactive centers, promoting the formation of micro- and mesopores in AC during gasification reactions. Functional groups of lignin containing O, S, N atoms can be referred to these reactive centers [7].

It is possible to suggest that to convert oil slimes into AC effectively, the presence of components with a high content of oxygen functional group, being an intermediary product of topochemical reactions during steam activation is necessary [8].

In case of lignin – oil slime mixture activation, lignin, having a high amount of oxygen ($O^{\text{daf}} 33.0 \%$), becomes a supplier of the mentioned functional groups: methoxyl, carboxyl, ether, carbonyls and others [7].

Thermochemical transformations of lignin – oil slime mixture have been studied in the

presence of another solid carbon substance – brown coal, which as well as lignin, has a high content of oxygen functional groups (O^{daf} 17.8 %). But coal is more thermostable and it has stronger rigidity of a carbon framework due to the presence of condensed 2-3 ringed arenes and larger number of three dimensional linkages between structural elements [9].

Table 1 compares the yield and specific surface area for ACs, produced from brown coal and brown coal – oil slime mixture.

In case of brown coal, the largest surface area development is registered after 15 minute activation, while in case of lignin activation, only after 30 minutes [4]. The maximum of surface area ($290 \text{ m}^2/\text{r}$) of AC from brown coal is several times lower than that of AC produced from lignin ($650 \text{ m}^2/\text{g}$ according to [4]).

Let us compare AC yield from the mixture of brown coal and oil slime (Table 1) with the AC yield from brown coal. Taking into account the low AC yield from oil-slime, the estimated AC yield from brown coal – oil slime is two times lower than of experimental yield. Thus, non-additive effect based on oil slime participation in AC structure formation while brown coal – oil slime mixture activation is observed.

The value of specific surface area of AC produced from brown coal is not high (Table 1) and reaches $290 \text{ m}^2/\text{g}$. Activated carbons from brown coal – oil slime mixture have less developed surface ($230 \text{ m}^2/\text{g}$), which is much lower the surface values for AC produced from lignin – oil slime mixtures.

We can suppose that the observed differences are the consequence of structural peculiarities of lignin and coals.

Lignin consists of low-branched phenylpropane chains, aggregated into a three-dimensional framework with easily destructed intermolecular bonds [7]. Because of this, lignin structure acquires a high conformation mobility

and can easier transform under the action of oil slime components both during mixing and under conditions of AC framework formation during activation.

Brown coals structural elements have lower conformation mobility, are more densely packed, resulting in a less porous structure of the produced AC. Besides, the composition of oxygen functional groups for brown coal and lignin is qualitatively different [7, 9], thus making influence on the interaction of brown coal and lignin with oil slime during activation.

The behavior of triple mixture lignin – brown coal – oil slime (1:1:1) was compared in the aspect of estimation of mutual influence of mixture solid components on AC formation. AC yield from a triple mixture is lower than that from brown coal – oil slime, but higher than that of lignin – oil slime mixture.

This result shows the lack of mutual influence of lignin and brown coal in the mixture during activation process. For a triple mixture under the conditions of a one-stage activation process the high AC yield, typical for brown coal – oil slime mixture was not reached. Nevertheless, it is possible to produce AC with the surface area about $400 \text{ m}^2/\text{g}$ (Fig. 3) and yield of 15-20 % from a triple mixture. It is necessary to stress that the reached yield and surface area values are enough for the industrial use of AC produced from the studied carbon-containing waste.

The comparison of lignin and lignin – oil slime samples microstructure before and after their thermal activation was made (Fig. 4). The microstructure of the initial hydrolytic lignin was presented in fragments of lignified walls of cells, observed from different cuts – horizontal, vertical an diagonal, cell cavity being empty.

In the cross cut the pore diameter is from 5 to 20 mkm, cell wall thickness is from 2 to 10 mkm, the inner cell wall surface is characterized by the presence of ultrathin pyritization and

Table 1. Yield and specific surface area of active carbons produced by one-stage activation of brown coal and brown coal – oil slime mixture

Activation temperature, °C	Activation time, min.	AC yield, wt. %	Specific surface area, m ² /g
Brown coal			
600	15	39.8	170
650	15	36.2	210
700	15	33.0	220
750	15	28.6	270
800	15	22.8	290
850	15	20.9	290
900	15	17.1	280
800	0	32.1	120
800	10	27.3	230
800	15	22.8	290
800	30	18.5	280
800	45	16.1	270
800	60	15.7	260
Brown coal – oil slime mixture (1:1)			
800	0	32.0	100
800	10	26.8	210
800	15	23.7	225
800	30	23.0	220
800	45	18.1	220
800	60	16.3	220

pyrite single crystals 2-3 mkm. Lignin color in different cuts is dark brown, dark grey, black. Lignin reflection indices are 0.26 – 0.37%, mean value is 0.30%.

Under a microscope observation lignin – oil slime mixture looks in a different way in comparison with pure lignin: cell walls are thicker with occluded cell cavities. Some cell cavities are occluded with a dark substance (oil slime), while lignin in a sample has a higher reflection index R (0.38 %).

Lignin in the lignin – oil slime mixture, heated at 240 °C during 3 hours is characterized by irregular changes in microstructure and a wide range of R values in different fragment points. About 50 % of lignin is characterized by R values from or 0.27 up to 0.60 %, the

rest values are up to 1.70 %, single fragments– 1.9-2.00 %.

With increasing R index the peculiarities of lignin microstructure become more evident: differences in color gradations disappear; aggregations of fine-fragmented lignin gets a denser structure with pores of irregular shape taking place of cavities between lignin fragments containing some bitumen inclusions. In some areas the thermolignin homogenous structure replaces fine-fragmented lignin aggregations.

Lignin – oil slime mixture, thermolyzed at 400 °C during 3 hours, is characterized by the presence lignin of light grey color with a variety of colors from grey to white and bright white. Accordingly, lignin in the sample has

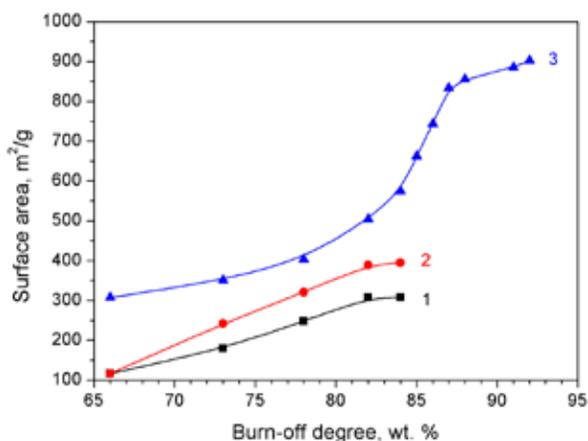


Fig. 3. Dependence of activated carbon specific surface area on the burn-off degree: 1 – brown coal – oil slime mixture (1:1); 2 – triple mixture of lignin – brown coal – oil slime (1:1:1); 3 – lignin– oil slime mixture (1:1)

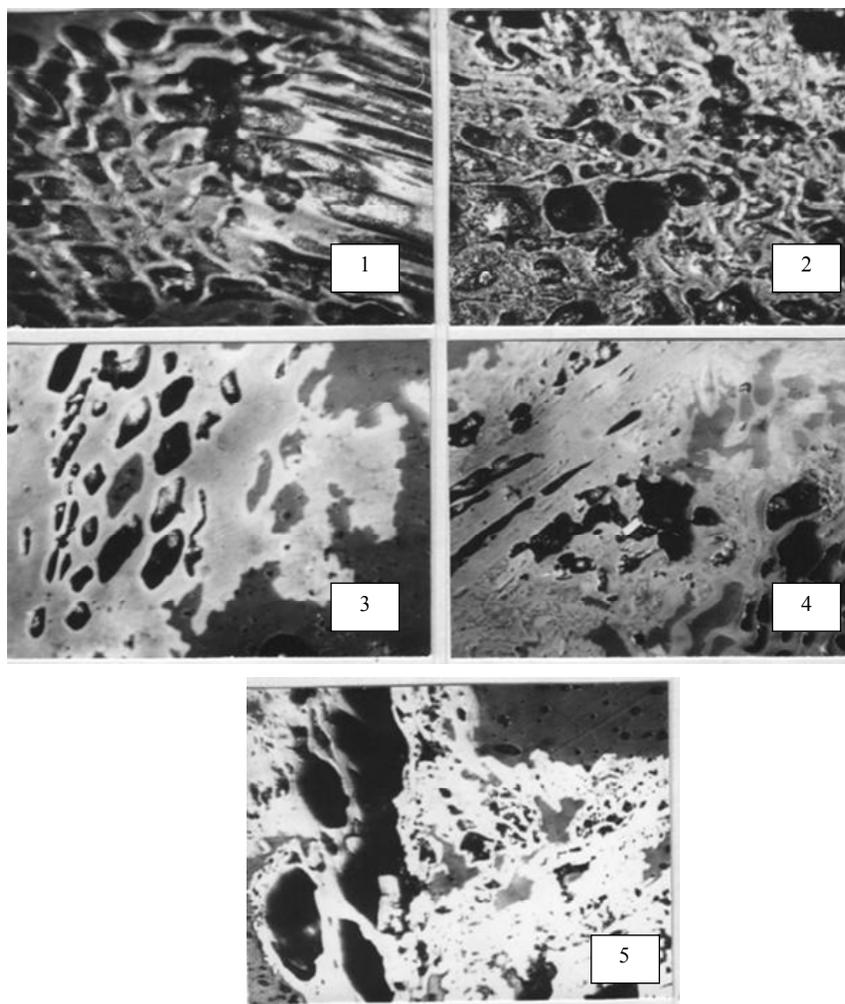


Fig. 4. Lignin and lignin – oil slime mixture microstructure before and after thermolysis: 1 – lignin; 2 – (lignin – oil slime mixture); 3, 4 – (lignin–oil slime mixture) at 240 °C after 3 h; 5 – (lignin–oil slime mixture), at 400 °C, after 3 h

high reflection indices, raised in comparison with the initial values from 0.57-0.55 up to 1.24 and 1.13 % and are equal to R of coking coals. Thermally changed lignin is isotropic, porous substance with dense smooth cell walls and pore walls. Lignin fragments with equal reflection values prevail, a number of lignin fragments with higher or lower reflection indices being rather small. There are two different pore types in lignin fragments. The first of them is present by natural pores of empty cell cavities and larger pores with sizes from 10 up to 100 mkm. The second type of pores is likely formed as a result of thermolysis. They have rounded, of irregular shape and rather homogeneously distributed and substantially smaller in size (from 2 to 40 mkm). Accordingly, the pores of the first type have thicker cell walls of 10-50 mkm as compared to pores of the second type – 2-15 mkm. The ratio of these two types of porosity is more or less equal in all samples.

Conclusion

As a result of the accomplished research it was found that oil-slimes can play the role of binding and structure forming component in thermal transformation of lignin and

brown coal. Active carbons, produced from oil slime – lignin – brown coal mixtures are coked particles, considerably different from powdery active carbons produced from lignin and brown coal.

AC produced from double mixture oil slime – lignin has highest specific surface area. The observed differences in yield and specific surface area between AC from lignin – oil slime mixtures and lignin – brown coal mixtures are likely to be the result of different content of oxygen functional groups, providing interaction of components in mixtures during thermal transformation processes, as well as availability of arenes in brown coal, which are more condensed than in lignin, and a larger number of three-dimension bonds, providing a higher rigidity of a carbon framework in coal.

The following benefits of active carbons, produced from hydrolytic lignin, oil slime, brown coal mixtures – well developed mesoporous structure with narrow range of mesopores sizes, high rather specific surface area, the possibility to produce AC of different geometric shape – open good perspectives to use the considered above active carbons as carbon sorbents, carriers and catalyst supports.

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