THERMODESTRUCTION OF BLENDS FROM CARBON-CONTAINING WASTES OF DIFFERENT ORIGINS

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Introduction

Up to now the search of new low cost natural abundant carbon-rich materials for production of solid porous carbon materials is actual. From our point of view one of the perspective way in this connection is to use carbon-containing wastes as the precursors for ACs production [1-5].

Pyrolysis and carbonization of different carbon-containing wastes are the first stage of activation process of raw materials for adsorbents obtaining. Knowledge of main regularities of substances decomposition is the direct way to predict the the result of activation [2].

For porous materials obtaining the following raw materials were chosen: biomass wastes (sawdust and lignin), cut oil (heavy washing off petroleum wastes (WPW) [3,5].

WPW were accumulated in the settlers near the stations for the unloading and transportation of oil (such as Odessa port) for tens years. They create some ecological problems there. WPW are the emulsion with water content ~50%, they have molecular mass 750- 1100c.u., average aromaticity- 9.4-17.2%. There are ~ 500 000 tons of WPW in Ukraine. WCW can be considered as the binder (or plastificator) of solid materials and as own precursors of sorbents. Lignin resources in Ukraine are more than 500 000 ton, but rational industrial ways for it utilization have not developed [6].

The goals of our work are:
- the investigation of features of decomposition of wood biomass and binary system (L+WPW),
- the examination of the influence of cooper on thermolysis of blends and its transformation during carbonization.

Experimental

For investigation of carbon-containing raw materials the following methods have been used: optical microscopy, X-ray diffractometry, thermogravimetry, IR- spectroscopy and chemical functional analysis (according to Boehm method). Acetate of copper was chosen as the catalytic addition. Thermogravimetric characteristics of initial lignin, petroleum wastes, coal and their blends was studied with apparatus MOM-1500 (V = 10^0/min, m_0 = 0.5g, in atmosphere of own gases).

Results and Discussion

Lignin (L), aspen, larix, pinus wood (sawdust), washing off petroleum wastes (WPW) and low rank coal were compared at considering their pyrolysis (thermogravimetric analysis) (Figure) and carbonization (400^0C, 3 hr).

For the blend of lignin and WPW temperature of main maximum of decomposition of the blend (L+WPW) decreases and conversion degree (CD) raises significantly.

Copper addition (by impregnation) leads to new low temperature maximum in range ~ 160^0C and some decreasing (2-4%) of conversion degree.

Initial blends of wastes have two or three maximums of thermal decomposition of organic mass: 1 and 2- (at temperature ~240 and 370 ^{0}C) correspond to destruction of lignin structure, 3 - (at temperature~420-500^{0}C) corresponds to disintegration of petroleum wastes. In the blends the maximums of organic mass decomposition (M_{DOM}) are more closed (at 265 and 385 ^{0}C). As for binary (L+WPW) system the synergetic effect concerning conversion degree of raw blends at L:WPW =20:80 has been observed (η=84 against theoretic 66%).
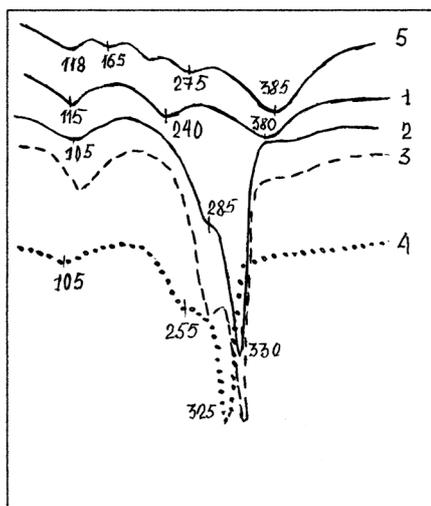
Figure. DTG- curves of :
1- lignin, 2- pine, 3- larix, 4 - aspen sawdust, 5 -
lignin + WPW + Cu(Ac)$_2$

The influence of catalytic addition of Cu(Ac)$_2$ is concluded in:

- the change of conversion degree (η)
- the change of beginning temperature of thermodestruction
- the shift of M $_{DOM}$ into the side of higher temperature
- the appearance of new maximums (at 165, 220^{0}C) on DTA-curves .

These facts are the evidence of the creation of new chemical bonds in the system, which can determine the formation of *other* carcass and porous structure of resulted PCM. IR- spectroscopy and Boehm method's data confirm our conclusion concerning new compounds formation .

Appropriate chemical interactions between components were found. For the systems they are:

- substitution of protons in COOH and OH $_{phen}$ - groups in Cu case,
- interactions of different functional groups in the system L+WPW, L+WPW+Cu.

The X-ray phase analysis of initial samples and blends has been carried out. In the composition of initial lignin the reflexes were detected characterized for following compounds: Cu SO$_4$. 5H$_2$O (d= 4,70; 3,99; 2,72; 2,44; 2,02; 1,96å), SiO$_2$ (d= 4,25; 3,35; 1,82å), BaSO$_4$ (d= 3,93; 3,09; 2,72å), clayey minerals and hydromica (d = 10- 6å). For initial WPW following minerals were found: clays (d = 12- 6 å), MgSO$_4$.6H$_2$O(d = 5,5; 5,1; 3,42; 2,92; 2,74; 2,50 å), CuS (d = 4,47; 3,01; 2,71 å), perhaps (KNaFe)$_5$ Fe$_3$ (SO$_4$)$_6$ (OH)$_2$. 9H$_2$O (d = 8,96; 8,07 å) and hematite FeS$_2$ (d = 2,52; 4,13 å). In the blend L+WPW=1:1 practically the same reflexes are detected which are characterized for initial components, but in different proportions. Besides that there are some others reflexes with d = 12,2; 4,2; 2,90 å, which are characterized for minerals tamarugite NaAl(SO$_4$)$_2$.6H$_2$O and yarosite KFe^{+3}[SO$_4$]$_2$ (OH)$_6$ (5,36; 5,16; 2,78 å).

In the case of impregnation of this blend with solution of Cu(Ac)$_2$ the diffractogrammes have weak reflexes of this reagent (d =5,35, 1,98, 1,89å) and new reflexes related to CuS (d = 3,06, 1,98Å).

At the heating of this blend in atmosphere own gases at 240^{0}C during 3 hours Cu(Ac)$_2$ disappeared. On diffractogrammes of chars the reflexes which are characterized for CuSO$_4$.5H$_2$O (d =2,86, 2,69, 2,62, 2, 58å), SiO$_2$ (d= 4,25; 3,35; 1,82å) increase and new reflexes appear (d=2,08, 2,76).

It has been established the dependence of burn off degree at two-step activation from the rate of principal thermal decomposition (according to DTA-data) for all the samples. It is closed to exponential. These data allow approximately to predict the surface area of resulted ACs.

Carbonization of initial lignin at 300-400^{0}C during 1-2h leads to activated carbons (ACs) with S$_{BET}$ ~ 3 m^2/g and burn off up to 35%. The maximum S$_{BET}$ = 120 m^2/g was observed for burn off ~ 45% (3h carbonization at 400^{0}C). These conditions of carbonization were chosen for the next experiments.

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