

FRUIT STONES CARBONS: OPTIMIZATION OF PROCESSES TO PREPARE ACTIVE AND OXIDIZED FORMS

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Introduction

Taking into account limited raw resources of the Ukraine at the creation of own industry of active carbons (AC), use the fruit stones and nuts shell is represented to one of priority. So, a trial preparation technology of stones AC (KAU-type) with the high operational characteristics, satisfying requirements of many practical tasks including medical application (hemoperfusion, adsorption preparates) is developed [1]. At the same time heterogeneity of initial raw material on structure, use of various preparatory operations and modes of carbonization puts a problem of technological parameters optimization for process of steam activation to produce the adsorbents of required quality [2]. It was represented not less important to optimize the process of KAU-carbons oxidation by damp air, supplying the synthesis of ionites on the basis of oxidized carbons (OC) with the rather high and reproduced characteristics on cation exchange capacity [3].

Experimental

Steam activation process of raw-charcoal from the crushed apricot stones was carried out on semi-pilot vertical furnace of a boiling layer. Initial volume of raw-charcoal made 4 dm³, primary granular size of an initial product made 1-3 mm, and bulk density (D_{in}) was in limits 0.5-0.6 g/cm³. Temperature and exposure modes have made 830-870 °C and 2.5-4.5h. At realization of work have spent measurements: mass and volume of obtained product (M_{ac}, V_{ac}), mass and volumetric distribution of particles on the sizes, yield of a product on mass and volume (R_m, R_v), burn-off (w), bulk density (D_{ac}) on the total and on separate fractions, sorption pore volume on benzene (W_s).

Oxidation of AC was carried out in quartz tube, placed in the tubular horizontal furnace with adjustable electrical heating, in a current of damp air at periodic hashing. Volume of an initial sample made 0.1 dm³, charge of air with 100% by humidity made 18 dm³/h. Temperature and exposure modes were varied in intervals

410-450 °C and 2-10 h, respectively. The controllable characteristics of obtained samples were: burn-off (w), bulk density (D), sorption pore volume on benzene (W_s), total exchange capacity (TEC) and exchange capacities on functional groups - strong acid carboxylic (SEC), weak acid carboxylic (WEC) and phenolic (PEC). Differences in ion exchange capacities were determined by fractional titration with solutions of NaHCO₃, Na₂CO₃ and NaOH, proposed by Boehm.

On the basis the received data mathematical models within the framework of the elementary algorithm - complete factor experiment of the first order at two levels (temperature, exposure) in view of factor interaction were constructed. The analysis of efficiency of process of activation on W_s, volumetric parameter of porosity (W_s•D_{ac}) and yield of a product (W_s•R_m and W_s•D_{ac}•R_m), and also process of oxidation on TEC, SEC, WEC and PEC as well as their appropriate parameters, connected to yield of a target product (EC•R_m) was spent.

Results and Discussion

Reception of AC. Received results have allowed to calculate some parameters of process of activation. Thus, the speed of burn-off (dw/dt) progressively grows with increase of temperature. Factors of decrease of the relation of yield on weight to yield on volume (-d(R_m/R_v)/dw), describing a parity between processes of pore formation (1) and burning (0), are close to 0.5, that testifies to the about equal contribution of these processes to integrated process of activation in a researched interval of temperatures. Thus parameters of increase of sorption pore volume (dW_s/dw) and the decrease of bulk density (-dD/dw), and accordingly the factor of development of porosity (dW_s/|dD|) best are at temperature 830 °C. The general analysis of the received data testifies that the primary size of particles after activation at burn-offs up to 60% practically same, as in initial raw-charcoal. At large burn-offs shift of distribution on sizes on a step below is possible).

At construction of factor model the equations as $Y = b_0 + b_1T + b_2t + b_{12}Tt$, where Y was W_s,

Ws•D, or Ws•D•Rm were received. The analysis of the equations enables to calculate threshold temperature of activation, which has made 770 °C. The appropriate three-dimensional diagrams are received which allow to choose optimum temperature-exposure modes for reception of AC with required porosity (in relation to mass or volume) and yield of a target product. The model allows also to construct two-dimensional diagrams T-t and to definite a field of the temperature-exposure modes of AC reception under condition of restriction operational (Ws, Ws•D) or economic (Ws•Rm, Ws•D•Rm) parameters, and also burn-off (w).

Reception of OC. The analysis of the received data has shown, that at all investigated temperatures during the first two hours burn-off is about identical and does not exceed 15%. Then sharp distinction in speeds of burn-off is markedly increase with growth of temperature. Just in this period alongside with during there is the increase of bulk density of substance at the expense of connection of oxygen. Account shows that bulk density of OC is compared to one of initial carbon accordingly at burn-off 45 (410 °C), 53 (430 °C) and 65% (450 °C). It means that effect of a "set of mass" at the expense of formation of surface oxides move in the party of lower temperatures, at which the oxidation is conducted. Dependences TEC on oxidation exposure (t) have the "sated" character as $C = C_{max} [1 - \exp(-bt)]$, where C_{max} - limiting TEC at indefinitely long oxidation, b - parameter of curvature of function, describing the kinetics of process. The character of dependences for various temperatures in an interval 410-450 °C is very close. Rather quickly (during 10h) TEC reaches 2-2.2 meq/g (i.e. 80-90% from limiting), but thus the yield of a product on mass Rm sharply falls with growth of temperature and in an investigated interval of temperatures the samples with identical TEC can differ on burn-off on 10-30%.

By consideration of factor model the same parameters were used, as at study of activation process, i.e. T and t, and as Y are considered TEC, SEC, WEC and PEC, as well as the same parameters, adhered to an yield of a product (•Rm). It is obvious, that it was not meaningful to bring parameters as volumetric, as bulk density of strong oxidized samples is close to bulk density initial ones. The analysis of the equations has enabled to calculate threshold temperatures of oxidation. So, total exchange capacity begins to be formed at 289.6 °C. Thus strong acid carboxylic groups owe, according to model, to begin to be formed already at 170 °C, and phenolic - at 406.5 °C. Weak acid carboxylic

group should completely be spreaded out after 457.2 °C. As well as in a case with reception of AC, the model enables to construct the three-dimensional diagrams and to choose optimum of temperature-exposure modes for reception of OC with required exchange capacity (total and on separate groups), referred to mass of a product, and also on yield of a target cationites. It is also possible more simple variant - construction of appropriate two-dimensional diagrams T-t and definition of a field of modes for reception of OC under condition of restriction of given parameters and burn-off (w). An example of diagram is shown on fig. 1.

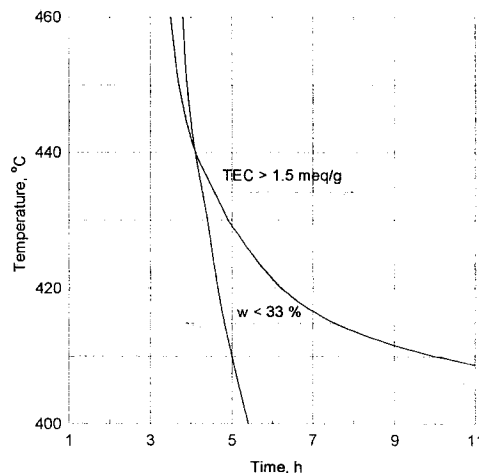


Figure 1. Temperature-exposure field to prepare OC which are characterized by TEC more than 1.5 meq/g at burn-off less than 33%.

Conclusions

Conditions of preparation of AC on porosity and yield, and also OC on exchange capacity, including differentiation as exchange centres and yield of a target product are optimized. The received peculiarities with use of mathematical modeling of processes enable creations of the appropriate technologies of carbon materials with required functional parameters and high yields of target products - adsorbents and cationites.

References

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