

# POSTER

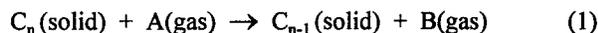
## MODELING OF KINETICS OF CARBON PORE STRUCTURE FORMATION BY STEAM ACTIVATION

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### INTRODUCTION

Most of the commercial active carbons (AC's) are prepared by steam or gas activation. Such activation agents ( $H_2O$ ,  $CO_2$ ,  $O_2$ ) reacts at high temperature with carbonaceous material:



The products formed are removed out of reaction zone. Activation causes changes in existing pores, initiating of new pores, coalescence of pores into one, changes in surface area and pore volume.

Modeling of kinetics porosity formation in AC's by activation allow to reveal optimal processing characteristics [1].

### EXPERIMENTAL

Synthetic active carbons described here are prepared by steam activation in quartz tube reactor at 1073, 1123, 1143 K and pressure 0.1 MPa. Starting material used for preparation of synthetic active carbons was raw carbon produced from porous styrene-divinylbenzene copolymer [2]. The benzene (273 K) and nitrogen (77 K) adsorption isotherms are used to characterize the porous structure of carbons. Volume, size and surface area of micropores are evaluated using Dubinin-Stoeckli equation. Mesopore surface area was estimated by  $\alpha_s$ -method and by mercury intrusion method.

### MODELING

By modeling of porous structure of AC's we consider that AC's particles consists of the portions of solids and pores. The model of a spherical shape pores which randomly distributed in carbon matrix and overlapping is supposed (Random Pore Model) [3, 4].

The most important characteristic of AC's is the pore size distribution (PSD) function  $f(r, t)$ . In our approach

PSD is normalized, so as  $f(r, t)dr$  is the number of pores having a radius lying between  $r$  and  $r+dr$  at the time  $t$  per unit volume of carbons. Studing of evolution of PSD fuction during activation is more convenient to carry out in terms of mathematical moments of PSD function

$$M_n = \int_0^{\infty} r^n f(r, t) dr$$

If we assume that number of pores is quite few and pores don't overlap, than effective characteristics per volume unit of porous solid are:

$$\begin{aligned} N(t) &= M_0 && \text{- number of pores;} \\ L_E(t) &= M_1 && \text{- specific total length of pores radii;} \\ S_E(t) &= 4\pi M_2 && \text{- specific total surface area of pores;} \\ V_E(t) &= 4/3\pi M_3 && \text{- porosity.} \end{aligned}$$

We will consider that pore size is changed because of chemical reaction (1) occuring on pore walls («corrosive» growth) [1, 3] and number of pores is increased because of initiating of new pores. Decreasing of number of pores during pore coalescence is not taken into consideration. Then the evolution of PSD function obey pore continuity equation (the pore population balance equation) [1, 3, 4]:

$$\partial f(r, t) / \partial t + \partial / \partial r \{ f(r, t) \partial r / \partial t \} = I(t) \delta(r - r_c) \quad (2)$$

$$\begin{aligned} \text{with initial conditions} & \quad f(r, 0) = f_0(r) \\ \text{and boundary conditions} & \quad f(r, t) \partial r / \partial t \Big|_{r=r_c} = I(t) \end{aligned}$$

where  $I(t)$  is the rate of new pores initiation (nucleation) per volume unit;  $\delta(r - r_c)$  is the Dirac delta function;  $r_c$  is the critical size of pore nucleus (minimal pore size).

In most cases analytical solution of population balance equation is not possible. In order to avoid this difficulty is often suggested a procedure which reduces equation (2) to a set of first-order differential equations for the moments of the PSD function. After multiplying eq. (2) by  $r^n$  ( $n \geq 0$ ) and further integrating from 0 to  $\infty$  we obtain a set of ordinary differential equations in terms of the

moments of the PSD function with initial conditions:

$$\begin{aligned} dM_0/dt - I(t) &= 0 & M_0(0) &= N_0 \\ dM_1/dt - WM_0 - r_c I(t) &= 0 & M_1(0) &= L_E(0) \\ dM_2/dt - 2WM_1 - r_c^2 I(t) &= 0 & M_2(0) &= S_E(0)/4\pi \\ dM_3/dt - 3WM_2 - r_c^3 I(t) &= 0 & M_3(0) &= V_E(0)/(4/3)\pi \end{aligned} \quad (3)$$

where  $W = dr/dt$  is the rate of the single pore growth.

When penetration of activation agent is not controlled by diffusion, the growth rate of isolated pore may be written as:

$$W = k_e C_A^m \exp(-E_A/RT) \quad (4)$$

where  $k_e$  is the effective constant of pore rate growth,  $E_A$  is the activation energy,  $m$  is the order of heterogeneous reaction (1),  $C_A$  is the activation agent concentration.

As the reaction (1) progresses, existing pores of carbon are increased in size, new pores are initiated and effect of pore overlapping is occur. As number of pores is increased and coalescence is took place. This effect led to decreasing of actual characteristics: porosity ( $\varepsilon$ ), surface area of pores ( $S$ ), length of pores ( $L$ ). According to RPM dependences between effective and actual characteristics of AC's are [4]:

$$\varepsilon = 1 - \exp(-V_E), \quad S = S_E(1 - \varepsilon), \quad L = L_E(1 - \varepsilon) \quad (5)$$

If the size of AC's particles is decreased by activation in very small degree the burn-off ( $X$ ) and apparent density ( $d$ ) of AC with a small amount of ash connected with porosity by:

$$X = (\varepsilon - \varepsilon_0)/(1 - \varepsilon_0) \quad (6)$$

$$d = d_0 (1 - \varepsilon)/(1 - \varepsilon_0) \quad (7)$$

where  $\varepsilon_0$ ,  $d_0$  are the initial porosity and density.

Combining a set of equations (2) with eqs. (4)-(7) we can get dependences for pore radii, surface area of pores, density, burn-off and porosity on time when the function of new pores initiation is known.

## RESULTS AND DISCUSSION

Microporous and bimodal (micro- and mesoporous) model of synthetic AC's were used. For the first model it was assumed that new pores were not initiated. In this case is possible to obtain the analytical solution of equations (3). For the gasification rate, surface area and average micropore radius the following equations were obtained:

$$dX/dt = W S d_0 (1-X)/(1-\varepsilon_0) \quad (8)$$

$$S = S_0 (1-X) \{1 + \ln(1-X)/\ln(1-\varepsilon_0)\}^{2/3} \quad (9)$$

$$\bar{r} = \bar{r}_0 \{1 + \ln(1-X)/\ln(1-\varepsilon_0)\}^{1/3} \quad (10)$$

For bimodal model and heterogeneous law of pores nucleation

$$I(t) = I_0 \exp(-k_i t) \quad (11)$$

the solution of eqs. (3) is possible only by numerical methods with computer using. This model can describe more precise the dynamic changes in porous structure of carbons than the first one.

Steam activation up to low burn-off results mainly in micropores development. Mesopore surface area and mesopore volume approximately linear depends on activation time. The total surface area of carbons with initial porosity (or burn-off) lower than critical value increases firstly, passes through the maximum and then decreases with conversion. The micropore size is lineary changed with activation time without nucleation and passes through the minimum in the case of nucleation. The dependences for burn-off have «S-form» during activation. Using above model it was found from experimental data that activation energy of the gasification reaction of synthetic AC's is about 200 kJ/mole.

Practical considerable conclusion is the possibility to predict the peculiarities of kinetics porosity formation and to control the activation process.

## REFERENCES

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