ORIGINAL RESEARCH PAPER

Investigation of Activation Time on Pore Size Distribution of Activated Carbon Determined with Different Methods

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Abstract

Three activated carbons are synthesized in a rotary reactor at different activation times. The adsorption isotherms of the samples are measured The pore size distribution of the samples is determined using combined Saito and Foley method, BJH method. An average potential function has been determined inside the cylindrical pores. The effect of activation time on the pore size distribution samples was investigated. In the micropore size range, as the reaction started, the SF method show the initial micropore was generated. As the activation reaction progress, the micropore volume is developed and widened and therefore area under the PSD curve is increased. Improving the reaction, the pore overlapping was carried out and this occurrence causes decreasing in micropore volume. In the mesopore size range, mesopore volume is increased as the reaction progress. It is acceptable because both developing and overlapping of pores causes improvement of mesopore (and macropore) volume.

1. Introduction

Pore size distribution (PSD) is a main factor of porous material in adsorption capacity which is used in several systems such as heterogeneous catalysts, mass transfer in porous materials, separation processes, removal of various pollutants, gas storage and physical adsorption. There were several methods to calculate the PSD, more works was done on activated carbon adsorption and desorption of N_2 at constant temperature of 77 K [1]. It is difficult to compare one adsorption isotherm with another one, but determination of the deviation of isotherm from the representative comparison plots are the t and α plots

[2]. A method is derived by Horvath and Kawazoe 1983 to determine the micropore size distribution from standard data is called comparison plot. The (HK) in linear get important information about the adsorption phenomena. The plot constructed with the aid of the information of experimental isotherm data the average potential energy for a slit shape pore. Later, Saito and Foley (SF) extended this method for cylindrical pores [3]. Barret-Joyer-Halenda (BJH) in 1951 proposed a method for calculated PSD in mesopore range basis on Kelvin equation [2]. In this paper the PSD factor of activated carbon synthesized at different time was determined using two methods and the effect of activation time on the PSD of the product was studied.

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Nomenclature

A_a constant in Lennard–Jones (J molecule^{-1})

A_A constant in Lennard–Jones (J molecule^{-1})

A_p area of each pore

d arithmetic mean of diameters of adsorbate and

k Avogadro's number (molecule mol^{-1})

L distance between nuclei of two layers (nm)

Na number of atoms per unit area of adsorbent (atom cm^{-2})

N_A number of molecules per unit area of adsorbate (molecule cm^{-2})

P Pressure (pa)

P_0 saturation pressure of N_2 (Pa)

r_k Kelvin radius (nm)

r_p pore radius(nm)

R gas constant (J mol^{-1} K^{-1})

t adsorbed layer thickness (nm)

T Temperature (K)

V_p Pore volume

ΔV is the observed volume of gas desorbed

Δt change in thickness

Greek Symbols

α_k parameter (—)

β_k parameter (—)

μ (W.m^{-1}.K^{-1})

σ distance between a gas atom and the nuclei of the surface at zero interaction energy (nm)

π two-dimensional pressure (N m-1)

2. Modeling study

2.1 BJH method:

The Kelvin equation provides the relationship between the pore radius and the amount of adsorption at a relative pressure. Many researchers developed a method for the calculation of the pore size distribution on the basis of the Kelvin equation with a correction term for the thickness of the multilayer adsorbed film. This method have been widely used for such calculations [2,4].

$$r_p = r_k + t \tag{1}$$

$$V_{pn} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} C_j A_{p_j} \tag{2}$$

In these equations, all parameters are functions of relative pressure (p/p$_0$), defined in the literature [4]. Therefore in any relative pressure, the pore size and pore volume as a point of pore size distribution can be calculated.

The pore size (r_p) is defined as a distance between walls of the pore rather than the distance between centers of atoms, which form first layers of the opposite pore walls.
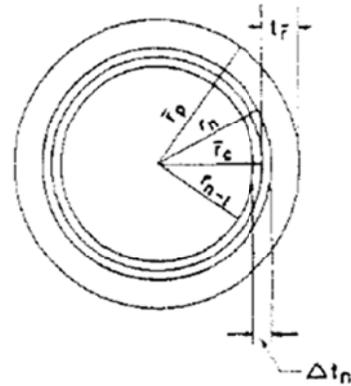

Fig. 1. Relation of VΔt to r$_p$ at n$_{th}$ step [4].

2.2 Horvath–Kawazoe method:

In the HK method, the interaction energy between molecules of adsorbate and adsorbent in a slit shape pore is considered using Lennard-Jones potential. This relation and adsorption isotherm data is used to determination of effective pore size [5]. The potential energy is shown in the figure 2.

Following equations is presented to obtain PSD basis on the HK method [6]:

$$RT \ln\left(\frac{p}{p_0}\right) = K \frac{N_a * A_a + N_A * A_A}{\sigma^4 (L-d)} *$$

$$\left[\frac{\sigma^4}{3\left(L-\frac{d}{2}\right)^3} - \frac{\sigma^4}{3\left(\frac{d}{2}\right)^3} - \frac{\sigma^{10}}{9\left(L-\frac{d}{2}\right)^9} + \frac{\sigma^{10}}{9\left(\frac{d}{2}\right)^9} \right] \tag{3}$$
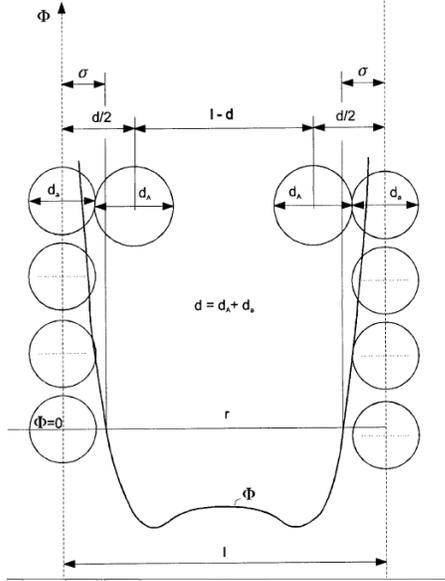
Fig. 2. Potential function in a slit-like pore [7]

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Note that increasing in the adsorption pressure causes increase in the effective pore width, but the HK method has a high accuracy in the micropore size range and not in mesosize range [4].

Later, Jaroniec et al. [8] developed an equivalent procedure based on the adsorption potential (A) distribution which is used in this study. In this procedure, with assumption of the condensation approximation, the pore volume distribution $J(r_p) = dV/dr_p$ can be related to the adsorption potential distribution through the following equation:

$$J(r_p) \equiv \frac{dV}{dr_p} = \left(\frac{dV}{dA}\right)\left(\frac{dA}{dr_p}\right) \qquad (4)$$

The adsorption potential is equal to the change in the Gibbs free energy of adsorption with the minus sign of $A = -\Delta G = RT\ln(p_0/p)$. This relation with equation 3 are used to determination second term of equation (4). The first term in equation (4) can be calculated from the isotherm data of adsorption.

As Saito and Foley theory developed the cylindrical pore shape of the HK method. The cylindrical shape of pore is shown in the figure 3 [7].

In the SF method, the cylindrical potential is line averaged. Calculation of PSD by this average potential is the same of HK method. Therefore, the following equation can be presented for the SF method.
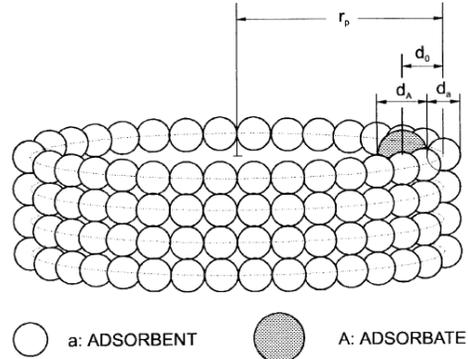

Fig. 3. Explanation of Saito–Foley model [7].

$$\ln\left(\frac{p}{p_0}\right) =$$
$$\frac{3}{4}\frac{\pi k}{RT}\frac{(N_a * A_a + N_A * A_A)}{d_0^4} \sum_{k=0}^{\infty}\left[\frac{1}{2k+1}\left(1 - \right.\right.$$
$$\left.\left.\frac{d_0}{r_p}\right)^{2k}\left\{\frac{21}{32}\alpha_k\left(\frac{d_0}{r_p}\right)^{10} - \beta_k\left(\frac{d_0}{r_p}\right)^4\right\}\right] \qquad (5)$$

3. Experimental study

The selected coal sample is a bituminous coal from Goltoot mine which is located in the Kerman province in Iran. The proximate analysis of the as-received coal sample is shown in Table 1. The proximate analysis was carried out with LECO instrument model MAC-400 and sulfur analysis with LECO instrument model SE-32. The coal with particle size 0.35-0.7 mm was selected as raw material. Washing in heavy media is used for ash washing of the coal samples with the final ash content about 8%. The low ash coal is used as raw material for the experiments. The process of pre-oxidation, charring and activation of the coal samples carried out in a rotary kiln reactor. The reactor was a quartz glass tube with a 25 mm diameter and 100 mm length heating zone. The charring step of the samples as heating of oxidized coal at 410 oC in the nitrogen flow stream during for 1 hr are good enough to yield a char without softening and swelling at high operating condition of the activation process. Pore development during activation within carbon matrix of char is the most important step for char activation. By these experiments, the effects activation time on porous structure of activated carbon are studied. The adsorption isotherm was measured by nitrogen adsorption at 77 K with Autosorb AP-1 apparatus (Quantachrome Corp.) [9].

Table 1
Proximate analysis of as-received coal sample

Volatile matter	Fixed carbon	Free moisture	Ash	Total sulfur
%16	%25	%2.5	%56.5	%1

4. Result and discussion:

Activation of the char sample was carried out at 920°C at different activation times. The isotherm data of the three synthesized samples were shown in Figure.4.
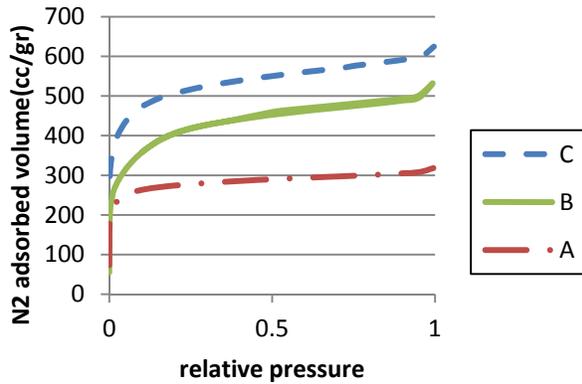

Fig. 4. adsorption isotherms of activated carbons produced by steam activation at resident time (A) 3.5 hr, (B) 5.5 hr and (C) 7.5 hr

The PSD data of the samples is determined by programming code in Matlab software using the isotherm data and the equations of BJH and SF methods. The results are shown in Figures 5 and 6. As it shown in the section 3 and the figures, the BJH and SF methods are covered the mesopore and micropore size respectively.

In the micropore size range, as shown in the figure 5, the SF method show different behavior of activation progress. In 3.5 hr activation time, the initial micropore was generated. As the activation reaction progress to 5.5, the micropore volume is developed and widened and therefore area under the PSD curve is increased. Improving the reaction to 7.5 hr, the pore overlapping was carried out and this occurrence causes decreasing in micropore volume.

In the mesopore size range as shown in the figure 6, mesopore volume is increased as the reaction progress. It is acceptable because both developing and overlapping of pores causes improvement of mesopore (and macropore) volume.
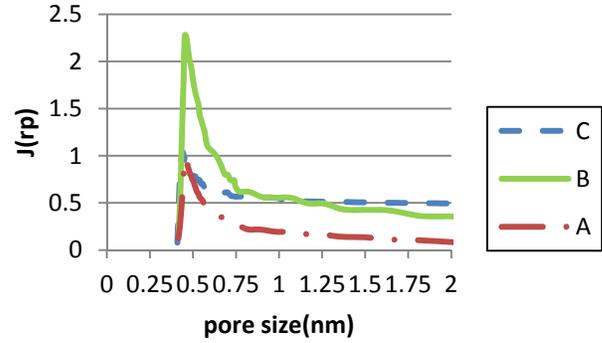

Fig. 5. SF pore size distributions of activated carbons produced by steam activation at resident time (A) 3.5 hr, (B) 5.5 hr and (C) 7.5 hr
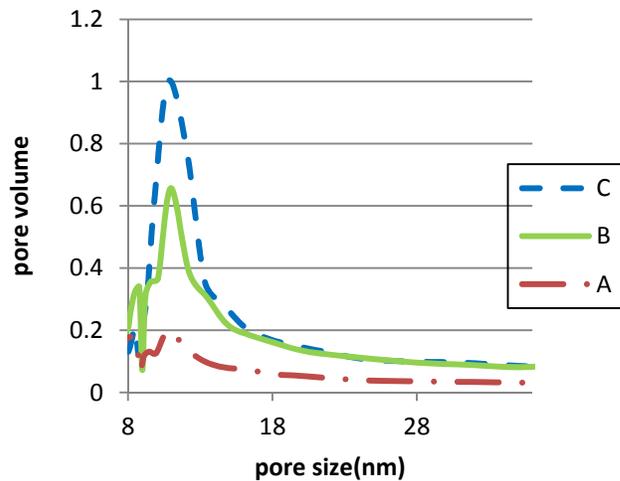

Fig. 6. BJH pore size distributions of activated carbons produced by steam activation at resident time (A) 3.5 hr, (B) 5.5 hr and (C) 7.5 hr

5. Conclusions

The activated carbons synthesized in different activation time show different PSD calculated using SF, and BJH methods. Improvement in activation time causes different changes in the micro and meso pore size range. These methods introduce different mechanism of pore size changes (pore developing, widening and overlapping) within the porous solid phase.

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