Research Article

Pore Size Distribution Analysis of Coal-Based Activated Carbons: Investigating the Effects of Activating Agent and Chemical Ratio

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The present study attempts to investigate the effects of different chemical agents and chemical ratios on pore structure of coal-based activated carbons. The adsorption isotherm data of two series of activated carbons prepared from bituminous coal by chemical activation with potassium hydroxide and zinc chloride were used. Four well-known models of Dubinin-Stoeckli, Stoeckli, Horvath-Kawazoe, and improved Horvath-Kawazoe were applied for the characterization of these porous solids. Although the results showed some differences among the models that arise from their fundamental assumptions, in general they are found to be comparable. Results showed that samples activated by ZnCl 2 provide higher-adsorption capacity than those from KOH. In each series, it was shown that the pore volume increases with increasing impregnation ratio, ranging from 50% to 200%. Activated carbons obtained at low chemical ratio in ZnCl 2 series (up to 100%) showed microporous structure, while those with higher ratios became predominantly mesoporous. In the KOH series, increasing KOH created more micropores in the carbon structure in the whole range of studied chemical ratio.

1. Introduction

Activated carbon (AC) is among the important carbon based materials that find widespread use in almost every industrial field. They are employed in different applications such as purification, recovery, decolorization, deodorization, separation, catalyst, catalytic support, and gas storage due to the large internal surface area and specific pore structure. On this basis, activated carbon adsorption is of interest to many economic sectors and areas such as chemical, food, pharmaceutical, automobile, petroleum, petrochemical, and gas industries [1–4].

Coals have become the main precursor for the production of activated carbons because of their inherent microstructure and surface chemical properties [5]. Low cost of production and unlimited resources as well as specific beneficial properties, such as well-developed internal pore structure and high surface area, high mechanical and chemical resistance, ease of degradation, and good ion-exchange properties are main reasons for increasing interest in the use of activated carbons obtained from coals [6–8]. Furthermore, coal products are in greater demand since they have greater density and corrosion endurance than other carbons [9, 10].

Important parameters that greatly affect the adsorption performance of a porous carbonaceous adsorbent are porosity and pore structure. Consequently, the determination of pore size distribution (PSD) of coal-based adsorbents is of particular interest. For this purpose, various methods have been proposed to study the structure of porous adsorbents [11–41].

A direct but cumbersome experimental technique for the determination of PSD is to measure the saturated amount of adsorbed probe molecules which have different dimensions. However, there is uncertainty about this method because of networking effects of some adsorbents including activated
isotherms and PSD of porous solids. However, the proposed methodology needs further improvement to provide high-accuracy predictions besides mass of computations that is needed.

There is also a different approach based on a single adsorption isotherm. Here, total adsorption amount which is simply a summation of the adsorbed molecules on various adsorption sites is equal to an integral of the local adsorption on particular sites multiplied by a PSD function, integrated over all sizes:

$$\theta(P) = \int_0^\infty \theta(L, P) f(L) dL,$$

where $\theta(L, P)$ is the local adsorption isotherm (kernel) evaluated at bulk pressure $P$ and local pore size $(L)$, and $F(L)$ denotes the PSD of the heterogeneous solid adsorbent. Solving for the PSD function is an ill-posed problem unless the form of function is defined. Various models by assuming different kernels (Langmuir, Freundlich, BET, DR, DA, Sips, Toth, Unilan, Jovanovich, Fowler and Harkins,…) and mathematical functions (Gaussian, Gamma,…) for PSD have been presented. For instance, the Dubinin-Stoeckli (DS) and Stoeckli models which have been proposed based on the Dubinin theory of volume filling of micropores (TVFM) implement gaussian and gamma type of mathematical function, respectively [35, 36]. The advantage of these models is that they are experimentally convenient and do not need complicated PSD calculations.

In 1998, Bhatia [37] successfully applied the combination of finite element collocation technique with regularization method to extract various double peak PSDs from synthetic isotherm data points contaminated with 1% normally distributed random errors using DR isotherm. They applied the constraint of nonnegativity of solutions by simply utilizing a Newton-Raphson technique. Although they reported that “the method is stable over a wide range of values of the regularization parameter,” the application of nonnegativity constraint usually provides unrealistic solutions [38].

Sun [39] proposed a new method based on the modification of DR equation by introducing adsorption density and correlating between the pore filling pressure and critical pore size for nitrogen adsorption at 77 K. The results are found comparable with other popular PSD methods such as MP, JC, HK, and DFT. In addition to uncertainty about the general performance of this model as a result of some assumptions in the model derivation, it is relatively complicated and the procedure for obtaining PSD is cumbersome.

The average diameter of the mesopores is usually calculated from the nitrogen adsorption data using Kelvin equation [40]. Recently, Shahsavand and Shahrak [38, 41] proposed two new methods for reliable extraction of PSD from adsorption and condensation branch of isotherms. According to their results, it seems that these two methods have also some limitation similar to the other previous ones. The regularization technique that used for obtaining optimum value of regularization parameter is challengeable in these methods. In addition, the basis of these methods is
Kelvin equation which unlikely provides reliable PSD for microporous solids.

Although much has been done to address the PSD of porous adsorbents, up to now, no general reliable theory is available leading to the conclusion that for microporous carbons the extensive investigation should still continue.

In the present study, we have tried as a novel work to extend the analysis on PSD of porous adsorbents by investigating the effects of different chemical agent and chemical ratios for two series of chemically coal-based activated carbons using KOH and ZnCl₂. Two well-known models based on Dubinin’s TVFM, namely, Dubinin-Stoeckli (DS) and Stoeckli models were used to investigate the effects of these two chemical agents and impregnation ratio on the porosity of AC samples, and the results were compared with the two widely used methods of Horvath-Kawazoe (HK) and improved Horvath-Kawazoe (IHK) for the determination of PSD of microporous solids. The first two models were derived based on benzene as a reference adsorbate, because it provides more accurate estimations than other adsorbates. On this basis, adsorption isotherm data of benzene at 30°C were used to determine the PSD of each sample. Finally, comparison of the PSD results from each model is also made for KOH and ZnCl₂-activated carbon series.

2. Methods

Finding a reliable, accurate, and flexible method for the determination of PSD of porous adsorbents still remains an important concern in the area of characterization of porous materials. Although a large number of researches have been done in this area, some constraints such as type of adsorbate, adsorbent characteristics, adsorption temperature, applicable range of pore size, and range of relative pressure limit the applicability of each model in all cases [42]. The lack of such method is tangible by rapid development of new porous materials and their wide applications in various fields. In the present study, the following three well-known models were used in order to obtain PSD for two series of chemically activated carbons and the results are compared.

2.1. Dubinin-Stoeckli (DS) Model. The adsorption of vapors by microporous carbons was described by the following fundamental equation of Dubinin-Astakhov (DA) [43–45]:

\[ W = W_0 \exp \left( - \left( \frac{A}{E} \right)^n \right). \]  

(2)

Here, \( W \) (mmol·g⁻¹) represents the amount adsorbed at relative pressure \( P/P_0 \), \( W_0 \) denotes the limiting amount of micropores filling, and \( A \) is the differential molar work of adsorption defined as \( A = RT \ln(P_0/P) \) at temperature of \( T \). One may write that \( E = \beta E_0 \), where \( \beta \) is the affinity coefficient depending on the adsorbative only, and it has been assumed that for benzene as a reference \( \beta = 1 \).

In general case of heterogeneous microporous adsorbents, the adsorption is described by the Dubinin-Stoeckli (DS) adsorption equation of [35, 46]:

\[ W = \frac{W_0}{2\sqrt{1+2m\delta^2/A^2}} \exp \left( - \frac{m\chi A^2}{1+2m\delta^2/A^2} \right) \times \left[ 1 + \text{erf} \left( \frac{x_0}{\delta\sqrt{2/(1+2m\delta^2/A^2)}} \right) \right]. \]  

(3)

Which implies a normal half-width (\( x \)) distribution of micropore volume for the slit-like pores as:

\[ \frac{dW}{dx} = \frac{W_0}{\delta\sqrt{2\pi}} \exp \left( - \frac{(x-x_0)^2}{2\delta^2} \right), \]  

(4)

where, \( x_0 \) is the half-width of a slit shaped micropore which corresponds to the maximum of the distribution curve, and \( \delta \) is the variance. The letter \( m \) is a constant coefficient for a given vapor:

\[ m = \left( \frac{1}{\beta K} \right)^2. \]  

(5)

For benzene as the reference vapor, the constant \( K \) equals to 12 KJ·nm·mole⁻¹. Using (3) to fit the experimental data, three parameters of \( W_0, x_0 \) and \( \delta \), can be extracted. Knowing these parameters, the micropore size distribution in terms of volume can be calculated from (4).

2.2. Stoeckli Model. Another approach for the determination of PSD of porous adsorbents which is also based on the Dubinin’s TVFM is Stoeckli method [36]. It had been shown by Stoeckli et al. [36, 47] that for the ideal slit-shaped microporous materials, a good estimate of the adsorption isotherm can be obtained by:

\[ W = W_0 \left[ \frac{a}{a + (A/\beta K_0)^\nu} \right]^2 \]  

(6)

The \( a \) and \( \nu \) are constant parameters that are related to the mean and width of the distribution, respectively, \( K_0 \) is calculated using (7). This is applicable over a range of pore size from 0.4 to 2.0 nm [48].

\[ K_0 = \frac{10.8E_0}{(E_0 - 11.4 \text{ KJ mol}^{-1})}. \]  

(7)

After obtaining the model parameters using (6), pore size distribution can be determined using the following gamma type distribution of the mean pore width (\( L = 2x \)):

\[ \frac{dW}{dL} = \frac{3W_0a^\nu L^{3\nu-1} \exp(-aL^\nu)}{\Gamma(\nu)}. \]  

(8)

2.3. Horvath-Kawazoe (HK) Method. Horvath and Kawazoe [15] developed a rather simple means of characterizing the pore structure of porous materials. This model provides a simple, one-to-one correspondence between the pore size
and relative arguments at which the pore is filled. Using thermodynamic arguments and applying the potential obtained by Everett and Powl [49], Horvath and Kawazoe derived the following expression:

$$RT \ln \left( \frac{P}{P_0} \right) = N_{AV} \frac{N_a A_d + N_A A_A}{\delta^4 (L - 2d_0)} \times \left[ \frac{\delta^4}{3(L - d_0)^3} - \frac{\delta^{10}}{9(L - d_0)^7} - \frac{\delta^4}{3d_0^3} + \frac{\delta^{10}}{9d_0^6} \right],$$  \hfill (9)

where \( L \) represents the micropore width \( (L = 2\delta) \), \( N_{AV} \) denotes Avogadro’s number, and \( R \) and \( T \) are gas constant and temperature, respectively. \( A_d \) and \( A_A \) are dispersion constant characterizing adsorbate-adsorbent and adsorbate-adsorbate interactions, \( N_a \) and \( N_A \) are the number of atoms per unit area of adsorbent and the number of molecules per unit area of adsorbate, \( d_0 \) is the arithmetic mean of the adsorbate molecular diameter and the adsorbent atomic diameter, and \( \delta \) is the distance between a gas molecule and an adsorbent atom at zero interaction energy at relative pressure of \( P/P_0 \).

From the amount adsorbed at relative pressure of \( P/P_0 \), (9) yields the corresponding slit-pore width, \( L \). Thus, a plot of adsorbed volume versus \( L \) is a cumulative pore-volume curve, the slopes of which give the differential PSD.

2.4. Improved Horvath-Kawazoe (IHK) Method. The HK equation is widely used for calculating the micropore size distribution (MPSD) from a single adsorption isotherm measured at subcritical temperature (e.g., \( N_2 \) at 77 K). In the HK model, the ideal Henry’s law (or linear behavior) is assumed for the isotherm.

Cheng and Yang (1994) modified the HK formulation by assuming the nonlinearity of the isotherm equation. This has improved the HK model significantly with the advantage of maintaining the PSD calculation simple [23]. The nonlinearity assumption also results in sharpening PSD [11]. Considering the mentioned nonlinearity correction, Cheng and Yang (1995) derived the improved HK equation (IHK) for three different pore geometries. For the slit-shaped pores, the IHK equation is derived as [11]

$$RT \ln \left( \frac{P}{P_0} \right) + \left[ RT - \frac{RT}{\theta} \ln \frac{1}{1 - \theta} \right] = N_{AV} \frac{N_a A_d + N_A A_A}{\delta^4 (L - 2d_0)} \times \left[ \frac{\delta^4}{3(L - d_0)^3} - \frac{\delta^{10}}{9(L - d_0)^7} - \frac{\delta^4}{3d_0^3} + \frac{\delta^{10}}{9d_0^6} \right].$$  \hfill (10)

The influence of this term and thus \( \theta \) depends on \( P/P_0 \) where the adsorption occurs and also the shape of the isotherm. In the initial part of the adsorption isotherm, where \( \theta \) is small and \( \theta \)-dependent term (second term in LHS of IHK equation) approaches zero, the IHK model approaches HK. By increasing \( \theta \), the pore filling term \( RT - (RT/\theta) \ln[1/(1 - \theta)] \) becomes more negative. In the meantime, as the relative pressure is increased, the free energy term \( RT \ln(P/P_0) \) increases [11]. The increase in free energy term is partly offset by the pore filling term. So, the LHS of the IHK equation is increased at a slower rate as compared with the original HK equation. Consequently, the calculated pore size is increased at a slower rate, resulting in sharpening the pore size distribution [11]. In the present study, \( \theta \) has been calculated from the following DR equation.

$$\theta = \frac{C_A}{C_{in}} = \exp \left[ -\frac{1}{(\beta E_0)^2} \left( R_T \ln \frac{P}{P_0} \right)^2 \right].$$  \hfill (11)

3. Experimental

A bituminous coal with medium ash content was used as a precursor for the preparation of chemically activated carbons with KOH and \( ZnCl_2 \). The influence of different chemical natures, a strong base (KOH) and a Lewis acid (\( ZnCl_2 \)), on the structure of the prepared activated carbons were investigated. The characteristics of precursor and detailed experimental procedure were described in our previous work [10]. In brief, 10 g of dried coal (212–250 \( \mu \)m) was well mixed with a concentrated solution of KOH or \( ZnCl_2 \) with the chemical ratio ranging from 50 to 200% (mass basis) for about 5 min, and then the resulting homogeneous slurry was dried at 110°C for 14 hrs. The resulting chemical loaded samples were heated (5°C/min) to the final carbonization temperature in nitrogen flow of 150 cm³/min. Samples were held at the final temperature for carbonization times of 1 hr, \( T = 500°C \) in \( ZnCl_2 \) series and \( T = 700°C \) in KOH series, before cooling down under nitrogen. The products were washed sequentially with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters, and then dried at 110°C. In all runs of chemical activation, heating rate and nitrogen flow were kept constant and nitrogen was passed through a copper turning bed at 480°C as well as a molecular sieve bed to remove the trace of oxygen and water content in the gases before entering the reactor.

After preparing samples, adsorption of benzene at 30°C and nitrogen at −196°C were performed to evaluate the adsorptive properties of the activated carbons. The benzene adsorption isotherms were determined in a conventional high accuracy volumetric adsorption rig and the nitrogen isotherms were obtained using Autosorb-1, Quantachrome.

4. Results and Discussion

Two series of activated carbons with different chemical ratios of 50, 75, 100 and 200 were prepared by chemical activation of a bituminous coal with potassium hydroxide and zinc chloride. Figure 1 shows benzene adsorption isotherms of the prepared samples with different chemical ratios at 30°C. Nitrogen isotherms of both carbon series at −196°C are also presented in Figure 2. The shape of adsorption isotherm can provide preliminary qualitative information about the adsorption mechanism as well as the pore structure of activated carbons. These isotherms clearly show that the KOH mainly created microporosity in the carbon samples for the whole range of chemical to coal ratio studied here.
Zinc chloride, on the other hand, produced a wide range of porosity and high ratio of this chemical changed the form of isotherm from type I to type II which is an indication of mesoporous carbon [42, 50, 51].

To clarify the differences between the mechanism of KOH and ZnCl₂ on pore evolution, mesopore volumes and pore half-width of the carbons have been plotted versus chemical ratio in Figure 3. The mesopore volumes are calculated by subtracting the micropore volumes (deduced from the DR equation) from the amount adsorbed at \( P/P_0 = 0.95 \) of N₂ isotherm at 77 K and pore half-widths are obtained using DS equation. This figure shows that the high ratio of ZnCl₂ increases mesoporosity in the resulting carbon, while KOH creates more micropore and the mesopore contribution in this series is almost constant.

The pore width and pore volume were increased steadily and samples became mesoporous with increasing ZnCl₂ ratio, while mesopores volumes are almost constant in the case of KOH. It is evident from Figure 3 that ZnCl₂ is not only responsible for the development of new micropores, but also for the enlargement of existing micropores to mesopores, while in the case of KOH activation, the micropore creation still plays an important role in the entire range of chemical ratio studied here.

As discussed elsewhere [10, 52], in carbonization of bituminous coals with ZnCl₂, by increasing chemical ratio the mechanism of pore evolution is changed and the dependence of pore evolution on the chemical ratio can be divided into three different zones. In the first zone with \( R < 50\% \), microporosity creation is predominant which is

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**Figure 1**: Benzene isotherms at 30°C on the prepared samples with different chemical ratio: (a) samples activated with KOH, (b) samples activated with ZnCl₂.

**Figure 2**: Nitrogen isotherms at −196°C on the prepared samples with different chemical ratio: (a) samples activated with KOH, (b) samples activated with ZnCl₂.
reflected by the sharp rise in the micropore volume versus chemical ratio. For the range of $50% < R < 100%$ there is competition between the microporosity creation and the widening of microporosity into the range of mesoporosity (Figure 3). Benzene and nitrogen isotherms of these carbons with chemical ratio less than 100% show that the resulting carbons are mainly microporous (Figures 1 and 2). In the third zone where the chemical ratio is greater than 100%, larger widening of porosity, mainly in mesopore range, increases the pore volume to some extent. In the case of KOH, the mechanism of pore creation is different [10]. Here, micropore and mesopore contribution that is almost constant and chemical to precursor ratio does not seem to have significant effect on the average pore size (Figure 3).

Undoubtedly, pore size distribution is one of the most important aspects for characterization of structural heterogeneity of porous materials employed in industrial application. Based on the results of benzene adsorption isotherms, the PSD of prepared samples chemically activated with KOH and ZnCl$_2$ at different chemical ratios were calculated using four well-known models, and the results are presented in Figures 4 and 5, respectively. In these figures, a comparison can also be made among different models in characterizing the AC porous structures.

By fitting the experimental adsorption isotherms to the DS and Stoeckli models, the parameters were obtained using a nonlinear optimization technique and presented in Table 1. Parameters of the HK and IHK models for benzene adsorption were taken from Terzyk and Gauden [53].

With regard to the values presented in Table 1, the DS model shows higher limits for micropore filling than that of Stoeckli model. Also, increasing the chemical ratio enhanced the adsorption limit of the prepared ACs. It is obvious that chemical ratio plays an important role on the pore structure of chemically activated carbons.

Pore size distribution of the prepared samples chemically activated by KOH obtained from DS, Stoeckli, HK and IHK models is presented in Figure 4. As expected from benzene and N$_2$ adsorption isotherms (Figures 1(a) and 2(a)), all samples in the KOH series showed microporous structure. Moreover, by increasing impregnation ratio the pore volumes were also increased. However, there is a difference between the PSDs calculated using DS, Stoeckli, HK and IHK models which are related to their fundamental assumptions on describing the porous structure and/or mechanism of adsorption.

The PSDs calculated from the Stoeckli model shift slightly to larger pore diameters in comparison to the DS model but with a similar trend. Furthermore, one can notice that the method proposed by Horvath-Kawazoe shows slightly lower pore diameters in comparison to the DS results (Figure 3). As mentioned above, the fundamental assumptions of each model are responsible for the differences in the results. Although DS and Stoeckli models are both based on the TVFM, implementing different mathematical functions and local isotherms, as mentioned before, causes the differences. The idealization of the micropore filling process of HK method in addition to completely different approach for characterizing porous solids is the main reasons for differences among the PSDs predicted by HK and IHK methods compared to those of DS and Stoeckli models. However, the differences are not so significant, and the results are comparable. Malformed predicted PSDs by HK and IHK methods are due to lack of experimental data especially in low range of
relative pressure. Although the HK and IHK methods showed some different pore volumes, they provided similar mean pore size predictions for all the investigated adsorbents.

The PSD of samples activated with ZnCl₂ is depicted in Figure 5. As it can be clearly seen in the figure, ZnCl₂ provides larger pores than KOH, which leads to pore widening and mesoporous structure at higher chemical ratio. Similar to the results of KOH activated samples, the DS model indicates larger pore diameters in comparison with the Stoeckli model and HK and IHK methods.

As seen in Figure 5, with increasing the chemical to coal ratio (up to 100%) in the ZnCl₂ series, the micropores are widened with a very fast rate, and further increase of ZnCl₂ changes the micropores to mesopores. However, this behaviour is not seen in the results of Stoeckli model (Figure 5(b)). This model is recommended for characterization of microporous materials, and it does not provide good PSD estimation of mesoporous solids [42, 47].

In general, the comparison of the data of two activated carbon series (Figures 1 to 5) revealed that, at the same chemical ratio, samples activated by ZnCl₂ have more adsorption capacity than those from KOH.

5. Conclusions

Activated carbons were prepared from bituminous coal by KOH and ZnCl₂ chemical activation at different chemical ratios. From Benzene and nitrogen adsorption data, the KOH series showed similar behavior to type I isotherms in the whole range of chemical to precursor ratio studied here, while activated carbons in the ZnCl₂ series illustrated the combination of types I and II isotherms. Pore characteristics of the prepared porous samples in terms of PSD were determined using four well-known models of DS, Stoeckli, HK, and IHK. The effect of different chemical activating agents and ratio of chemical to coal precursor on PSD of the
Figure 5: Pore size distribution of chemically activated carbons with ZnCl$_2$ calculated using: (a) Dubinin-Stoeckli (DS) model, (b) Stoeckli model, and (c) Horvath-Kawazoe (HK) method and (d) Improved Horvath-Kawazoe (IHK) method.

Table 1: DS and Stoeckli model parameters for the prepared AC samples.

<table>
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<th>Impregnation ratio</th>
<th>DS model parameters</th>
<th>Stoeckli model parameters</th>
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<tr>
<td></td>
<td>$W_0$ (mmol·g$^{-1}$)</td>
<td>$x_0$ (nm)</td>
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<td>KOH activated samples</td>
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<td></td>
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prepared samples were also investigated. Increasing impregnation ratio increases the pore volume of activated samples, and ZnCl₂ resulted in ACs with more adsorption capacities than those of KOH. This increase for KOH chemical agent will create more micropores with insignificant variations of average pore size, while in the case of ZnCl₂ it creates wider pores, and after a specific impregnation ratio (100%) it begins to create mesopores in the carbonaceous structure.

References


