Pore Development of the Activated Carbon Prepared by Steam Activation Process

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(Received June 3, 1998; Accepted August 15, 1998)

Abstract: Activated carbon was prepared using bituminous coal by steam activation process in a laboratory scale rotary type furnace. The physical properties and porosity of the chars were investigated. The optimum conditions of manufacturing process of activated carbon were suggested by observing the development of pores during the activation process. Generally, the adsorption capacity of activated carbon decreased with increasing the activated carbon yield (AC yield). However, the adsorption capacity and the pore characteristics such as BET surface area or pore volume etc., showed a similar tendency. It was found that the maximum adsorption capacity and pore development were obtained from the activation process showing about 35~40% AC yield, which was strongly affected by raw materials and activation condition.

Keywords: activated carbon (AC), activation process, porosity, bet surface area, adsorption capacity, pore development.

1. Introduction

Commercially available activated carbons are prepared from some carbonaceous materials containing source materials such as coal, lignite, wood, coconut shell, petroleum and sometimes synthetic polymers. These materials are first pyrolyzed and carbonized. During this process, the volatile components and low molecular products of pyrolysis are removed, subsequently the residuals undergo the following activation process using oxidizing gas, such as steam or CO₂.

Activated carbon has being produced for a specific use through adjusting activation process using various raw materials. Even though the optimum conditions has been providing in production, yet it was difficult to describe the relationship among surface area, pore size distribution, carbonization and activation clearly. Some works have been performed concerning the change of pore structures during the activation process in recent. Watanabe [1] prepared, respectively, activated carbon from coal and phenol-formaldehyde resin in which reported the relation between the growth of pores and the activation conditions. Also, Kawahata and Walker [2] activated an anthracite coal with CO₂, using a laboratory scale fluidized-bed reactor and researched the pore characteristics such as pore surface area, pore volume, and pore size distribution.

In this work it was discussed that the optimum activation condition and pore characteristics of coal such as pore volume, pore size distribution, and surface area. Furthermore, the various factors which could ultimately specify the desirable pore volume and surface area were analyzed.

2. Activation Mechanism

2.1. Thermodynamic Background for Activation

Activated carbon is made through carbonization and activation process. During the carbonization pore
structure is developed and this structure leads to the development of porosity in the activation step using oxidizing gases, such as steam at higher temperature than 800 °C [3]. Among them, steam activated carbons are produced as follows, firstly the material is carbonized to an intermediate product, and in the next step the pore structure is enlarged. It is well known that the reaction of carbon with steam is thermodynamically endothermic [4] and the mechanism can be expressed as [5].

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{C}(\text{H}_2\text{O}) \]  
\[ \text{C}(\text{H}_2\text{O}) \rightarrow \text{H}_2 + \text{C}(\text{O}) \]  
\[ \text{C}(\text{O}) \rightarrow \text{CO} \]  
\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  

2.2. Correlation of Physical Properties

Generally a starting material of \( W_0 \) in weight decreases to \( W \) during activation. A burn-off (\( f \)) based on a mineral matter is defined as

\[ f = 1 - \frac{W}{W_0} \]  

The exterior of the sample particles is often eroded by gasification and abrasion of the particles in the reactor during the activation, which results in a decrease in particle radius from \( R_0 \) to \( R \). The decreasing ratio (\( R/R_0 \)) is calculated as [6]

\[ \frac{R}{R_0} = \left( \frac{1-f}{\rho/\rho_s} \right)^{1/3} \]  

where \( \rho_s \) and \( \rho \) are the particle densities before and after the activation, respectively. To estimate the optimum AC yield in practical applications, internal and external conversion are useful. The relative weight loss results from the change in the particle radius \( f_{out} \), which is defined as external burn-off, can be expressed as

\[ f_{out} = \frac{(R^3 - R_0^3)\rho_s}{R_0^3 \rho} = 1 - \frac{1-f}{\rho/\rho_s} \]  

On the other hand, the relative weight loss in the interior of the particle \( f_{in} \), which contributes to the formation and enlargement of pores, is expressed by subtracting \( f_{out} \) from \( f \) as

\[ f_{in} = f - f_{out} = (1-f) \left( \frac{\rho}{\rho_s} - 1 \right) \]  

This relative weight loss is here named as internal burn-off.

3. Experimental

3.1. Raw Material

The ultimate and proximate analysis of bituminous coal from Fushun are shown in Table 1. The shape of coal was noncaking and average size was under 1.65 mm in diameter. Their thermal behavior was observed with thermogravimetric analyzer.

<table>
<thead>
<tr>
<th>Coal</th>
<th>moisture [wt %]</th>
<th>ash [wt %]</th>
<th>volatile matter [wt %]</th>
<th>fixed carbon [wt %]</th>
<th>C [wt %]</th>
<th>H [wt %]</th>
<th>N [wt %]</th>
<th>S [wt %]</th>
<th>O [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fushun</td>
<td>4.17</td>
<td>6.11</td>
<td>42.0</td>
<td>47.72</td>
<td>73.82</td>
<td>5.34</td>
<td>1.34</td>
<td>0.5</td>
<td>12.89</td>
</tr>
</tbody>
</table>

3.2. Apparatus and Process Operation

The activation and carbonization of coal were carried out in a rotary kiln-type furnace. It was 7 and 160 cm in diameter and length respectively, and it was controlled to operating temperature by the PID (proportional integral derivative) type controlling electric heater. The schematic diagram for experimental apparatus was shown in Figure 1.

About 30 g of the raw coal was put into the sample container, which was maintained at a given temperature. The carbonization for the fresh coal samples was carried out under the nitrogen stream, with flow rate of 20 ml/min and heating rate of 3 °C/min.

![Figure 1. Rotary kiln type carbonization-activation reactor.](image-url)
The product was removed at any specialized time, as will be told later on, and cooled in a sand bath. The carbonization and activation were carried out under the following condition, that is, carbonization temperature was 700 °C and maintained for 60 minutes, activation temperature was varied from 800 to 950 °C, activation time for 240 minutes, the steam flow rate was in the range 0.75–3 g steam/g coal · hr, respectively [7].

3.3. Determination of Physical Properties and Adsorption Characteristics

To characterize the properties of the activated carbons at the several different burn-off the pore surface area, yield, iodine value and apparent density were measured experimentally. BET surface area analyzer [ASAP 2010, Micromeritics Co.], thermogravimetry analyzer [SDT 2960, TA Instrument], HPLC [Waters 600E, Waters Co.] and standard sieves were used for metering these properties. The AC yield and iodine value of prepared activated carbon were estimated with the method of KS-M 1802 [8].

The adsorption isotherm of benzene and methyl ethyl ketone (MEK) in aqueous solution were determined by batch experiments. To investigate the adsorption isotherms of them, granular activated carbon of 10–14 mesh having an apparent density of 0.42–0.48 g/ml from Fushun coal was used.

4. Results and Discussion

4.1. Pore Development and Operating Conditions

Coal based activated carbon was prepared in a rotary kiln type furnace and the optimum conditions of manufacturing process and the change in pore structure according to activation parameter were investigated. Steam was employed as the activation agent for this work. The major operating parameters for activated carbon were temperature, time, and amount of steam. Generally, the adsorption capacity of activated carbon increased with activation parameters, but AC yield decreased. The effect of the operating parameters are shown in Table 2.

The AC yield decreased with the activation temperature but the BET surface area increased in the range of 800 to 880 °C. And iodine value (I) and BET surface area are alike in trend. The maximum adsorption capacity was obtained at about 35–40% yield. Then, to analyze the burn-off the AC yield was defined as:

\[
\text{AC Yield} = \frac{W_p}{W_i} \times 100 \text{[%]}
\]

where \(W_p\) and \(W_i\) are the amount of product and feed after and before activation, respectively. The value of BET surface area was calculated with the modified technique of the BET procedure. To recommend the optimum condition of AC manufacturing process we have to consider both AC yield and adsorption capacity. Considering the experimental information for both factors, AC yield and adsorption capacity, 880–880 °C was suggested as the optimum activation temperature.

Figure 2 and 3 show the effect of heating rate (in the range of 2.3 to 4.7 °C/min) on Fushun coal’s AC yield and BET surface area. The data in this work were obtained from the activation temperature of 880 °C and steam amount of 1 g steam/g coal·hr. As the heating rate increased, AC yield, iodine value and BET surface area increased and reached a maximum value at the 2.9 °C/min, and then decreased over 2.9 °C/min. These trends were caused by the macropores developed above 2.9 °C/min and the pores of activated carbon blocked by ash below 2.9 °C/min.

Figure 4 and 5 show the development of pore and adsorption capacity with the activation. During the activation the relation between AC yield and adsorption capacity is as follows. The AC yield decreased and the development of pores increased with increasing steam amount, however BET surface area was decreased from 880 °C. Also, the pore volume increased with increasing BET surface area. This tendency is remarkable for the volatile matter and ash, because of blocking of the pore in the activation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating Rate</th>
<th>Temp. [°C]</th>
<th>AC Yield [％]</th>
<th>Iodine Value [mg/g]</th>
<th>BET Surface Area [m²/g]</th>
<th>(V_p) [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fushun Coal</td>
<td>2.9 °C/min</td>
<td>800</td>
<td>46.2</td>
<td>807</td>
<td>584</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>830</td>
<td>41.5</td>
<td>906</td>
<td>734</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>38.0</td>
<td>1047</td>
<td>1067</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>880</td>
<td>35.1</td>
<td>1069</td>
<td>1223</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>14.3</td>
<td>1154</td>
<td>1294</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>5.7</td>
<td>460</td>
<td>257</td>
<td>0.18</td>
</tr>
</tbody>
</table>

period. In the previous paper, the authors produced activated carbon from coal, and found that coal has the developed pores in the region of the micropore (near radius 10 Å) and mesopore in the region of radius 100–400 Å [9]. The pore size was dependent on how much it includes the volatile matter and ash of the carbonized materials. Consequently, it was found that pore size distribution and development of activated carbon were strongly affected by the raw materials.

Figure 6 shows the average pore size and BET surface area with the activation temperature. BET surface area was 1000 m²/g above and average pore size was developed near 20–30 Å at the activation temperature 850 °C over. It was found that pore distribution was changed from mesopore to micropore with activation temperature increasing. Figure 7 shows pore distribution curve of prepared activated carbon with activation temperature. In the range of 850–880 °C, the pore structure developed into micropore due to the opening of closed pore. However, in the lowest and highest activation temperature meso or macropore distribution was developed. This may suggest that the mesopore development was resulted from closed pore at the lowest activation temperature. Also, the surface area was decreased as the burn-off increased. These phenomena indicate that the coalescence of adjacent pores is more predominant than the formation of new pores.
Figure 6. Effect of activation temperature on average pore size and BET specific surface area.

Figure 7. Pore size distribution of activated carbon prepared with Fushun coal.

Figure 8. Pore development of activated carbon with activation temperature.
Table 3. Experimental Results of Internal and External Conversion

<table>
<thead>
<tr>
<th>f</th>
<th>ρ</th>
<th>ρ/ρ₀</th>
<th>f_in</th>
<th>f_out</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.96</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59</td>
<td>0.61</td>
<td>0.314</td>
<td>0.180</td>
</tr>
<tr>
<td>0.6</td>
<td>0.46</td>
<td>0.48</td>
<td>0.435</td>
<td>0.167</td>
</tr>
<tr>
<td>0.7</td>
<td>0.43</td>
<td>0.45</td>
<td>0.493</td>
<td>0.333</td>
</tr>
<tr>
<td>0.8</td>
<td>0.38</td>
<td>0.40</td>
<td>0.306</td>
<td>0.500</td>
</tr>
<tr>
<td>0.9</td>
<td>0.37</td>
<td>0.39</td>
<td>0.159</td>
<td>0.744</td>
</tr>
</tbody>
</table>

4.2. Internal and External Conversion

Table 3 shows f_in and f_out calculated by eq. 7 and 8, respectively. Generally, f_in shows a maximum value whereas f_out increases with the conversion ratio. This trend is due to the facts that steam diffusion into the inner pore causes to develop micropore then, the external conversion is more sensitive than internal conversion with temperature. To estimate the optimum AC yield in practical applications, eq. 7 and 8 are useful. The AC yield of 30~40% was obtained for Fushun coal.

4.3. Morphology with Activation Temperature

Pore distribution and shape of the activated carbon were observed by scanning electron microscopy (SEM). Figure 8 (a-d) are the SEM photography of activated carbon prepared at various activation temperatures (800~900 °C, 4 hrs, 1 g steam/g coal·hr), respectively. As shown in Figure 8 (b, c), the micropore (near radius 20 Å) was developed at 850~900 °C. On the other hand, when the activation temperature was high or low, they developed slightly not only in the region of micropore but in the region of mesopore. According to the above it was shown that the pore size distribution of activated carbon was greatly affected by activation temperature.

4.4. Liquid Adsorption Capacity

The various isotherms have been offered by many papers. Langmuir isotherm and Freundlich isotherm were applied to this work to test the adsorption capacity of AC prepared using Fushun coal. BET surface area was 1246.5 m²/g. Benzene and MEK were selected as adsorbates. 1000 ppm solution of them were adsorbed onto activated carbon at 5 °C, respectively, and Figure 9 and 10 show the effect of time. The adsorption for benzene and MEK took about 360 min and 180 min to reach equilibrium, respectively, at 80 cycle/min in stirring speed. The adsorption capacity of benzene and MEK was, respectively, 0.62 g/g and 0.18 g/g. Activated carbon is so hydrophobic that less water soluble material have a tendency to be adsorbed more, whereas more soluble material have a tendency to be adsorbed less. Consequently more water soluble MEK was adsorbed about three times comparing to benzene.

Figure 11 and 12 show comparisons of the two computed isotherms by eq. 10 and eq. 11 using the parameters obtained and the data measured.

\[ Q_e = \frac{ABC}{1 + BC} \]  

\[(10)\]

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isotherms seem to fit the measured data of adsorption of MEK equally well. The parameters obtained for adsorption isotherms are listed in Table 4. K and 1/n are characteristic constants. Generally, the value of K can be taken as a relative indicator of adsorption capacity, while 1/n is indicative of the energy or intensity of the reaction. We obtained 1/n which is acceptable to adsorption process in range of 0.1 ~ 0.5.

5. Conclusions

The feasibility of developing maximum pore volume and distribution in an activated carbon manufacturing process was investigated. During the activation process, the pore development was strongly affected by raw materials and activating condition, temperature and steam flow rate. The optimum pore development mechanism was proposed after testing the adsorption capacity. Consequently, it was found that the maximum adsorption capacity and pore development were obtained from the activation process in the range of about 35 ~ 40% activated carbon yield.

Nomenclature

\begin{align*}
A & : \text{Langmuir constant parameter [-]} \\
B & : \text{Langmuir constant parameter [-]} \\
C_{eq} & : \text{concentration of VOCs in equilibrium [mg/L]} \\
f & : \text{fractional gasification of char conversion [-]} \\
f_i & : \text{internal conversion [-]} \\
f_o & : \text{external conversion [-]} \\
K & : \text{Freundlich constant parameter [-]} \\
1/n & : \text{Freundlich constant parameter [-]} \\
Q_e & : \text{equilibrium adsorption capacity [mg VOCs/g adsorbent]} \\
R & : \text{residual particle radius [cm]} \\
R_0 & : \text{initial particle radius [cm]} \\
V_p & : \text{pore volume [cm}^3/\text{g]} \\
W & : \text{residual weight of fixed carbon in char sample [g]} \\
W_i & : \text{initial weight of fixed carbon in char sample [g]} \\
W_f & : \text{amount of feed before activation [g]} \\
W_p & : \text{amount of product after activation [g]}
\end{align*}

Greek letters

\begin{align*}
\rho & : \text{particle density of activated carbon [g/cm}^3] \\
\rho_o & : \text{particle density of char [g/cm}^3]
\end{align*}

Acknowledgement

The financial support from DKU Research Foundation...
dation of Dankook University is greatly appreciated.

References