Effect of Temperature on the Surface Area Change and Formation of Crystal Structures During Activated Carbon Production from Fir (Abies bornmulleriana) Wood

Billur Sakintuna\textsuperscript{1} Sevil Çetinkaya\textsuperscript{2}, Zeki Aktaş\textsuperscript{3}, and Yuda Yürüm\textsuperscript{1}

\textsuperscript{1}Faculty of Engineering and Natural Sciences, Sabancı University, Tuzla, Istanbul 34956, Turkey
\textsuperscript{2}Department of Chemistry, Hacettepe University, Beytepe, Ankara 06532, Turkey
\textsuperscript{3}Department of Chemical Engineering, Ankara University, Tandoğan, Ankara 06100, Turkey
Introduction

- The physical and chemical characteristics of activated carbons make them interesting materials for use in many industrial processes.

- They are prepared by carbonization and activation of natural carbonaceous materials.

- The sorbent characteristics of activated carbons are related to their high surface area and pore volume and their particular pore size distribution.
Chemical and physical activation:

Physical activation: thermal treatment in an inert environment and activation of the resulting char by steam or CO$_2$. 
The turbostratic structure of carbon was suggested by Warren in 1934. Currently used X-ray diffraction techniques for the measurement of graphene sheet size and turbostratic crystallite thickness were developed by Warren in 1941.

The most widely accepted model of the structure of “turbostratic” carbon the atoms are arranged in layers but stacked randomly instead of the order ABABA... Sequence of graphite and interlayer spacings also occur randomly.

Warren BE. X-ray diffraction in random layer lattices. Phys Rev 1941;59(9):693–8
Experimental Procedure

Materials: Bark-free Fir (Abies bornmulleriana) wood dust (from Bolu forests (northwest Anatolia) in Turkey) ground and sieved to below 175 µm (~80 mesh) size.

Carbonization: Samples dried at 100°C with ultra high pure nitrogen. Heated at 700, 800, 900 and 1000 °C, 10 °C/min, under N₂ flow (100 ml/min).

Activation: Carbonized sample at 700 °C activated under CO₂ flow (100 ml/min).
Analysis

Surface Analysis : Quantachrome NOVA 2200 Series volumetric gas adsorption instrument
(Relative pressure range : 0.05 – 0.3)

X-Ray Diffraction : Bruker axs Advance powder diffractometer, Siemens X-ray gun, Cu Kα, Bruker axs Diffrac PLUS software
(0.3° step angle, 7s step time, 2θ = 10°-90 °, generator: 40kV at 40mA)

FTIR Analysis : Bruker EQUINOX 55 FT-IR spectrometer, KBr pellets, 200 scans at a resolution 2 cm⁻¹
# Proximate and Ultimate Analysis of Fir Wood Sample

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>%, (as received)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatiles</td>
<td>85.5</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>10.5</td>
</tr>
<tr>
<td>Ash</td>
<td>0.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>3.7</td>
</tr>
<tr>
<td>Ultimate Analysis</td>
<td>%, daf</td>
</tr>
<tr>
<td>C</td>
<td>47.2</td>
</tr>
<tr>
<td>H</td>
<td>6.1</td>
</tr>
<tr>
<td>N</td>
<td>0.3</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>46.7</td>
</tr>
</tbody>
</table>
# BET Surface Area of Carbonized Samples and Activated Sample

<table>
<thead>
<tr>
<th>Sample no</th>
<th>BET surface area m²/g</th>
<th>t-method external surface area, m²/g</th>
<th>t-method micro pore surface area, m²/g</th>
<th>BJH method cumulative desorption pore volume, cc/g</th>
<th>t-method micro pore volume cc/g</th>
<th>BJH method desorption pore diameter, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(700 °C)</td>
<td>432.8</td>
<td>197.1</td>
<td>235.7</td>
<td>0.1667</td>
<td>0.1121</td>
<td>34.93</td>
</tr>
<tr>
<td>(800 °C)</td>
<td>484.1</td>
<td>110.3</td>
<td>373.7</td>
<td>0.1047</td>
<td>0.1947</td>
<td>35.12</td>
</tr>
<tr>
<td>(900 °C)</td>
<td>451.3</td>
<td>95.90</td>
<td>355.4</td>
<td>0.0738</td>
<td>0.1838</td>
<td>39.51</td>
</tr>
<tr>
<td>(1000 °C)</td>
<td>609.1</td>
<td>125.4</td>
<td>483.7</td>
<td>0.1081</td>
<td>0.2485</td>
<td>39.49</td>
</tr>
<tr>
<td>(700 °C, activated carbon)</td>
<td>514.2</td>
<td>240.4</td>
<td>273.8</td>
<td>0.2357</td>
<td>0.1410</td>
<td>35.02</td>
</tr>
</tbody>
</table>
At first, the increase in heat treatment causes formation of smaller pores in solid particles and resulted in higher surface area. Combination of inaccessible smaller pores starts to create larger ones at further increase in temperatures.
Gas adsorption/desorption isotherms for the sample carbonized at 700°C

- Adsorption isotherms of N₂ at 77 K

- The shape of hysteresis may be related to the dominant pore shape in the mesoporous solid.
Gas adsorption/desorption isotherms for the sample carbonized at 800ºC
Gas adsorption/desorption isotherms for the sample carbonized at 900°C
In the nitrogen adsorption there is initially a very rapid uptake, followed by a slow approach to equilibrium, and so the most reasonable explanation for this behavior is that there is significant adsorption capacity and very little diffusion resistance within the mesoporous. The macropore surface equilibrates rapidly in the first instances. This is followed by slow diffusion into the micropores where most of adsorption occurs.
Gas adsorption/desorption isotherms for the sample activated at 700°C

- Activation with CO₂ increases the amount of N₂ adsorption, especially in the range of high relative pressures.
The samples have almost mesopores of which diameters are between 20-500 Å.

FTIR spectra of the Wooddust

- **Aliphatic C-H stretching**: 2822 cm⁻¹
- **OH Groups**: 3429 cm⁻¹
- **Uranic acid and acetyl groups**: 1743 cm⁻¹
- **Aromatic C-H**: 1461 cm⁻¹
- **β-pyranose ring**: 883 cm⁻¹
FTIR spectra of Carbonized Samples

- O-H stretching
- \(-\text{CH}_3, \text{CH}_2-\)
- C=O stretching
- ketones, aldehydes, lactones or carboxyl groups.
- C–O stretching

900 °C
800 °C
700 °C
1000 °C
1039 cm\(^{-1}\)
1559 cm\(^{-1}\)
1826 cm\(^{-1}\)
2854 cm\(^{-1}\)
2921 cm\(^{-1}\)
3417 cm\(^{-1}\)
FTIR spectra of the Activated sample at 700 °C

- O-H stretching
- \( \text{CH}_3, \text{CH}_2 \) stretching
- C=O stretching
- C–O stretching
XRD of the Carbonized samples

Shterenberg L. and Bogdanova S., Inorg Mater, v15, p 632, 1979
McCready D., Powder Diff., v9, p 93, 1994
XRD of the Carbonized samples, 3D

1000 °C

700 °C
XRD of the Activated sample at 700 °C
**FWHM, \( L_a \) and \( L_c \) Calculations**

- The position of the interplanar spacing \( d_{002} \) obtained by direct application of Bragg’s law.

\[
\begin{align*}
L_c &= 0.90 \lambda / \beta \cos \theta_{002} \\
L_a &= 1.94 \lambda / \beta \cos \theta_{10} \\
n &= L_c/d
\end{align*}
\]

\( \beta \): Full Width Half Maxima, FWHM (in radians of \( \theta \))

\( n \): # of graphene sheets

For the dimension of turbostratic crystallites perpendicular to the graphene sheets, \( L_c \) data is used and const. equals 0.9. For the dimension in graphene sheet planes, \( L_a \) data is used and const. equals 1.94.
$d_{002}$ spacing is app. 0.38.

Carbonization Temperature had no significant effect on the size of particles, $L_a$ of graphene sheets
Effect of Carbonization Temperature on $L_a$

$L_a$ values increased with $T_{\text{carb}}$

$L_a$ growth effect would cause a lower FWHM.
- Carbon atoms in one layer interact with carbon atoms in adjacent layers by means of dispersion interactions
- \( N \) and BET surface area were almost inversely proportional.

Effect of Carbonization and Activation on $L_c$ and $N$ at 700 °C

- $L_c$ and Number of layers were increased upon activation.

<table>
<thead>
<tr>
<th>$L_c$ (nm)</th>
<th>$N$ (av. Number of layers per stack)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
</tr>
</tbody>
</table>

![Graph showing the increase of $L_c$ and $N$ upon activation](image-url)
Conclusions

- Heat treatment markedly affected \( N_2 \) adsorption characteristics of the samples. However, the general shape of the isotherms stayed at the same.

- Inaccessible smaller pores starts to create larger ones at further increase in temperatures.

- BET surface areas were increased with increasing carbonization temperature and with activation.

- As expected from the adsorption isotherms, the pore volume and average pore diameter generally increase upon activation.

- The samples have almost mesopores of which diameters are between 20-500 Å.

- FTIR spectra of the wooddust and carbonized samples indicated the loss of functional groups during pyrolysis reactions.
Conclusions (Con’t)

- In XRD, peaks which are belongs to C60, carbon fullerite C60, C70 and mainly C was observed.

- Crystalline structures were changed with carbonization temperature. Upon activation crystalline structures were destroyed.

- $L_c$ and $N$, number of graphene sheets, had no significant change, whereas $L_a$ was increased with increasing carbonization temperature.

- $L_c$ and $N$ and $N_2$ adsorption were increased upon activation process. The porous of molecular sieve materials are usually considered to be slits between two carbon layer planes.
THANK YOU