THERMAL TREATMENT OF ACTIVE CARBONS:
A COMPARISON BETWEEN MICROWAVE AND ELECTRICAL HEATING

J. A. Menéndez, E M. Menéndez, A. García, J. B. Parra and J. J. Pls

Two commercial activated carbons were subjected to thermal treatment in a N₂ atmosphere using a microwave multimode resonant cavity and a conventional electric tube furnace as heat sources. The temperature of the carbon bed during the microwave treatment was monitored using an infrared pyrometer and an Inconel shielded type-K thermocouple. A comparison between both methods of measuring temperature was made. When similar treatment temperatures are used, both techniques produce similar changes in the textual and chemical properties of the activated carbons. However, microwave treatment is much less time-consuming than conventional heating. Microwave treatment in an inert environment seems to be an efficient and attractive way of removing oxygenated functionalities from carbon surfaces and of increasing the hydrophobicity and basicity of carbons.

Key Words: Activated carbon, Surface oxygen complexes

Industry requires activated carbons which have not only optimum physical properties (e.g., surface area, porosity, pore size distribution, hardness, etc.) but also specific chemical properties. Thermal treatment in different gaseous environments is useful for eliminating oxygen functionalities from the carbon surface and thus obtaining carbons with a low oxygen content, basic properties [Menéndez, et al, 1996; Menéndez, et al, 1997; León y León, et al, 1992], a highly hydrophobic character and resistance to aging [Boehm and Voll, 1970; Bansal et al, 1971]. Generally speaking, these thermal treatment must be carried out at relatively high temperatures (> 800°C) while flowing an inert or reducing gas (e.g. N₂, H₂) over a suitable carbon precursor.

In this work thermal treatment on activated carbons was carried out in an atmosphere of N₂ using both an electrical tube furnace and a multimode resonant microwave cavity. The main difference between conventional methods of heating and microwave heating is the way in which heat is generated. In the conventional approaches, the heat source is located outside the carbon bed, and the bed is heated by conduction and/or convection. A temperature gradient is established in the material until conditions of steady state are reached. In the microwave method, microwaves supply energy to the carbon particles. This energy is converted by dipole rotation and ionic conduction into heat inside the particles themselves.

Microwaves are used in various technological and scientific fields in order to heat dielectric materials [Zlotorzyński, 1995]. Yet, in the particular case of carbon materials, there are relatively few publications that describe the use of microwaves for producing (Troll, 1991; Norman and Cha, 1996) and regenerating [Haque, et al, 1991; Holland, 1994; Kong and Cha, 1996; Bradshaw, et al, 1997; Price and Schmidt, 1997] activated carbons. The main advantage of using microwave heating is that treatment time can be considerably reduced. This means that the consumption of inert gas can also be reduced. An additional advantage is that microwave furnaces are, in general, smaller than conventional furnaces.

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The aim of this work was to study the potential of microwave-induced treatment for selectively removing oxygen-containing groups from the carbon surface in order to produce carbons with a low oxygen content (i.e., more hydrophobic carbons). A more specific goal was to establish a procedure which would make it possible to measure the temperature inside the carbon bed as well as the changes produced in this temperature during microwave treatment.

**Experimental**

Two commercial activated carbons, BPL (5.71 wt% ash content) and Norit c (0.54 wt% ash content), were used as starting materials (named as BPL and Ne respectively). Sub-samples (ca. 3-4 g) of these two carbons were placed in a quartz reactor (20 mm i.d.), which in turn was placed either inside a multimode resonant microwave cavity or in an electrical tube furnace. Treatments in the electrical furnace were carried out by heating the carbon samples at a rate of 25°C/min to a temperature of 950°C, and maintaining this temperature for 3 h. An inert atmosphere was maintained during treatment and cool-down intervals by passing a N₂ flow of 100 mL/min through the sample bed. Microwave treatment consisted in subjecting the samples to microwave action for 5 minutes. As in the case of the treatment carried out in the electrical furnace a 100 mL/min flow of N₂ was flushed through the sample bed in order to ensure an inert atmosphere. The resultant samples were labeled sample-ef or sample-mw respectively. The input power of the microwave equipment was set at 1000 watts and the microwave frequency used was 2450 MHz. The most common microwave frequency used in Europe is 2450 MHz ± 2% due to restrictions imposed by international laws to avoid disturbances in telecommunications.

A diagram of the multimode resonant microwave cavity employed in this work is shown in Figure 1. Basically, it consists of a commercial microwave oven, which was adapted for this particular use. This arrangement is not a very efficient way (from the point of view of energy consumption) of carrying out the treatment, because the volume of the sample loaded is too small given the relatively large volume of the oven cavity. The use of a single mode resonant microwave cavity or much larger amounts of sample would increase the efficiency of the treatment [Zlotorzynski, 1995]. Nevertheless, the results obtained with this apparatus could serve as a good indication of the possibilities offered by the use of microwaves in this kind of treatment, since the changes observed in the surface chemistry of the carbons could be expected to resemble quite closely those that a more efficient device might produce.

After these thermal treatments carbon surfaces are very reactive due to the presence of unsaturated carbon atoms at the edges of the basal planes [Menéndez et al. 1996; Menéndez et al., 1997] leading to a relatively quick re-oxidation (i.e., formation of new oxygen-containing surface groups) during the first few days. After this period, samples reach a stable degree of oxidation upon atmospheric exposure [Menéndez et al., 1996; Menéndez et al., 1997]. In order to give the carbon samples sufficient aging time, the resulting carbons were exposed for two weeks to the atmosphere before their characterization was carried out.

Specific surface areas were determined in an ASAP 2020 volumetric system (Micromeritics) by physical adsorption measurements with N₂ at 77 K. The surface areas were obtained from N₂ adsorption data using the BET equation. The t-plot method [Lippens and de Boer, 1953] was used to estimate the micropore and mesopore volume of the samples. T-plot have been constructed using a very low area active carbon as a reference [Sellés-Pérez and Martín-Martínez, 1991]. Elemental analysis of all the samples was carried out in a LECO CHNS-932 analyser coupled to a LECO VTF-900, which makes it possible to determine the oxygen content directly. The point of zero charge ($pH_{pzc}$) of each sample was determined using a modified version of a simple method proposed by Noh and Schwarz [1990].
FIGURE 2: Relation between the temperature measured directly and through the microwave window with the optical pyrometer.

referred to as reverse mass titration [Menéndez, et al., 1996]. slurries of 10 wt% were prepared by mixing particles of carbon (< 0.3 mm) with an appropriate amount of distilled water in a bottle sealed under N₂. The pH of the slurry was measured after shaking for 24 h. Some distilled water was subsequently added, and the previous procedure was repeated for slurries of 8, 6, 4, 2 and 1 wt%. A plot of the equilibrium pH vs. solid weight fraction, yields a curve and the pH equilibrium at the plateau of the curve corresponds to the pH_{eqc}. The assumption that the pH_{eqc} can be taken as being equivalent to the pH_{eqc} of the carbon has recently been confirmed by Wang and Lu [1998].

Results and discussion

Temperature measurement during microwave treatment

The temperature reached in the carbon bed depends on the nature of the carbon (dielectric properties) as well as on the microwave power applied to the sample. For a given carbon, the temperature can, in principle, be maintained by adjusting the input power. In the present work, a constant input power of 1000 watts was used in all the experiments. Under these conditions active carbons became incandescent (exhibiting a bright-red color) approximately one minute after commencement of the treatment, and remained incandescent for the entire period of treatment.

Direct measurement of the carbon bed temperature during the microwave treatment presents certain difficulties which are related with the electromagnetic field. In relation with the use of thermocouples there are reports [Liu, et al., 1994; Roussy, et al., 1995] that a thermocouple introduced normal to the direction of the electromagnetic field does not influence the electromagnetic field distribution. However, other researchers [Chen, et al., 1995], have concluded that the effect of interference from the electromagnetic field on metallic thermocouples makes them unsuitable for use in a microwave heated reactor. In the present work, two different thermocouples, a ceramic sheltered type-S thermocouple and a Inconel sheltered type-K thermocouple (2 mm thick), were tested. Blank experiments, i.e. where only the thermocouple is placed inside the microwave cavity, showed that the ceramic thermocouple absorbs microwave radiation. As a consequence of this absorption the temperature registered after a few minutes was > 1000°C. This kind of thermocouple was, in consequence, discarded. The blank experiment with the type-K thermocouple showed that the temperature registered after 5 minutes was ca. 100°C. Taking these results and the above considerations into account we used the type-K thermocouple along with an optical pyrometer (Minolta/Land, Cyclops 52) to determine the temperature of the carbon samples during microwave treatment.

The use of the optical pyrometer also presented some technical difficulties, since any window built into the microwave cavity has to be protected with a < 2 mm grid in order to prevent microwave release to the outside. Such a window would not be completely transparent and therefore some of radiation released by the incandescent carbon would be adsorbed by the window (see Figure 1). In order to overcome this problem, different known temperatures of irradiated bales were measured through the same window of the microwave cavity. By using this ‘calibration procedure’ it was possible to establish a correlation between the temperature measured directly by the optical pyrometer and that measured through the microwave window (see Figure 2). Application of this correlation to the temperature measured by the optical pyrometer through the microwave window provides quite a good estimation of the temperature of the carbon bed during microwave treatment.
FIGURE 3: Variation in the temperature of the samples with time during microwave treatment. $T_{PR}$: Temperature measured with the pyrometer. $T_{TC}$: Temperature measured with the thermocouple.

Another point of discussion is the homogeneity of the temperature in the carbon bed during treatment. A study of the heating uniformity in a multimode microwave cavity was carried out by Bradshaw et al. [1997] and it was found that for a granular activated carbon bed, the field was concentrated at the top of the reactor. In addition, microwave treatment can be expected to 'heat' surface dipolar functional groups more readily than the carbon substrate itself. Moreover, local 'hot spots' may be generated inside the carbon particles as a consequence of mineral impurities. In the present work, we found that differences of temperature (measured with the optical pyrometer) between the top and the bottom of the carbon bed (ca. 50 mm height) were less than 10°C, at the average temperature of the treatment (ca. 950°C), the temperature, in fact, being slightly higher at the top of the carbon bed. Taking these variations into account, the optical pyrometer was focused on a zone located approximately half way up the carbon bed in all the experiments.

Although the treatment time of the carbon samples was about 5 minutes, in order to obtain a more accurate estimation of the variation of the temperature with treatment time, the temperature was monitored for 10 minutes during the preliminary tests. The variations in the temperature during the treatment time, for both activated carbons, are shown in Figure 3. As can be seen, in both cases the maximum treatment temperature obtained with the optical pyrometer (ca. 950 ±10°C for BPL, 940 ±10°C for Nc) was reached only about 1 minute after the commencement of the treatment. This temperature remained relatively constant for about 4 more minutes and then it underwent a decrease during the next 2 minutes to reach another temperature plateau to the minute 10. The temperature drop was more significant in the case of Nc than carbon BPL and this is thought to be due to changes in the dielectric properties of the carbon as a consequence of the thermal treatment. One objection to this method of measuring the temperature could be that the measured temperature is an average of that of the outer surface of the quartz tube and the carbon inside the tube [Perry, et al. 1997]. In addition, the temperature measured with the optical pyrometer is also that of the external part of the carbon bed, which is not necessarily the same as the temperature inside. So, in order to measure the temperature of the inner part of the carbon bed, the type-K thermocouple was inserted to a point near the center of the carbon bed. The variations in the temperature with time registered by this method are shown in Figure 3. In the case of carbon Nc, the thermocouple seems to show a quicker response to variations in the temperature than the optical pyrometer. Otherwise, the temperature curves follow a similar trend to those obtained with the pyrometer, i.e. a very rapid increase in temperature at the beginning, a more or less steady temperature zone and a slight decrease in temperature about five minutes after the commencement of the treatment. The most significant difference, however, is
that temperatures measured with the thermocouple are about 100°C higher than those measured with the optical pyrometer. With the present experiments it cannot be discerned if these discrepancies are due to an actual higher temperature inside the carbon bed or to a field concentration around the thermocouple, as reported by Janney and Kimrey [1992]. Blank experiments suggest that this difference of 100°C may not be real and so the difference in temperatures between the inner and external part of the carbon bed might be less than 100°C (i.e. more homogeneous). In subsequent experiments (5 min treatment) the thermocouple was removed from the carbon bed. In these experiments, it was found that the variation in temperatures with the treatment time recorded by the optical pyrometer (not shown) is almost identical to that recorded when the thermocouple was present (Figure 3). This suggests that the presence of the thermocouple does not affect, at least, to any significant degree, the temperature of the carbon bed.

Modification of carbon surface chemistry by thermal treatments

Table 1 shows the main textural properties of the as-received and treated carbons. In the case of the BPL sample, neither the thermal treatment carried out in the electrical furnace nor the treatment carried out with microwaves seems to produce any important modification in the textural properties. Both treatments give rise to a small increase in the BET surface area and mesopore volume. This is probably due to a ‘cleaning’ of the pore entrances through the elimination of certain oxygen-containing groups. Very different, however, is the case of sample Nc. Here, thermal treatments seem to cause a partial collapse of the porous structure of the carbon, which gives rise to a relatively important decrease in the BET surface area, micropore and mesopore volume. However, both treatments seem to affect the changes in the porous texture in a similar way, the changes produced by the microwaves being less pronounced than those produced by treatment in the electrical furnace.

As stated above, our main concern was to reduce the oxygen content of the carbon samples and so the amount of oxygen-containing groups. This, in turn, would increase the hydrophobicity of the activated carbons [Müller et al., 1996; Bradley and Rand, 1993]. The results of the chemical analysis and the pH correspond-

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m²/g)</th>
<th>Micropore volume (mm³/g)</th>
<th>Mesopore volume (mm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPL</td>
<td>1080</td>
<td>475</td>
<td>50</td>
</tr>
<tr>
<td>BPL-MW</td>
<td>1110</td>
<td>472</td>
<td>50</td>
</tr>
<tr>
<td>BPL-ef</td>
<td>1142</td>
<td>494</td>
<td>59</td>
</tr>
<tr>
<td>Nc</td>
<td>1224</td>
<td>621</td>
<td>161</td>
</tr>
<tr>
<td>Nc-mw</td>
<td>1111</td>
<td>543</td>
<td>90</td>
</tr>
<tr>
<td>Nc-ef</td>
<td>1122</td>
<td>543</td>
<td>90</td>
</tr>
</tbody>
</table>

(1) Calculated from N₂ adsorption, isotherm data at 77 K.

(2) Calculated using the t-plot method.

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**Table 2:** Chemical characterization of the as received (BPL, Nc) and treated carbons.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%O</th>
<th>%S</th>
<th>pH&lt;sub&gt;irp&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPL</td>
<td>95.2</td>
<td>0.4</td>
<td>0.6</td>
<td>2.9</td>
<td>0.9</td>
<td>7.1</td>
</tr>
<tr>
<td>BPL-mw</td>
<td>97.0</td>
<td>0.3</td>
<td>0.6</td>
<td>1.2</td>
<td>0.9</td>
<td>9.3</td>
</tr>
<tr>
<td>BPL-ef</td>
<td>95.6</td>
<td>0.3</td>
<td>0.6</td>
<td>2.5</td>
<td>0.9</td>
<td>8.9</td>
</tr>
<tr>
<td>Nc</td>
<td>82.1</td>
<td>2.7</td>
<td>0.2</td>
<td>15.0</td>
<td>0.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Nc-mw</td>
<td>94.0</td>
<td>0.7</td>
<td>0.2</td>
<td>5.2</td>
<td>0.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Nc-ef</td>
<td>93.9</td>
<td>0.7</td>
<td>0.2</td>
<td>5.1</td>
<td>0.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

*Weight % by elemental analysis (dry, ash-free normalized to a 100% basis).

ing to the point of zero charge (pH<sub>irp</sub>) are shown in Table 2. Both types of thermal treatment are effective not only in eliminating oxygen functionalities from the carbon surface, but also in keeping the oxygen content to a lower level than in the untreated samples even after two weeks of aging in the laboratory atmosphere (see above). The reduction in oxygen content is more significant in the case of the Nc sample. However, since in the Nc sample there are no important differences between the effect of the type of furnace used, in the case of sample BPL microwave treatment seems to be more effective in reducing the oxygen content. Finally, this reduction in oxygen content also gives rise to an increase in the pH<sub>irp</sub> of the treated samples which suggests the elimination by thermal treatment of some of the oxygen-containing surface groups that have an acidic nature (i.e. carboxyl, lactone and phenol groups).

**Conclusions**

Both electric and microwave heating in an inert atmosphere of carbon samples produce similar changes in textural and chemical properties. The main advantage of using microwaves is that the treatment can be performed in a relatively short period of time, which means a lower consumption of inert gas and energy. The combination of thermocouple and optical pyrometer permits the estimation of the temperature of the carbon during microwave treatment. Temperature variation with time indicated a very rapid initial heating rate and also showed that the temperature in the carbon bed remains relatively constant at its highest value for about 4 out of the 5 minutes of microwave treatment. Microwave treatment in an inert environment seems to be an efficient way of removing oxygenated functionalities from carbon surfaces and of obtaining materials with specific properties. Depending on the characteristics of the carbon sample, microwave-induced treatment can remove most of the oxygen-containing surface groups in a matter of minutes.

**References**


