Developing a new carbonization process using high pressure and temperature to treat medical and municipality wastes for coal production

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ABSTRACT

A new process of carbonization was used to carbonize different waste such as expired drugs, wood, fruits, and polymer of β-cyclodextrin. The carbonization process was performed at 400 °C and under pressure of 10 bars. The chars obtained were characterized and compared to the commercial activated charcoal. Mercury porosimetry and nitrogen adsorption were used to characterize the specific surface and porosities of the chars obtained by the carbonization of the four products. The surface area is lower for the fruit (S BET = 13 m²/g) than for the drugs, wood and polymer samples (S BET = 285, 150, 40 m²/g respectively). The char obtained from expired drugs represent a relatively large surface area without any treatment, traditionally followed to prepare activated charcoal. The different samples have similar macropore diameters with mean values between 30 and 40 µm. The specific surface of the expired drug coal was relatively important and triggered a curiosity to develop the characterization studies of this type of coal.

Key words: Carbonization, organic solid waste, high pressure and temperature, high specific surface, zero waste.

Introduction

Activated carbons are widely used as adsorbents in both gas-phase and liquid-phase separation processes and can be produced from various carbonaceous materials, for instance, coal, coconut shell, wood, and polymer scrap (Demirbas, 2006). It has been reported that activated carbons can also be obtained from municipal and industrial wastes such as PET waste (Hernandez-Ramirez and Holmes, 2008) and refuse derived fuel (Nagano et al., 2000). Waste tires represent another interesting source for activated carbons because of its high carbon content. As the production of activated carbon from waste tires changes hard-to-dispose waste to pollution-cleaning adsorbents, it is thought to be a very effective method to relieve environmental pollution. The pyrolysis of tires in an inert atmosphere at 450-900°C has been studied by many researchers, and the effects of pyrolysis conditions on the product yields (gases, oils and char) have been reported (Leung et al., 2002; Zabaniotou and Stavropoulos, 2003; Barbooti et al., 2004). As the BET surface areas of chars obtained through the pyrolysis of waste tires are extremely low (30–90 m²/g), several attempts have been made to increase their surface areas by activation (Ariyadejwanich et al., 2003; Yuan et al., 2004). The influence of operating conditions on the porous properties of the obtained activated carbons has also been investigated (Manocha, 2003). Several researchers studied dye adsorption on activated carbon (Lin 1993; Jumasiah et al., 2005; Mohammed et al., 2007; Malarvizhiet al. 2010) and pointed out that the presence of mesopores together with micropores in the activated carbon granules and fibers, enhance their adsorption capacities, especially against the large adsorbates (Cazorla-Amoroset al., 1996; Tamaiet al., 1999; Hsieh and Teng 2000; Hu et al., 2001). Therefore, several methods for the preparation of mesoporous activated carbons have been developed. For instance, through the catalytic reaction (Lebodaet al., 1998; Liu et al., 1999; Hu and Srinivasan 2001), the pre-treatment of precursor chars followed by steam activation (Tamon et al., 1999), and the chemical activation (Lebodaet al., 1998; Liu et al., 1999).

The technique of preparation of activated carbon requires costly physical and chemical processes. The traditional mechanisms for producing the activated carbon can be achieved by physical reactivation and chemical activation. Prior to carbonization, the raw material is impregnated with certain chemicals. The aim of the present work is to evaluate the chars obtained by a simple carbonization using a home-made reactor based on the heating of the materials (400°C) at a high pressure (10 bars of air) and a heat catalytic diffuser.
The new technique produces coal from organic waste and also create new sources of energies.

Materials and Methods

2.1. Raw materials to be carbonized:

Several types of organic solids have been tried with the idea of treating these compounds as organic solid waste. The raw materials tested are: expired drugs, wood, fruits and polymer of β-cyclodextrin.

2.2. Apparatus:

2.2.1. Reactor:

The apparatus used for the carbonization is a home-made machine. The main elements of the apparatus are: 1. cylindrical stainless steel reactor, 2. Electrical heating system (2000 W), 3. high pressure compressor and 4. heat diffuse catalytic.

2.2.2. Flash EA 1112 elemental analyzer:

The elemental analyzer is equipped with two combustion columns, one for the analysis of the carbon, nitrogen, hydrogen and sulfur under high oxygen conditions, while the other column is set up for the oxygen analysis in an oxygen-free environment. All of the samples were weighed into either tin or aluminum cups for CHNS analysis or into silver cups for oxygen analysis. This was done on a Mettler Toledo balance that can weigh down into the microgram range and reads directly via a computer. Several standards are available to run samples against.

2.3. Determination of surface area and pore distribution:

Two methods were used to characterize the surface area and the pore distribution of the carbonized materials as follows:

2.3.1. Nitrogen adsorption-desorption:

The surface area, pore dimensions and volumes of the carbonized samples were determined by nitrogen physisorption measurements. Nitrogen adsorption-desorption isotherms were obtained at 77 K, over a wide relative pressure range from 0.01 to 0.999, with a volumetric adsorption analyzer TRISTAR 3000 manufactured by Micromeritics. The samples were degassed under vacuum for several hours at 120 °C before nitrogen adsorption measurements. The micropore volume and the external area were calculated by the t-plot approach (Brunauer et al., 1938). The mesopore diameter and the mesopore size distribution were determined by the BJH (Barret, Joyner, and Halenda) method (Barret et al., 1951). The corresponding BJH pore size distributions was derived from the desorption branch. Although it is well-known that this method gives an underestimated pore size and that some new methods have been developed (Jaroniec et al., 1998), we used it here for the sake of simplicity, and this mathematical algorithm does not significantly affect the results as it is a systematic comparison.

2.3.2. Mercury porosimetry:

Mercury porosimetry was performed on the carbonized samples to characterize pores larger than 5 nm in diameter by using the Washburn equation. Here, a contact angle of 130° was assumed in the pore size calculations. A Micromeritics PoreSizer 9320 measured the Hg porosimetry data. All samples were dried overnight at 120 °C before weight and Hg porosimetry measurements. Mercury porosimetry measures both inter-particular and intra-particular pores. It has shown to be a reliable method to characterize pore size distributions and pore structure.

Results and Discussion

3.1. Carbonization of the raw material:

About a 100 g of the raw materials was transferred into the reactor. After setting the temperature at 400 °C and pressure at 10 bars, the samples were kept under these conditions, for about 20 min. As shown in Figure 1.
The shape of the coal obtained from expired drugs is a black powder without any smell. Elemental analysis of coal shows that the product contains more than 98% of carbon. Table 1 provides a detailed description of the elemental analysis.

Table 1: Elemental analysis of charcoal obtained after carbonization of different solid waste.

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>%N</th>
<th>%C</th>
<th>%H</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Expired drug</td>
<td>0</td>
<td>98.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>wood</td>
<td>0</td>
<td>99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Fruits</td>
<td>0.5</td>
<td>96</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>β-cyclodextrin polymer</td>
<td>0</td>
<td>98.2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3.2. Effect of the temperature on the yield formation of coal:

Under the pressure of 10 bars and temperatures ranging from 150 ºC to 400 ºC, the same mass of expired drug is subjected to carbonization. The elemental analysis was performed by using a Thermo Flash EA 1112. The carbonization time was fixed at 20 minutes. The mass of carbon obtained in each sample was plotted in function of the temperature. It has been observed that when the temperature reaches 400 ºC, the carbonization becomes 98%, as it is illustrated in Figure 2.

Fig. 2: The percentage of the carbon generated when setting the pressure to 10 bars and increasing the temperature from 150 ºC to 400 ºC.

3.3. Effect of the pressure on the yield formation of coal:

Temperature carbonization system was set at 450 ºC, while the pressure ranges from 1 bar to 10 bars. For each pressure value, the mass of carbon obtained as well as the ash were determined using elemental analysis already described. The evolution of the state of carbonization shows that from 5 bars, the raw material is completely transformed into coal, while ash cannot be observed. It is important to note that under the pressure of 1 bar, materials were burned and the ash was only the final product. Figure 3 shows the evolution of the carbonization function of pressure change.
3.4. Characterization of coal obtained by carbonization at 450 °C and 10 bars:

3.4.1. Nitrogen porosimetry:

Figure 4 shows the nitrogen adsorption-desorption isotherms of four coals prepared from drug, wood, fruit and polymer. The specific surface area $S_{BET}$ and the constant $C_{BET}$ determined from the nitrogen adsorption data (from the BET method) are listed in Table 2.

<table>
<thead>
<tr>
<th>Carbonized samples from</th>
<th>BET surface area $S_{BET}$ (m$^2$/g)</th>
<th>$C_{BET}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drug</td>
<td>286</td>
<td>12341</td>
</tr>
<tr>
<td>Wood</td>
<td>148</td>
<td>79</td>
</tr>
<tr>
<td>Fruit</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>Polymer</td>
<td>40</td>
<td>149</td>
</tr>
</tbody>
</table>

The isotherms are significantly affected by the nature of the raw materials. The nitrogen porosimetry experiments performed on the samples produce different isotherms which can be mainly classified in three groups according to the IUPAC classification (Sing et al., 1985).

For drug (Fig. 4a) and wood (Fig. 4b) carbonized samples, it was noticed that both adsorption-desorption isotherms almost have no hysteresis loop and exhibit “Type I” isotherm. The reversible Type I isotherm is concave to the $p/p_0$ axis and the volume adsorbed approaches a limit value as $p/p^o$ is close to 1. Type I isotherms are given by microporous solids having relatively small external surfaces, the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area. The two adsorption isotherms demonstrate the normal shape for activated carbons with extensive microporosity and limited mesoporosity (Kercher and Nagle, 2003). The upper limit of 2.0 nm in diameter (D) for the micropore width was put forward as part of the IUPAC classification of pore size. In addition, the shapes of the two isotherms are quite similar, as a result of analogous kind of porosities in the two activated carbons. A high adsorbed amount of nitrogen is observed at approximately $p/p_0 = 0.2$, which is a result of the filling of the micropores due to the capillary condensation. However, the extent of porosity (micropore volume, Table 2), as well as the pore size distribution, vary between the two samples thus providing evidence of the important effect of the initial nature of the carbonized sample on the properties of the activated products. The larger nitrogen uptake during the physisorption on drug sample compared to that obtained with wood indicates that it possesses a larger degree of microporosity. The high value of the constant $C_{BET}$ for the drug sample, namely $C_{BET} > 200$, is also attributed to the micropore filling during the monolayer-multilayer formation. In addition, the lack of hysteresis loop in the adsorption-desorption isotherms shows the absence of mesoporosity. The BET surface areas of the carbonized samples are also given in Table 1. The surface area is naturally larger for drug activated carbon ($S_{BET} = 285$ m$^2$/g) than for the wood carbonized sample ($S_{BET} = 150$ m$^2$/g).

The nitrogen adsorption-desorption isotherm obtained from a carbonized sample from fruit displays a different behavior (Fig. 4c).
Fig. 4: Adsorption-desorption isotherms of carbonized samples from (a) drug, (b) wood, (c) fruits and (d) polymer. The inset in (d) shows the zoom of the adsorption-desorption isotherm of carbonized sample from polymer for relative pressures $p/p_0$ ranging from 0.6 to 1.

We can observe a Type II isotherm, according to the IUPAC classification. The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent (D > 50 nm). The Type II isotherm represents unrestricted monolayer-multilayer adsorption. The specific surface area is equal to 13 m$^2$/g. The lack of hysteresis loop in the adsorption-desorption isotherm confirms the absence of mesoporosity. The surface area is lower for the fruit ($S_{BET} = 13$ m$^2$/g) than for the drug and wood carbonized samples ($S_{BET} = 150-285$ m$^2$/g) due to absence of micro and mesoporosity.

Another trend is reported with polymer activated carbon. An intermediate between a Type IV and a Type II isotherm is obtained by nitrogen adsorption-desorption analysis (Fig. 4d). Characteristic feature of the Type IV isotherm is its hysteresis loop, which is associated with the capillary condensation taking place in the mesopores. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. The isotherm cannot be strictly classified as Type IV because the adsorption isotherm does not reach a plateau when the relative pressure approached unity. Neither does this adsorption isotherm correspond to Type II, because of the steep adsorption at high relative pressures. The isotherm has also a hysteresis. The hysteresis loop is fairly narrow with nearly vertical and parallel adsorption and desorption branches, but in this case the hysteresis loop does not finish in a plateau at high relative pressures. This fact prevents us from classifying this loop as Type H1, but the narrow loop and steep branch does not fit in with the rest of the IUPAC types. So this type has been named as Type H1 without plateau (Julve et al., 2011). The plateau of the hysteresis loop of Type H1 and H2 would indicate that the material has no pores in the macropore region and that the biggest pore size does not reach the upper limit of the mesopore region. In the present case, the hysteresis is associated with the capillary condensation of N$_2$ during filling and emptying of mesopores in the structure (Garcia-Garcia et al., 2003). For polymer that produces hysteresis loop Type H1 without plateau, it is likely that the pore size distribution continues in the macropore region, but the disappearance of the plateau, caused by the appearance of macropores, do not allow the bigger pore size to be followed by nitrogen porosimetry. The corresponding pore size distribution of the sample is displayed in Fig. 5.
The pore diameter distribution is quite broad in the range of pore diameters between 2 and 50 nm. The BJH desorption method confirms the presence of non-ordered mesopores. Nitrogen adsorption-desorption isotherm of polymer-waste-activated carbons indicates that they are mainly mesopores. Fig. 5 shows the consequences of applying the BJH method (which is suitable for the analysis of mesoporous materials) to a sample containing both meso and macropores. The existence of macropores distorts the pore size distribution obtained with the BJH method. The BJH method cannot detect macropores since they are not filled by capillary condensation. The appearance of macropores results in the absence of a plateau in the nitrogen adsorption curve and this causes a distortion of the pore size distribution calculated using BJH method. The specific surface area value is 40 m$^2$/g.

The relative increase of the surface area compared to fruit sample is mainly attributed to the presence of the mesopore. However, despite the mesoporosity, the surface area remains lower ($S_{\text{BET}} = 40$ m$^2$/g) than for the drugs and wood carbonized samples ($S_{\text{BET}} = 285-150$ m$^2$/g), due to the difference in pore size and density. The increase of the surface area for the later is mainly attributed to the large micropore volume.

Typically, any practical activated carbon should have a BET surface area of more than 500 m$^2$/g (Garcia-Garcia et al., 2003; Sricharoenchaikul et al., 2008). From the analysis above, it may be proposed that only activated carbon obtained from drug may be considered as potential functional activated carbon.

3.4.2. Mercury porosimetry:

Mercury porosimetry determines larger pores, which are not within the detection range of nitrogen adsorption. Due to different measurement ranges, pore volume values obtained with nitrogen adsorption and mercury porosimetry methods are in general not equal. Mercury porosimetry measures both inter-particular and intra-particular pores. Two representations of the mercury intrusion data are used to emphasize the different aspects of the pore size distributions. Fig. 6 shows the cumulative (Fig. 6a) and differential pore size distributions (Fig. 6b) of the four carbonized samples.

The experiments performed on the drug, fruit and wood samples produce intrusion curves with similar shape (Fig. 6a). This particular shape is characterized by one steep intrusion step that ends in a plateau at relatively low pore diameter (D < 10 µm). The pore diameter at which the plateau region is reached slightly depends on the activated carbon used. The corresponding differential pore size distribution of the 3 carbonized samples is compared in Fig. 6b. All the samples show the same trend. Each sample exhibits a broad peak centered at 30-40 µm. The different samples have similar macropore diameters with mean values between 30 and 40 µm depending on the initial composition of the activated carbon. We believe that these peaks arise from the inter-particle porosity induced by the aggregation of particles. It is well established that the size of the inter-particulate macropores between close packed spheres can be determined by mercury porosimetry (Smattet et al., 2008). The packing of these particles creates an interconnected network of inter-particle voids of different sizes. The macropores measured are the voids between powders particles. On the other hand, the samples exhibit no mesoporosity since the differential pore volumes (dV/dD) are equal to zero in the diameter range between 2 and 50 nm (i.e. 0.002 and 0.05 µm in the figure). This result is in accordance with the nitrogen adsorption-desorption analysis (Figs. 4 and 5). Note also that the nitrogen adsorption-desorption method determines smaller pores than does mercury porosimetry, so that the micropores observed in the nitrogen porosimetry cannot be detected with mercury porosimetry because they are not within the detection range of mercury porosimetry.
The shape and the evolution of the intrusion curve with the polymer activated carbon displays a different behavior (Fig 6a). The intrusion curve becomes less steep and does not reach a plateau at low pore size. The resulting pore size distribution is presented in Fig 6b. The sample exhibits a well defined broad peak centered at ca. 5 µm. This peak corresponds mainly to inter-particle intrusion and is attributed to the inter-particulate porosity. In addition to the first peak located at 5 µm, the sample displays a second non-negligible signal in the region situated at 0.01-0.1 µm (D = 10 - 100 nm, see inset in Fig. 6b). The pore size distribution of the intra-particulate pores is fairly broad, with a non-negligible differential pore volume (dV/dD) for pores with dimensions of about 10–100 nm. We believe that a new pore population appears and arises from the mesoporosity. In addition to the macropores resulting from the inter-particulate voids, the sample also contain a mesoporosity with pores in the range of 10-50 nm. The continuous rise and the lack of plateau of the mercury intrusion curve at low pore diameter suggest that a significant part of the pores are mesopores. Thus, the mercury porosimetry results mirror those obtained by nitrogen adsorption-desorption analysis (BJH), and gives further support for a mesoporous sample.

Conclusion:

In this work, we studied the carbonization of various organic materials and its conversion into coal recoverable. This new technique is based on the principles of high pressure and high temperature and also on a catalytic heat diffuser.

The organic materials are transformed into coal for a short time (10-20 minutes) without emission of toxic materials. This technique can be envisaged for the treatment of all types of organic waste and as being a way to produce coal from some type of wastes that can form a potential hazard to the environment and human health if recycled in traditional ways i.e expired drugs.

Certain products such as expired drugs showed obtaining coal having a specific surface area (285 m²/g) close to that of charcoal and this, though without recess no treatment usually adapted for the preparation of activated charcoal.
This technique can identify several objectives at the same time. We produce coal from organic waste, some of which possesses a high specific surface area and also we create new sources of energies from the organic waste, within a short time and without generating any toxic emissions.

References


