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Characterization, Analysis and Comparison of Activated Carbons Issued from the Cryogenic and Ambient Grinding of Used Tyres

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Activated carbons were obtained from the cryogenic grinding of used tyres using the liquid nitrogen as agent of freezing and compared to those obtained by the ambient grinding,. These products were prepared using the chemical activated method. It consists of impregnation of the powder obtained from the cryogrinded and ambient grinded used tyres by phosphoric acid, followed by a carbonization at 600 °C in inert atmosphere. It was found that the surface area and total pore volume of are around 400 m^2/g and 0.44 cm^3/g respectively for both the cryogrinded and ambient grinded used tyres, with a small advantage for the cryogenic grinding.
In order to prove the viability of the cryogenic grinding and the using of chemical activation, physicochemical properties of the activated carbons obtained from the pyrolysis of used tyres were investigated by several techniques including Scanning Electron Microscopy (SEM), Thermogravimetric analysis and Fourier Transform Infrared (FTIR).

1. Introduction

As a result of the great increase in the use of automobiles, the number of scrap tyres will increase considerably. It was estimated that approximately 1.5 10^9 of used Tyres are discharged worldwide every year. With the new mode of consuming in the developing countries, the cars demand has considerably increased in the last five year. It was estimated that the total number of waste Tyres in Algeria has already reached more than 10 million pieces by the end of 2010, and the amount project for the next five years will be over 20 million.
Since that used Tyres are throw in the nature, put in the land fill, stockpiled or simply dumped, they have become a serious source of environmental pollution.
In this way the used Tyres also present a source for breeding several animals and flies like mosquitoes, rats, mice or vermin which can be in turn sources of diseases being able to affect seriously the human health.
Activated carbons are materials composed mainly of carbon, and have a high adsorption capacity; this is due essentially to their large surface areas and to their highly developed microporous texture.
These intrinsic properties allow them to be used in various applications including storage and gas separation, storage of energy (Mui 2010), water treatment (Betancura 2009), bleaching, retention of impurities (Aylon 2012) and separation of pharmaceutical compounds (Amutio 2012).
Activated carbons can be obtained from carbon-rich materials of plant, animal or mineral. Their method of preparation can be achieved in two ways: by physical activation (Ko 2004, Lopez 2012) or chemical activation (Mui 2004, Roiqul 2009).
This study consists of using an alternative method for preparing activated carbons from the scrap Tyres, which is essentially focused on the cryogenic grinding (cryogrinding) by using the liquid nitrogen as refrigerant agent. This cryogenic recovery process, which achieves separation through the freezing, the hardening and the embritteling of the tyre and then using a grinder to break the materials apart, may offer

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a cleaner and more effective separation of rubber, steel, and fibbers than many other processes. The cryogenic grinding process produce finely smooth surface and generate little or no heat resulting in high yield of usable products and little loss of rubber

The obtained powder from the cryogenic grinding and the ambient grinding of the used tyres can be used as is or as raw materials for producing carbon black and activated carbon.

The activated carbons from scrap tyres are obtained after the chemical activation with potassium hydroxide acid and then by carbonisation in a muffle furnace.

2. Materials and methods

2.1 Preparation of raw material

A used Tyre has been shredded with a chainsaw to get sliced roughly 4x15cm size and then reduced into pieces of varying size through a mechanical shearing (see photos in Figure 1).

As a result, the pieces are put in liquid nitrogen at a temperature of -196 ° C for 15 min to harden and embrittled. Finally, the grinding took place in a disc type grinder SODEM containing within its walls a certain volume of liquid nitrogen. In order to obtain better performance in the cryogrinding operation the grinder was filled with a certain volume of liquid nitrogen. A time of 2 minutes was required to reduce the sample of 5 g to the desired powder (see also Figure 1). Once grinded, the obtained powder requires different additional operation to clean it from all the impurities and undesirable parts as fibbers and steels. These last were separate first by hand and then by magnetic sorting.

We proceed with the same manner by using the same grinder to prepare powder from ambient grinding of the used tyres. No liquid, of course, is used for this method.

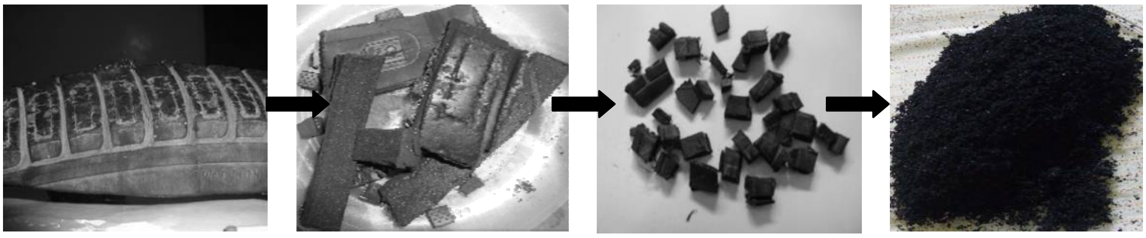

Figure 1: The steps for preparing the raw material

2.2 Preparation of activated carbon

For the production of the activated carbon, we used fractions of powder sized between 0.063mm and 2mm obtained from cryogenic and ambient grinding.

The impregnation with phosphoric acid was performed for about an hour. Then the mixture was placed in an oven at 110 ° C (± 5 ° C) for 2 h.

5 grams of dried and impregnated powder is placed in a stainless steel tubular reactor. And then introduced in a muffle furnace.

After that we proceeded to the carbonization in an inert atmosphere of nitrogen, at a temperature of 650 °C with a residence time of 2 h 30 min.

The resulting product is washed with distilled water until pH 7 and then dried in an oven at 110 °C for 24 h, it is then stored in a dry place in a container.

2.3 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG) are commonly used to determine the tyre pyrolysis kinetics. Due to their characteristic and the complexity of Tyre composition, DTG curve measurements are proposed as an identification method for rubber mixtures. The pyrolysis of waste tyre components was carried out in a TGA measurement apparatus SETARAM TGA92. A typical sample mass of 30 mg was heated up to 700 °C at a constant heating rate of 10 °C/min. Purified nitrogen (99.999%) at a flow rate of 100 mL/min was used as the carrier gas to provide an inert atmosphere for pyrolysis and to remove the gaseous and condensable products.

3. Results and Discussion

3.1 Scanning Electron Micrograph: before and after carbonization

The scanning electron micrograph (SEM) images of cryogrinded and ambient grinded activated carbons (Figure 2) allowed us to visualize and assess the surface chemistry of these samples. The surface texture and porosity are clearly indicated before and after the carbonisation.

This figure shows that the active carbon absorbent issued from cryogrinding has a regularly porous surface, indicating a high surface area of mesoporous dimensions, while the activated carbon obtained from ambient grinding is less porous and the pores are not regular. The SEM has also enabled us to evaluate an average pore size, less than 100 nm and less than 60 nm for ambient and cryogrinded activated carbon.

The scanning electron micrograph-assisted electron microprobe (EDS) also permits to determine the elements constituting the composition of our activated carbon (see Table 1 and Figure 3). We note the presence of oxygen, which is mainly due to inadequate washing of the material. It's clear that the carbon is the predominant component in both cryogrinded and ambient grinding indicating the carbonaceous nature of matter.

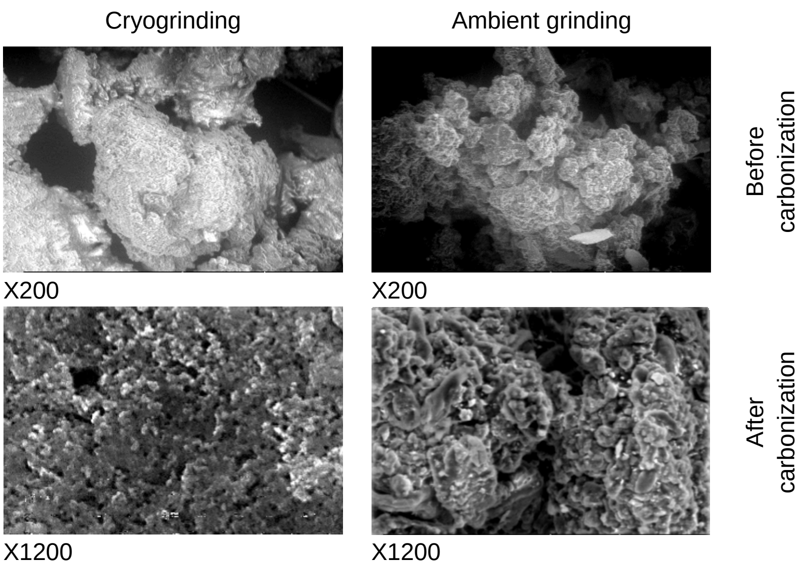

Figure 2: SEM: Photos of recycled tyres before and after carbonization

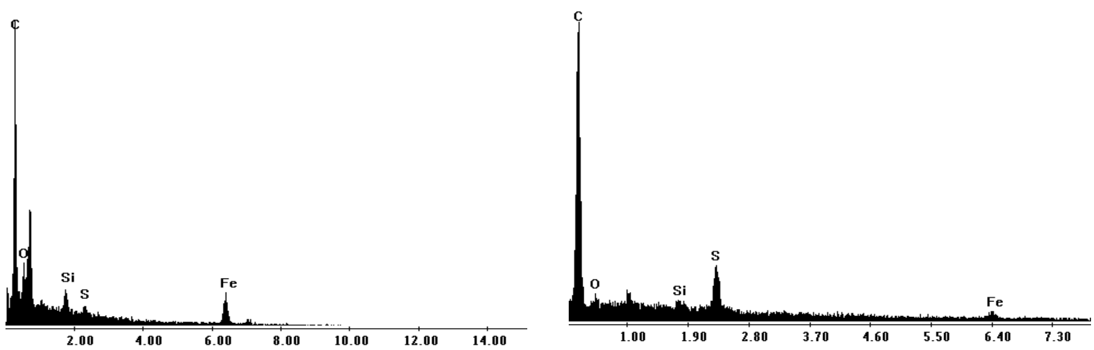

Figure 3: the principals elements constituting the composition of the activated carbons obtained by cryogrinding and by ambient grinding.

3.2 Fourier Transform Infrared

Infrared spectroscopy is ideal to confirm the presence of the functional groups in the samples. Table 2 and Figure 4 showing the spectra of activated carbon from cryogrinding an ambient grinding respectively indicating the presence of function normally detected on this type of products, such as hydroxyl acids, carboxylic acids, the aromatic rings, or bands corresponding to CH bonds.
This confirms the absence of surface features on activated carbon, and therefore justifies the neutral pH found.

Table1: comparison between the activated carbon obtained from the cryogrinding and the ambient grinding

Elements	cryogrinding Wt %	Ambient grinding Wt %
Carbon (C)	88.49	80.25
Oxygen (O)	1.26	7.62
Silicom (Si)	1.42	4.13
Sulfur (S)	2.54	1.01
Iron (Fe)	1.87	3.11

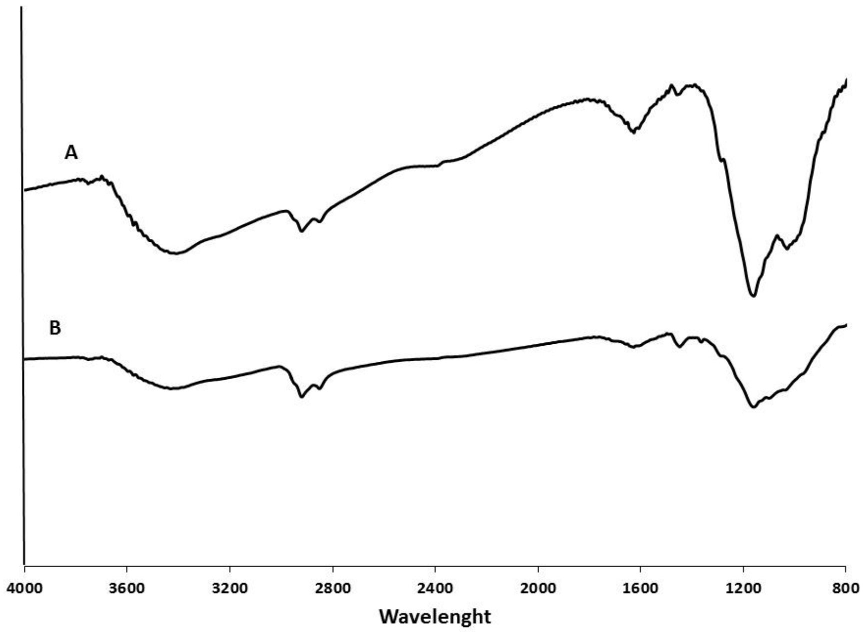

Figure 4: Activated Carbon obtained from cryogrinding(A) ambient grinding (B)

Table 2: FTIR spectra of the activated carbon obtained from the cryogrinding and the ambient grinding

Functional groups	Cryogrinding	Ambient grinding
(O-H)	3411.0	3400.0
(P-H)	2388.6	-
(C-F)	1003.3	1081.4
(C=C)	1627.2	1596.6
(C=C)arom.	-	1482.0

3.3 Thermogravimetric analysis

Thermogravimetric analysis of the used Tyres under a nitrogen atmosphere revealed that major thermal decomposition occurred around 250–500°C as shown in Figure 5.

From pyrolytic differential thermogravimetric (DTG) curve, increasing the temperature to over 500°C had little effect on the mass losses which means that all components in Tyre had been converted to gaseous volatiles, leaving carbon black as the residue. The most commonly used rubbers for Tyres are natural rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR). According to the thermograph, an initial degradation event around 270-350°C corresponds to natural rubber decomposition, followed by a second event at around 350 °C-500 °C, where the degradation of the mixture of styrene–butadiene rubber and butadiene rubber occurs.

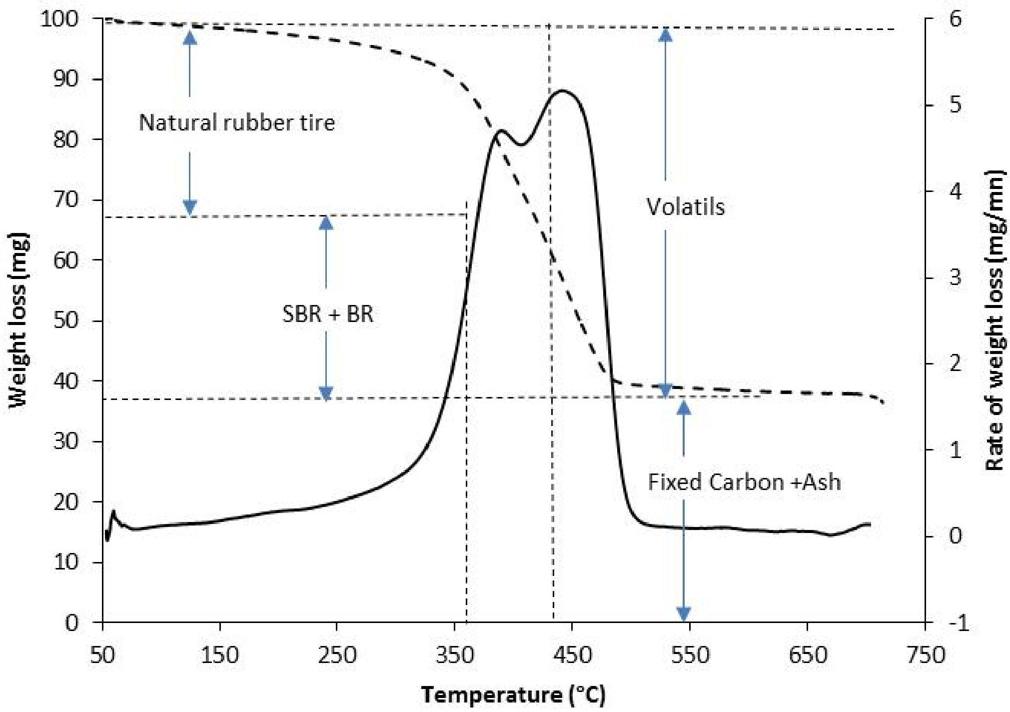

Figure 5: Thermogravimetric analysis of used Tyre under N_2 atmosphere

4. Conclusion

The cryogenic grinding was found to be an effective strategy to efficiently change the waste tyres into solid powder without any modification on their properties. With this process, spending time is significantly reduced and the powder size of the product is uniform. It was found that combination of cryogenic grinding and thermo chemical activation was able to yield carbon with excellent structural parameters. The activated carbon prepared by phosphoric acid. Chemical activation from used tyres attained a BET surface area and mesoporous volume of approximately 400 m^2/g of 0.44 cm^3/g; for both cryogenic and ambient grinding.

During the synthesis of activated carbon obtained from a powder grinding scrap tyres using liquid nitrogen, we noticed that the cryogenic grinding is more effective than the ambient grinding.

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