



Preparation of Adsorbents Derived from Waste Tires

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The production of activated carbons derived from waste tires has been carried out using steam and carbon dioxide as activation agents. The effect of temperature and activation time over the carbons prepared has been studied. The material subjected to activation has been char or residual carbon black obtained by continuous flash pyrolysis of waste tires carried out in a conical spouted bed reactor at 500 °C. The activation has been carried out at 850 and 900 °C using steam and only at 900 °C using carbon dioxide due to the slower kinetics of this process. The activation runs have been conducted in a fixed bed reactor. An essentially mesoporous structure is developed in the process, with BET surface areas above 500 m²/g for the carbons obtained with steam and above 370 m²/g in those obtained using carbon dioxide.

1. Introduction

The production of waste tires has continuously increased in the last decades, at present, a global generation of around 5 billion tones of waste tires is estimated (Karthikeyan et al. 2012). Given that they are considered a hazardous waste and there are regulations that forbid their landfill, considerable attention has been paid to waste tire management. The interest in recycling has opened new routes for their application, such as their use in asphalt surfacing and in the manufacturing of waterproofing systems and composites for construction.

Given the high calorific value of tires, an interesting alternative for their large-scale upgrading is incineration for energy recovery, although this has been a controversial solution due to the emission of particles, tars and PAHs generated in the process (Caponero et al. 2004).

The interest of the tire pyrolysis process lies in the fact that the products obtained by this process, gas, liquid, and solid, whose yields are around 10, 45, and 33 wt %, and the remaining 12 wt % is the metallic residue of the tire may be easily handled, stored, and transported and then valorised separately according to different objectives. The oil can be used as a fuel (Lopez et al. 2011; Murugan et al. 2008), and moreover it contains interesting chemicals such as limonene, isoprene, styrene etc. (Fernandez et al. 2012; Pakdel et al. 2001). The non-condensable gas is made up of light hydrocarbons (olefins and C₁-C₄ paraffins) together with H₂, CO, CO₂, and H₂S and can be used to provide the energy requirements of the process, contributing to the design of a cost-effective and thermally integrated process. The use in situ of an acid catalyst (HZSM-5, HY and H β zeolites) is efficient for increasing the content of light olefins (ethylene and propylene) and BTX fraction (Arabiourrutia et al. 2008; Olazar et al. 2008).

Activation is an alternative for producing high quality active carbons from waste tires (Troca-Torrado et al., 2011). Physical activation is commonly carried out by using steam or carbon dioxide as activation agents, but it may also be suitably carried out using NO and O₂ (Heras et al. 2012). Steam is

considered to be more active than carbon dioxide (Mui et al. 2004) and, moreover, the carbons obtained with steam have higher BET surface areas.

The active carbons obtained in the steam and carbon dioxide activation processes are mainly mesoporous with limited microporosity. In order to increase microporosity, an acid pre-treatment has been applied to the char prior to activation (Tanthapanichakoon et al., 2005). Carbons with high surface areas are obtained in the steam activation of tire chars, although important differences are found in the literature depending on the different experimental devices and pyrolysis conditions used in the process. Moreover, different trends have been observed in the evolution of the surface area with burn-off. Some authors (Cunliffe and Williams, 1999; Lopez et al., 2009b) have observed a maximum in the BET surface area with burn-off values of around 60% and an increase above these values gives way to a decrease in BET surface area. Others (Gonzalez et al., 2006) have observed a continued increase in the surface area up to burn-off values of 80 %. Nevertheless, activation processes with such a burn-off extension involve a major reduction in the amount of product obtained.

In this work the results obtained in a previous study using steam as activation agent (Lopez et al., 2009b) have been compared with those observed using carbon dioxide.

2. Experimental

The activation of tire char has been addressed using steam and carbon dioxide as activation agents. The char samples used in the activation have been obtained by continuous flash pyrolysis carried out in a conical spouted bed reactor described elsewhere (Lopez et al. 2009a; Lopez et al. 2010a; Lopez et al. 2010b). Operating at 500 °C, char yield reaches 34 %, which accounts approximately for the total amount of carbon black contained in the tire. This is due to the limited adulteration of this material related with the short residence time of the volatiles in the reactor and with the fast removal of the carbon black from the reactor. In fact, pyrolysis conditions are an important factor for porosity development throughout the activation process.

Figure 1 shows a schematic representation of the activation unit used in this study. The unit's main component is the fixed bed reactor where activation takes place. The reactor is placed inside a radiant oven that provides the heat to operate at temperatures up to 1000 °C. The unit is provided with a pressure meter to ensure that pressure in the reactor during the activation reaction is not higher than 1.2 atm. Both the reactor and the oven are located in a forced convection oven (hot box) maintained at 270 °C in order to ensure that water is vaporized before entering the reactor. Both nitrogen and carbon dioxide are fed to the reactor by means of mass flowmeters. The water flowrate is controlled by a high precision Gilson 307 pump.

A sample of 2-grams of residual carbon black has been used in each experiment. It is noteworthy that the carbon black particles obtained in the conical spouted bed are of the same size as the original tire particles used in the pyrolysis process, which are smaller than 1 mm. The carbon black sample is heated in an inert atmosphere (nitrogen) flow until the activation temperature is reached. Once this temperature has been reached, nitrogen flow is maintained for one hour in order to complete sample carbonization. The activation gas mixture, which is made up of steam or carbon dioxide and nitrogen at a ratio of 75:25, is then continuously fed into the reactor. The gas flowrate used under both inert and activation conditions is 400 cm³/min measured at normal conditions. When the reaction has finished, the activation mixture is replaced by nitrogen and the reactor is cooled. Finally, the sample is removed from the reactor and weighed in order to determine the burn-off undergone in the activation.

Surface area, and pore volume and size distribution, have been determined from nitrogen adsorption-desorption isotherms carried out in a Micromeritics ASAP 2000. The technique based on Hg porosimetry (Micromeritics Autopore II 9220) has been used to characterize macropores.

The composition of the active carbon samples obtained in the activation process has been determined in an LECO CHNS-932 elemental analyzer. Sulphur content is a parameter of great relevance, given that its application as active carbon or reuse as carbon black requires this content to be lower than 1 %.

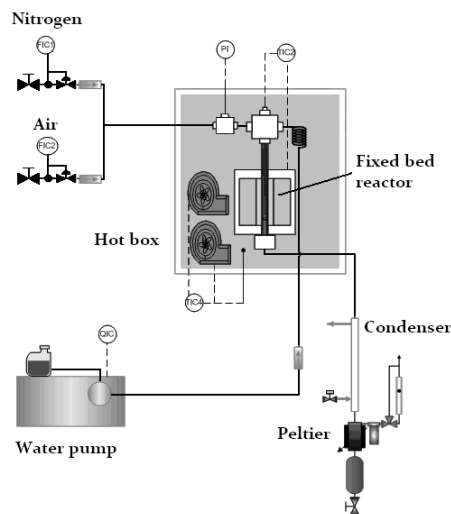


Figure 1: Scheme of the steam activation unit used in this work.

3. Results and discussion

Activation runs have been carried out at 850 and 900 °C using steam as activation agent. However, in the case of carbon dioxide the activation has only been conducted at 900 °C due to the lower reaction rate that gives way to long activation times at 850 °C. Figure 2a shows the evolution of burn-off with activation time for both temperatures and activation agents. As observed, the residual carbon black shows a high reactivity using steam as activation agent at both studied temperatures. However, the reaction rate obtained using carbon dioxide is much lower. In fact, the reaction rate with carbon dioxide is approximately four times lower than that observed using steam at the same temperature.

There is a clear increase in reaction rate with temperature, given that it doubles from 850 °C to 900 °C in the activation carried out with steam. In all the studied cases, the evolutions of burn-off with time are almost linear, Figure 2a. The burn-off curves do not start at zero, because there is a substantial mass loss during the carbonization step. These initial mass losses are 10.6 % at 850 °C and 12.0 % at 900 °C. Moreover, the BET surface areas of the carbon blacks grow during carbonization. Thus, the carbon black obtained in tire pyrolysis has a BET surface area of 65.2 m²/g, but the samples carbonized at 850 and 900 °C have 89.5 and 93.2 m²/g.

Figure 2b shows the BET surface area values obtained for the samples at different burn-off levels. As observed, the evolutions are very similar using steam as activation agent, so temperature affects mainly to the activation kinetics, but not porous structure development. In this case the maximum BET areas for both temperatures studied are higher than 500 m²/g. However, the results obtained with carbon dioxide are poorer (maximum BET area of 370 m²/g). In the same line, other authors have observed lower reaction rates and BET surface areas when the activation of tire chars is carried out with carbon dioxide (Gonzalez et al. 2006; Helleur et al. 2001). Concerning the BET areas published in the literature, they vary in a relatively wide range from 300 to 1000 m²/g. These differences are a consequence of several factors, such as the experimental device used for the activation process, the original tire characteristics, pyrolysis conditions (heating rate, residence time of the volatiles) and other factors that may affect the carbon black porous structure and reactivity.

The BET area increases steadily with burn-off until levels of around 60 %, when the maximum BET surface area values are obtained. For longer treatments, a reduction in surface area is observed. It suggests that the activation process consists of micropore formation, followed by pore enlargement. This trend is observed at the two temperatures and activation agents studied in this paper. This fact is due to the growth of micro and mesopores that gives way to the breaking of their walls and causes the

formation of macropores. Other authors have obtained a similar trend in the evolution of BET surface area with burn-off (Cunliffe & Williams 1999; Zabaniotou et al. 2004).

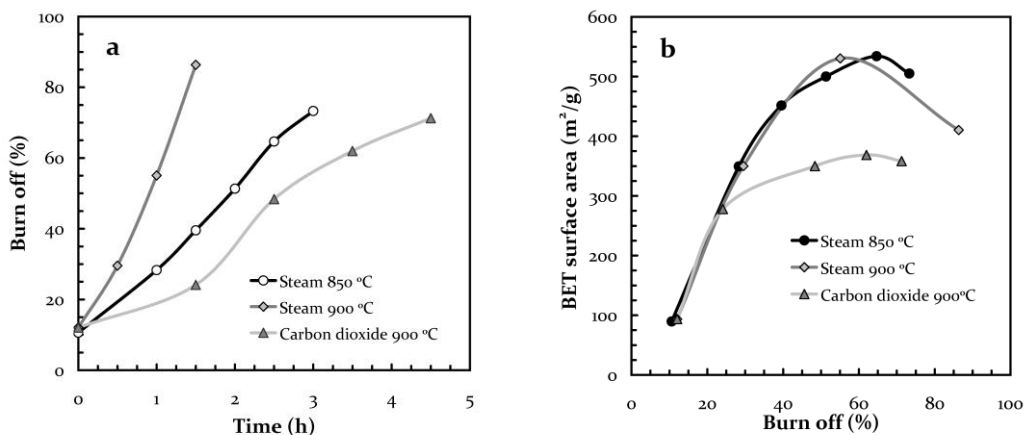


Figure 2: a) Evolution of burn-off in the activation process at the two temperatures studied with steam and carbon dioxide, b) BET surface area values of the active carbons obtained at different burn-off levels.

The shape of the adsorption isotherms gives useful information about the porous structure of the tire-derived-carbons. Figure 3a shows a comparison between the isotherms of the original pyrolytic char and the carbon obtained after 1-hour of steam activation at 900 °C. The active carbon predominantly exhibits a type IV isotherm, which is characteristic of mesoporous materials. The initial adsorption capacity at low relative pressures records limited micropore development. Moreover, an important mesoporous structure is created, as is evidenced by nitrogen adsorption at high relative pressures and by the typical hysteresis loop of mesoporous materials.

Figure 3b shows the evolution of the total pore volume and micropore volume of the carbons obtained for different activation times using carbon dioxide as activation agent. A similar trend has been observed in the experiments carried out with steam. As observed, the micropore volume represents a small fraction of the total pore volume, around 10% of the total pore volume. Both the total pore volume and micropore volume reach the maximum for burn-off values in the 50 to 60% range and longer activation times give way to lower values of these parameters.

Table 1 shows the elemental analysis of the original char and activated carbons obtained for different activation times and conditions. The residual carbon black obtained by pyrolysis has a similar composition to coal, mainly made up of carbon, with limited hydrogen and nitrogen contents. The ash content is in all cases around 10%, which is mostly ZnO. In fact, the starting material we used for pyrolysis is vulcanized rubber without steel chords or other additives. The pyrolytic tire char in the pyrolysis process has considerable sulphur content due to the addition of this compound as vulcanization agent. This content is a problem for pyrolytic char reuse as carbon black, given that sulphur content for this purpose must be lower than 1%. Apart from the improvement of char surface properties during the steam activation process, an important reduction in sulphur content is attained. In the case of the process carried out with carbon dioxide as activation agent the reduction in sulphur content is much lower, being the sulphur content above 1% in all cases. It should be noted that sulphur content is a specification of commercial active carbons, so the reduction in sulphur content could be the key for the industrial application of tire-derived-carbons.

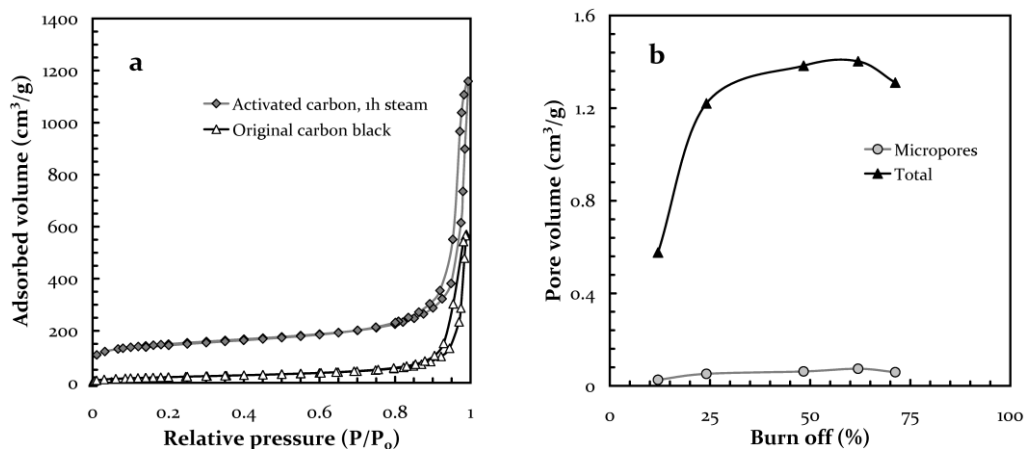


Figure 3: a) Comparison of adsorption-desorption curves of the original tire char with those of the active carbon obtained for 1-hour activation with steam at 900 °C. b) Evolution of the micropore and total pore volume throughout the activation process carried out at 900 °C with carbon dioxide.

Table 1: Elemental analysis of the original pyrolytic char and of activated carbon samples obtained with different burn-off levels, activation agents and temperatures.

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
Original Char	86.9	1.2	0.5	3.3
Steam 850 °C, 1 h	87.2	0.9	0.1	1.3
Steam 850 °C, 3 h	77.3	1.1	0.1	0.6
Steam 900 °C, 0.5 h	86.5	1.0	0.1	1.2
Steam 900 °C, 1.5 h	78.2	1.1	0.1	0.3
Carbon dioxide 900 °C, 1.5 h	87.6	0.5	0.1	2.3
Carbon dioxide 900 °C, 3.5 h	82.4	0.7	0.1	3.2

4. Conclusions

The activation of pyrolytic tire char obtained in a conical spouted bed reactor produces good quality active carbon. Commercial active carbons are microporous materials, but those obtained from activation of waste tire char are mainly mesoporous. The presence of mesopores and macropores makes pyrolytic tire char suitable for the adsorption of large molecular size compounds. The properties of the carbons obtained depend largely on activation time and activation agent, but temperature seems only to have a kinetic effect in the case of steam activation. Steam has shown a faster activation kinetic than carbon dioxide, approximately four times faster at the same temperature. Moreover, the activated carbons obtained with steam have a higher surface area than those obtained using carbon dioxide as activation agent. Steam activation has another important advantage, namely, sulphur removal from the char during activation. This removal is enhanced by the structure of the char obtained in the conical spouted bed reactor. This reduction in sulphur content may be the key for the industrial application of tire-derived-carbons, either as active carbons or as carbon blacks for tire manufacturing.

References

Arabiourrutia, M., Olazar, M., Aguado, R., Lopez, G., Barona, A., Bilbao, J., 2008, HZSM-5 and HY Zeolite Catalyst Performance in the Pyrolysis of Tires in a Conical Spouted Bed Reactor, *Industrial and Engineering Chemistry Research*, 47, 7600-7609.

- Caponero J., Tenorio J., Levendis Y., Carlson J., 2004, Emissions of batch combustion of waste tire chips: The hot flue-gas filtering effect, *Energy and Fuels*, 18, 102-115.
- Cunliffe A. M. Williams P. T., 1999, Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires, *Energy and Fuels*, 13, 166-175.
- Fernandez A. M., Barriocanal C., Alvarez R., 2012, Pyrolysis of a waste from the grinding of scrap tyres, *Journal of Hazardous Materials*, 203–204, 236-243.
- Gonzalez J. F., Encinar J. M., Gonzalez-Garcia C. M., Sabio E., Ramiro A., Canito J. L., Ganan J., 2006, Preparation of activated carbons from used tyres by gasification with steam and carbon dioxide, *Applied Surface Science*, 252, 5999-6004.
- Helleur R., Popovic N., Ikura M., Stanculescu M., Liu, D., 2001, Characterization and potential applications of pyrolytic char from ablative pyrolysis of used tires, *Journal of Analytical and Applied Pyrolysis*, 58, 813-824.
- Heras F., Alonso-Morales N., Jimenez-Cordero D., Gilarranz M. A., Rodriguez J. J., 2012, Granular mesoporous activated carbons from waste tires by cyclic oxygen chemisorption-desorption, *Industrial and Engineering Chemistry Research*, 51, 2609-2614.
- Karthikeyan S., Sathiskumar C., Moorthy S. R., 2012, Effect of process parameters on tire pyrolysis: A review, *Journal of Scientific and Industrial Research*, 71, 309-315.
- Lopez F. A., Centeno T. A., Alguacil F. J., Lobato B., 2011, Distillation of granulated scrap tires in a pilot plant, *Journal of Hazardous Materials*, 190, 285-292.
- Lopez G., Olazar M., Aguado R., Bilbao J., 2010a, Continuous pyrolysis of waste tyres in a conical spouted bed reactor, *Fuel*, 89, 1946-1952.
- Lopez G., Olazar M., Aguado R., Elordi G., Amutio M., Artetxe M., Bilbao J., 2010b, Vacuum Pyrolysis of Waste Tires by Continuously Feeding into a Conical Spouted Bed Reactor, *Industrial and Engineering Chemistry Research*, 49, 8990-8997.
- Lopez G., Olazar M., Amutio M., Aguado R., Bilbao J., 2009a, Influence of Tire Formulation on the Products of Continuous Pyrolysis in a Conical Spouted Bed Reactor, *Energy and Fuels*, 23, 5423-5431.
- Lopez G., Olazar M., Artetxe M., Amutio M., Elordi G., Bilbao J., 2009b, Steam activation of pyrolytic tyre char at different temperatures, *Journal of Analytical and Applied Pyrolysis*, 85, 539-543.
- Mui E., Ko D., McKay G., 2004, Production of active carbons from waste tyres - a review, *Carbon*, 42, 2789-2805.
- Murugan S., Ramaswamy M., Nagarajan G., 2008, Influence of distillation on performance, emission, and combustion of a DI diesel engine, using tyre pyrolysis oil diesel blends, *Thermal Science*, 12, 157-167.
- Olazar M., Aguado R., Arabiourrutia M., Lopez G., Barona A., Bilbao J., 2008, Catalyst effect on the composition of tire pyrolysis products, *Energy and Fuels*, 22, 2909-2916.
- Pakdel H., Pantea D., Roy C., 2001, Production of dl-limonene by vacuum pyrolysis of used tires, *Journal of Analytical and Applied Pyrolysis*, 57, 91-107.
- Tanthapanichakoon W., Ariyadejwanich P., Japthong P., Nakagawa K., Mukai S., Tamon H., 2005, Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires, *Water Research*, 39, 1347-1353.
- Troca-Torrado C., Exandre-Franco M., Fernandez-Gonzalez C., Faro-Dominguez M., Gomez-Serrano V., 2011, Development of adsorbents from used tire rubber: Their use in the adsorption of organic and inorganic solutes in aqueous solution, *Fuel Processing Technology*, 92, 206-212.
- Zabaniotou A., Madau P., Oudenne P., Jung C., Delplancke M., Fontana A., 2004, Industrial pyrolysis and bench scale activation with H₂O-CO₂ mixture, *Journal of Analytical and Applied Pyrolysis*, 72, 289-297.