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Pyrolysis of blends of coal and tyre wastes in a fixed bed reactor and a rotary oven

B. Acevedo, C. Barriocanal *, R. Alvarez

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

HIGHLIGHTS

- Pyrolysis of blends of two wastes from scrap tyres with coal were carried out in two ovens of different configuration.
- Mass balances were performed with gas and oil yields showing the greatest differences.
- Textural characteristics of the chars from the two ovens were similar.
- The oil produced in the rotary oven was more aromatic and contained smaller amount of oxygenated compounds.

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ABSTRACT

The pyrolysis of blends of two wastes from scrap tyres with a coal of 36 wt.% db volatile matter content was carried out in two ovens of different configuration in order to compare the characteristics of the products obtained. The rotary oven was expected to improve the blending of the raw materials and to promote a synergistic effect. Mass balances were performed with gas and oil yields showing the greatest differences. The chars obtained were studied on the basis of their true and apparent densities, Hg porosimetry and by determining their surface area under N_2 at 77 K and under CO_2 at 273 K. The chars were also examined by scanning electron microscopy (SEM). The oils were subjected to Fourier spectroscopy (FTIR). It was observed that the oils obtained in the rotary oven were more aromatic and contained smaller amounts of oxygenated functional groups due to their higher residence time in the hot zone of the reactor.

1. Introduction

More than 17 million tons of waste tyres are produced every year [1]. Finding a use for the huge amount of wastes derived from tyre rubber has been the subject of intensive investigation in recent years [2–8]. Combustion, gasification and pyrolysis have been proposed as the most appropriate technologies for exploiting a waste which contains a high amount of carbon and possesses a high calorific value. Tyres are made up of different types of rubbers. Apart from styrene–butadiene (SBR), these include natural rubber, nitrile, chloroprene and polybutadiene. In addition to rubbers, reinforcing textile cords, steel and carbon black are also included in the composition of tyres. The production of tyres requires the expenditure of a high amount of energy. SBR rubber entails energy consumption of the order of 156 MJ/kg (67,000 Btu/lb). Whereas, the energy required to make a retreaded tyre is less than a third of this. Similarly the energy used to produce reclaimed rubber from waste tyres, recover carbon black or to perform any of a number of recycling operations is considerably less than the energy needed for comparable virgin material operations [9].

Tyre material recycling is normally carried out by means of a shredding procedure that yields granulated rubber as the main product and steel and reinforcing fibre in the form of fluff as sub-products. Rubber crumbs are applied in sports surfaces and as an additive for asphalt, etc. but no use has been found for the fluff apart from that of sound absorber [10].

Pyrolysis is a process that allows the decomposition of waste tyres into gas, pyrolytic oil and char, all of which are highly useful products. Tyre pyrolysis gases have a very high calorific value and can be used as a source of energy for the pyrolysis process itself. The oil produced is a complex mixture of compounds that can be employed as a fuel. It may also be used as a source of chemical products such as benzene, xylene, toluene, styrene and limonene. The char produced also has various potential applications: (i) as a fuel, (ii) as low quality carbon black and (iii) as activated carbon. The co-processing of tyres and coals has been studied in the past to improve the production of liquid products from coal via a hydro-

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* Corresponding author. Tel.: +34 985 118958; fax: +34 985 297662.
E-mail address: carmenbr@incar.csic.es (C. Barriocanal).

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pyrolysis process [11]. A recent paper studied the production of liquid fuels from the pyrolysis of blends of scrap tyres and oily wastes [12]. Nevertheless, to our knowledge, no work has been carried out to try to improve the characteristics of the char obtained from scrap tyre by co-pyrolysis with coal.

The aim of the present research work is to study and compare the pyrolysis products obtained in two ovens of different configuration, (one fixed bed and the other rotary), from two wastes derived from the grinding of scrap tyre and their blends with coal with the aim of increasing the char yield and lowering the ash and sulphur content. The influence of the reactor type on the yields and characteristics of the products was also studied. The rotary oven was expected to improve the blend and to produce a synergistic effect.

2. Experimental

2.1. Materials

A low rank coal (G) was used for blending with two wastes derived from the grinding of scrap tyres. The wastes which were employed in the pyrolysis experiments, i.e. tyre crumbs (TC) and fibres used as reinforcing fibre in tyres, were obtained as a waste during the grinding and shredding of scrap tyres (RF). TC and RF were obtained from the processing of car and truck tyres. The reinforcing fibre was obtained during the process of mechanical grinding of the tyres after the metallic parts and the rubber had been removed. These wastes comprised a very heterogeneous material made up of a mixture of a fluff, fine rubber and pieces of cord with rubber adhered to it. Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was carried out by using a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144 DR (ASTM D-5016) for sulphur and a LECO VTF-900 for the direct determination of oxygen determination. Coal G was a low rank coal with a volatile matter content of 36.2 wt.% db.

2.2. Pyrolysis in a fixed bed (FB) and rotary oven (RO)

For each pyrolysis experiment a sample of 6–8 g of coal, each waste and blends of the coal and waste prepared in a proportion of 1:1 were introduced into a quartz reactor that was heated in a horizontal electrically-heated oven at 5 °C/min to a final temperature of 850 °C. During pyrolysis, the liquid products were collected using an ice-cooled trap. The char and liquid product yields were calculated relative to the starting material, while the gas yield was calculated by difference.

Around 40 g of sample was introduced into the quartz reactor of the rotary oven and heated to 850 °C at a rate of 5 °C/min. A trap situated at the end of the oven allowed the liquid products to be recovered. After the oil trap a column filled with a polymeric resin was used to collect the most volatile products. The product yields were calculated, as in the case of the FB oven. Fig. 1 shows a diagram of the configuration of the two ovens. In the FB reactor the gases left the reaction zone as they were produced but in the rotary oven, due to the larger diameter of the reactor in the hot zone, the residence time was longer, to allow more cracking and secondary reactions of the pyrolysis decomposition products.

The coal was crushed to less than 1.18 mm while the tyre crumbs and the fluff were used as received. The size of the tyre crumbs was smaller than 3 mm.

2.3. Characterization of the chars

The particle size selected to determine the porous structure of the materials was between 600 and 212 μm.

The true density (ρ_{He}) of the chars was measured by means of helium pycnometry in a Micromeritics Accupyc 1330 Pycnometer. Their apparent density (ρ_{Hg}) was determined with mercury at 0.1 MPa in a Micromeritics Autopore IV 9500 mercury porosimeter. From the true and apparent densities the open porosity and total pore volume corresponding to pore sizes smaller than 12 μm were calculated by means of the following equation:

$$\varepsilon\ (\%) = \left(1 - \frac{\rho_{\mathrm{Hg}}\ (\mathrm{g/cm^3})}{\rho_{\mathrm{He}}\ (\mathrm{g/cm^3})}\right) \cdot 100 \tag{1}$$

The total pore volume (V_T) was obtained from the equation:

$$V_T\ (\mathrm{cm^3/g}) = \left(\frac{1}{\rho_{\mathrm{Hg}}\ (\mathrm{g/cm^3})} - \frac{1}{\rho_{\mathrm{He}}\ (\mathrm{g/cm^3})}\right) \tag{2}$$

The pore size distribution was calculated by applying increasing pressure to the sample from 0.1 to 227 MPa. This resulted in pore sizes in the range of 12 μm to 5.5 nm as determined by the Washburn equation:

$$d_p\ (\mathrm{nm}) = \frac{1244}{P\ (\mathrm{MPa})} \tag{3}$$

Pore size was classified into three categories: macropores (12 μm > dp > 50 nm), mesopores (50 nm > dp > 5.5 nm) and micropores (dp < 5.5 nm). Microporosity was calculated by difference relative to the total pore volume.

The textural properties of the chars were studied by means of N_2 adsorption at 77 K on a Micromeritics ASAP 2420 apparatus. The software package provided with the equipment was used. The specific surface area (S_{BET}) was calculated by means of the BET method in the relative pressure range 0.03–0.1. The total pore volume (V_T -N_2) was measured at $P/P0 = 0.97$. The micropore volume was determined by applying the Dubinin equation to the lower relative pressure zone of the N_2 isotherm. The mesoporosity was calculated as the difference between the total pore volume (V_T -N_2) and the micropore volume. The mesopore volume was ascertained by applying the density functional theory (DFT) so as to obtain the pore size distribution.

The samples (0.25 g approximately) were degasified under vacuum at 200 °C for 24 h prior to adsorption to eliminate all the moisture and condensed volatiles. The IUPAC pore size classification that assigns a 2–50 nm size to mesopores and <2 nm size to micropores was used.

In order to determine the microporous structure of the chars, physical adsorption of CO_2 at 273 K was carried out in a Nova 4200e Quantachrome Instruments. Degassing for 24 h at 200 °C in a vacuum was performed prior to adsorption. The Dubinin–Radushkevich (D–R) equation was then applied to the CO_2 adsorption isotherms in order to obtain the volume of micropores (W_0) and the characteristic adsorption energy (E_0). Following the procedure of Stoeckli [13] the E_0 was related to the average width of the micropores (L), while the surface area of the micropores (Smi) was related to the volume W_0 by means of the following empirical equations:

$$L\ (\mathrm{nm}) = \frac{10.8}{E_0\ (\mathrm{kJ/mol}) - 11.4} \tag{4}$$

$$\mathrm{Smi}\ (\mathrm{m^2/g}) = \frac{2000 \cdot W_0\ (\mathrm{cm^3/g})}{L\ (\mathrm{nm})} \tag{5}$$

The topography of the fractured surfaces of the chars was studied on a Zeiss DSM 942 scanning electron microscope.