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Pyrolysis of a waste from the grinding of scrap tyres

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ABSTRACT

The fibres that are used to reinforce tyres can be recovered as a waste in the process of grinding of scrap tyres. In this paper beneficiation through pyrolysis is studied since the fibres are made up of polymers with a small amount of rubber because the latter is difficult to separate. The experiments were performed at three temperatures (400, 550 and 900 °C) in a horizontal oven. The three products – gas, oil and char – obtained from the pyrolysis were investigated. The composition of the gas was analyzed by means of gas chromatography. The oil was studied by gas chromatography and infrared spectroscopy. The char porous structure was determined by N_2 adsorption. In addition, the topography of the chars was studied by means of scanning electron microscopy (SEM). The products resulting from the pyrolysis of the fibres were compared with those obtained from scrap rubber.

1. Introduction

More than 2.7 million tonnnes of recyclable waste in the form of scrap tyres are generated every year in the EU. Tyres are mainly made up of rubber, carbon black, steel and textile components as reinforcing materials. The most commonly used tyre rubber is styrene–butadiene copolymer (SBR). Natural rubber and polybutadiene are also included in the manufacture of tyres. All the materials used are 100% recyclable. Moreover, their chemical and physical properties make them a highly valuable resource [1,2]. The present methods of tyre disposal include: landfill, energy recovery, export, retreading, and their reuse in low value products such as sports surfaces, noise barriers and roofing materials. Although a great deal of effort to promote the recycling of tyres has been made in recent years, efforts will inevitably intensify in the future due to increasing public and political pressure for stricter legislation, such as the European Landfill Directive, which strictly prohibits the disposal of rubber tyres on landfill sites. Tyre rubber has a high calorific value and can be used as fuel, although some problems may arise due to the emission of hazardous compounds and metals [3].

In contrast, pyrolysis is a process that allows the decomposition of waste tyres into gas, pyrolytic oil and char, all of which are highly useful products. Many authors have studied the pyrolysis of waste tyres [1,4–10]. Tyre pyrolysis gases have a very high calorific value and can even be used as a source of energy in the pyrolysis process itself. The oil produced is a complex mixture of compounds [5,11] that can be employed as a fuel. Furthermore, some of these compounds are present in sufficiently large amounts for them to be separated [12]. The char produced also has various potential uses [3,13–15]: (i) as a fuel, (ii) as low quality carbon black and (iii) as activated carbon.

The fibres that constitute the reinforcement of tyres have not until now received much attention in research journals. Nevertheless several authors have tried to identify and characterize them [16,17]. The aim of the present research work is to study the pyrolysis of the fluff that is recovered as a waste in scrap tyre recycling factories. This fluff comes from the fibres that are used as a reinforcing material in tyres. Because these fibres contain some rubber, tyre granules obtained in the shredding/grinding process were included in the study for comparison purposes.

2. Experimental

2.1. Materials

Typically in tyre recycling plants, about 65%, 20% and 15% of crumb rubber, steel and waste fluff are recovered, respectively [18]. The fluff consists of a mixture of polymeric fibres and rubber particulates that cannot be further separated and is disposed of at landfill sites.

The tyres are first fed into a shredder and reduced to a size of around 15 cm. The resultant pieces are then transported on conveyor belts to a second step where the tyre pieces are ground down to a size of <2 cm. This step enables the tyre rubber to be separated from the steel and fibres. The fibres are removed from the rubber in the grinding processes. A combination of cross belt

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magnetic separators, magnetic drums and suction systems helps to separate the various components at this stage of the process. Whereas some of the fibre retains its initial shape stuck to the rubber, other looks like microfibre.

The raw materials used for the pyrolysis experiments were the tyre crumbs (TC3) and the fluff/fibres obtained as a waste during grinding and shredding of scrap tyres (F3) obtained from the processing of car and truck tyres. 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 means of a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144 DR (ASTM D-5016) for sulfur and a LECO VTF-900 for direct oxygen determination.

2.2. Pyrolysis experiments

For each pyrolysis experiment a sample of 6–8 g was heated in a horizontal electrically heated oven at 5 °C/min to a final temperature of 400, 550 °C and 900 °C. After pyrolysis, the liquid products were collected using an ice-cooled trap and recovered by solvent extraction with dichloromethane (DCM). The char and liquid product yields were calculated relative to the starting material as follows:

$$\text{coke yield(wt\%)} = \frac{a}{w_s} \times 100$$

$$\text{tar yield(wt\%)} = \frac{b}{w_s} \times 100$$

a = weight of semicoke; b = weight of tar; W_s = initial weight of the sample.

The gas yield was calculated by difference. Since the fluff is a very heterogeneous material, at least four pyrolysis experiments were carried out to obtain the mass balances.

2.3. Characterization of the oil and gas resulting from pyrolysis

The pyrolysis oils were characterized by Fourier transform infrared spectroscopy, gas chromatography with flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS).

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-IR560 spectrometer equipped with a DTGS detector. The sample was deposited as a thin film between the NaCl windows and subjected to 64 scans at a resolution of 4 cm^{-1} to obtain the spectra.

Gas chromatographic analyses of the tars were carried out on an Agilent Model 6890 Series II gas chromatograph equipped with flame ionization and mass spectrometry detectors (GC–FID–MS). A detailed description of the procedure can be found elsewhere [19,20]. Briefly, the oil sample was heated from 50 to 295 °C at a rate of 4 °C/min. Helium was used as a carrier gas. The data presented are based on an average of at least 3 chromatograms.

The gas produced from the pyrolysis experiments was analyzed on a HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Two packed columns were used for the analysis: (i) a Porapak N (3 m × 1/8 in.) to separate C1, C2, C3, C4, H_2S and CO_2 and (ii) a molecular sieve TM13x (0.9 m × 1/8 in.) to separate O_2, N_2, and CO. The Porapak column was heated from 50 °C (maintained for 5 min) to 185 °C at a rate of 10 °C/min. The TM column was held at 50 °C throughout the experiment. Helium was used as carrier gas and the temperature of the detectors was maintained at 300 °C. Quantification was carried out using blends of gases of known composition. The amount of hydrogen was calculated by difference.

Table 1
Main characteristics of the raw materials used.

	TC3	F3
VM (wt% db)[a]	63.0	65.7
Ash (wt% db)	9.3	8.4
C (wt% daf)	87.6	83.6
H (wt% daf)	7.6	7.2
N (wt% daf)	0.3	0.3
S (wt% daf)	2.01	1.75
O (wt% daf)	3.1	7.8
C/H	0.96	0.97
Calorific power (kcal/kg)	8778	7856

[a] VM, volatile matter content on a dry basis (db).

2.4. Characterization of the chars

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

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 to determine the BET surface area (S_{BET}), the total pore volume (V_T) and the pore size distribution based on the density functional theory (DFT). The micropore volume was also calculated by applying the Dubinin equation to the lower relative pressure zone of the isotherm. The mesoporosity was calculated as the difference between the total pore volume (V_T) and the micropore volume. The mesopore volume also was also calculated by applying the density functional theory 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 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.

3. Results and discussion

3.1. Pyrolysis yields as a function of temperature

Table 1 shows the main characteristics of the raw materials used. It can be seen that both of them have similar ash and volatile matter contents, the main difference being the higher oxygen content of the fibres. Especially striking is their high calorific value, which is similar to that of a bituminous coal but higher than that of lignite. However, their use as a fuel in the combustion process to provide energy for cement kilns is rather problematic due to the emissions of hazardous compounds and metals [3].

After the mechanical process of grinding and shredding of scrap tyres some of the fibres retain their original form and have a cord-like appearance but most of them are obtained in the form of microfibres as shown in Fig. 1.

TC3 and F3 were pyrolyzed to a final temperature of 400, 550 and 900 °C. The oil, char and gas yields from the pyrolysis tests are shown in Fig. 2. At 400 °C the main product was char with values ranging between 60 and 70 wt%. When the temperature is increased to 550 °C the oil and gas content increases. A further increase to 900 °C produces no variation in the yields obtained from the rubber granules. However there is a slight decrease in char yield with the consequent rise in the tar and gas yields for the fibres as a consequence of higher thermal cracking. At the three temperatures selected for the experiment, the amount of char obtained from the tyre crumbs was greater than that obtained from the fibres. Moreover, whereas char from TC3 is mainly made up of carbon black, char form F3 will include also some char derived from the polymers that constitute the reinforcing fibre.