



Fuel-oils from co-pyrolysis of scrap tyres with coal and a bituminous waste. Influence of oven configuration



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HIGHLIGHTS

- Fuel-oils were prepared from two wastes from tyre recycling.
- The oils can be tailored by co-pyrolysis with coal or a bituminous waste.
- Blending with a low rank bituminous coal led to a higher aliphatic/aromatic ratio.
- Blending with a bituminous waste lowered the aliphatic/aromatic ratio.
- The influence of the oven configuration has been established.

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ABSTRACT

Two wastes from the tyre recycling industry – the fibers used as reinforcing material and tyre crumbs – were pyrolyzed in two ovens of different configuration. Blends with a low rank coal and a bituminous waste were also prepared to modify the composition of the oils obtained from the pyrolysis of the tyre wastes. Elemental analysis, calorific value, Fourier transform infrared spectroscopy (FTIR) and gas chromatography were used to determine the oil composition. A comparative study taking into account the configurations of the ovens and the raw materials was carried out. The oils produced in the rotary oven were found to be more aromatic and to have lower oxygen contents. Depending on the type of oven and the material used in the co-pyrolysis process it is possible to obtain a fuel-oil with a specific heating value and sulfur content. It is also possible to obtain oil with more than 20% limonene and 20% BTX (benzene, toluene, xylene). The amount of aliphatics can be increased by including a coal in the pyrolysis process and the amount of aromatics can be increased by co-pyrolysis with a bituminous waste.

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1. Introduction

End-of-Life Tyres (ELTs) is an increasing economic and environmental problem closely related with a rapid developing modern society. More than 3.3 million tons of used tyres are generated in the European Union each year. While 2.7 millions tons are considered to be ELTs the rest are reused, exported or retreaded [1]. European legislation on waste tyres has become more stringent since the year 2000 and, as a consequence, the amount of waste tyres has declined while the valorization of the material has been favoured either due to the greater number of uses for tyre crumbs or to the increasing use of this material in the production of energy [2].

Pyrolysis can be considered as an optimal and environmentally friendly method for thermo-chemical conversion of wastes such as

tyres. Three products are derived from pyrolysis: gas with a high calorific value, pyrolytic oil that can be used as fuel or as a source of benzene, toluene, xylene (BTX) or limonene and char that can be used as fuel, activated carbon or carbon black [2–7].

Scrap tyres are converted in tyre recycling plants into tyre crumbs, reinforcing fiber and steel. Styrene butadiene (SBR), polybutadiene (BR), nitrile (NiR) and chloroprene rubbers together with natural rubber (NR) are the main constituents of tyre crumbs [5,7–9]. Their chemical structure with aromatic and aliphatic constituents plays an important role in determining the composition of the oils derived from tyre crumbs. The reinforcing fiber is usually recovered as a heterogeneous fluff made up of polymeric fibers that contain a certain amount of rubber [3,10,11]. Until now little effort has been devoted to finding a procedure for recycling this fluff.

The co-processing of tyre crumbs with coal has been studied as a way to improve coal liquefaction [8,11–13]. But to our knowledge

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the co-pyrolysis of waste tyres with a bituminous waste has not been reported.

It has been well established [14] that the structural units of a coal increase in size with coal rank. Coal pyrolysis can be considered as a depolymerization reaction during which the weak bonds such as methylene and oxymethylene bridges are broken, resulting in tars that contain structures representative of the parent coals [15]. Tars from low-rank coals contain low-molecular weight compounds such as phenol, alkyl phenols and saturated aliphatics [16,17].

The configuration of the oven can give rise to differences in the composition of the pyrolysis oils [18,19].

Taking into account that the pyrolysis of a low-rank coal produces mainly aliphatic compounds, co-pyrolysis with tyre wastes can modify the composition of the oils so that it has a higher aliphatic/aromatic ratio. On the other hand, if the objective is to increase the percentage of aromatic compounds co-pyrolysis with a bituminous waste is the best option.

The objective of the present research work was to study the co-pyrolysis of waste tyres with a low rank coal and a bituminous waste in two ovens of different configuration to try to optimize the composition of the pyrolysis oils as a function of the oven configuration and the raw material used.

2. Experimental

2.1. Materials

The raw materials used for the pyrolysis experiments were tyre crumbs (TC) and fluff/fibers (RF) obtained as a waste during the grinding and shredding of scrap tyres obtained from the processing of car and truck tyres. For the co-pyrolysis test, a low rank coal used in blast furnaces for pulverized coal injection and a bituminous waste (BW) obtained from the benzol distillation column of a by-product section of a coking plant were employed.

RF is a very heterogeneous material composed of fluff, cord with tyre adhered to it and finely grounded crumbs of tyre [3,11]. The tyre crumbs with a particle size lower than 3 mm were used as received.

Proximate analyses were performed following the ISO562 e ISO1171, Standard procedures for volatile matter and ash contents, respectively. The elemental analysis was performed using a LECO CHN-2000 instrument for C, H y N (ASTM D-5773), a LECO S-144 DR instrument (ASTM D-5016) for sulfur and a LECO VTF-900 device for direct oxygen determination.

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

The pyrolysis experiments in the two ovens were carried out with the following samples: the two tyre wastes (RF and TC), their blends with the coal 1:1, and the RF/BW 1:1 blend. In the fixed bed oven samples of 6–8 g 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 the 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 cold trap (OT) and a column filled with amberlite resin (AMB) allowed the recovery of the condensable products. The product yields were calculated, as in the case of the FB oven. A diagram showing the configuration of both ovens has been published previously [11].

For the pyrolysis experiments the coal and the bituminous waste were ground to a size lower than 1.18 mm while RF and TC were used, as received.

2.3. Characterization of the pyrolysis oils obtained in the two ovens

The elemental analysis of the pyrolysis oils was determined as in Section 2.1. The calorific value was measured in a IKA – Calorimeter C4000 adiabatic, Analysentechnik Heitersheim apparatus.

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 in the 400–4000 cm⁻¹ range to obtain the spectra. Selected indices obtained from the FTIR data, using the integrated area (A) of different absorption bands were employed for the semiquantitative analyses (Table 1). The values of the indices were calculated as the average of four spectra obtained from two different droplets.

Gas chromatographic analyses of tars were carried out on an Agilent Model 6890 Series II gas chromatograph equipped with flame ionization and mass spectrometry detection (GC-FID-MS). The separations were carried out using a fused-silica capillary column (HP-5MS) of length 30 m and I.D. 0.25 mm. The temperature was programmed from 50 to 295 °C at a rate of 4 °C/min, the final temperature being maintained for 10 min. Helium was used as the carrier gas and split ratios of 1:200 and 1:50 were employed respectively in the front (MS) and back (FID) injectors. The detector and injector temperatures were 300 °C and the volume of sample injected was 1 µl. The quantitative analyses were based on peak area determinations. The data presented are the average of 2 chromatograms.

3. Results and discussion

Table 2 shows the main characteristics of the raw materials used. The coal presents the lowest volatile matter content while the other samples have contents higher than 65 wt.% db. The ash contents vary between 0.2 wt.% for BW and 7.5 wt.% for TC. The lowest carbon content corresponds to the reinforcing fiber which on the other hand has the highest oxygen content. In spite of its low rank (VM = 36.2 wt.% db) the coal exhibits the highest C/H atomic ratio. The differences in the elemental composition between the coal and bituminous waste may lead to variations in the compositions of the oils obtained from the tyre wastes that can be profitably exploited.

The highest sulfur content corresponds to the bituminous waste and the tyre crumbs. The sulfur present in the tyres is due to the vulcanizing procedure that allows rubber to be converted into more durable materials. In this procedure sulfur is added to form crosslinks between the polymer chains. In order to endow the rubber with superior mechanical properties [9,20].

3.1. Mass balances and main characteristics of the oils

Mass balances were carried out in the two ovens of different configuration used for the pyrolysis experiments. Fig. 1 shows the char, oil and gas yields obtained in the pyrolysis experiments. As was previously found the char yields of the two ovens were very similar, while the oil and gas yields varied depending on the type of oven used. The gas yield was always higher in the RO while the oil yield was higher in the fixed bed reactor [11]. The differences in the oil and gas yields from the two ovens arise from the fact that the oil was allowed a higher residence time in the hot zone of the reactor because of the reactor's dimensions. It was in the hot zone where the non-condensed oil yielded, a larger amount of

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