



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 N₂ 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.

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1. Introduction

More than 2.7 million tonnes 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, H₂S and CO₂ and (ii) a molecular sieve TM13x (0.9 m × 1/8 in.) to separate O₂, N₂, 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 N₂ 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 microfibrils 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 from F3 will include also some char derived from the polymers that constitute the reinforcing fibre.

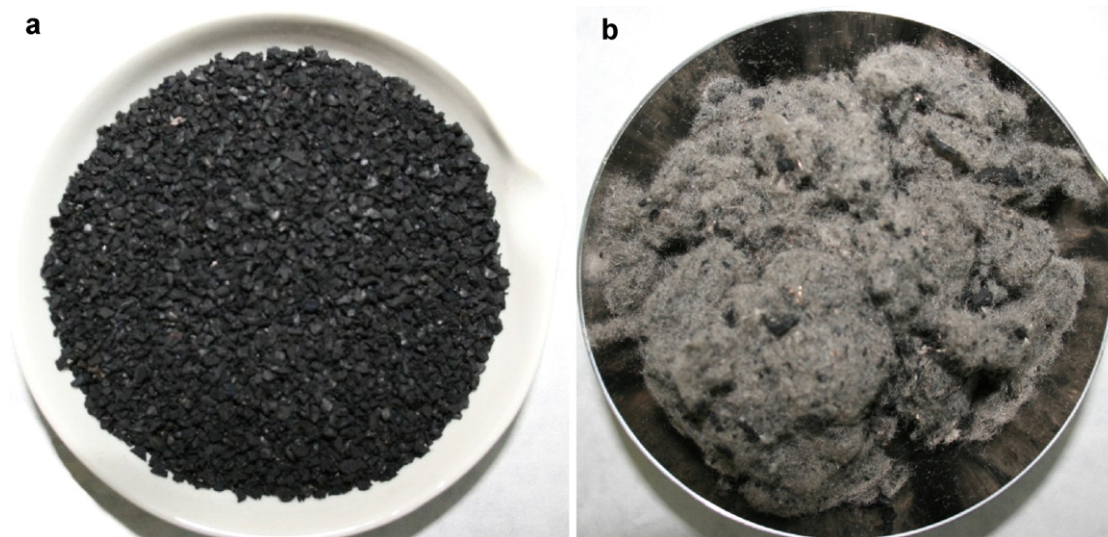


Fig. 1. General aspect of the tyre crumbs (a) and the fibres (b) used.

At 400 °C the decomposition of both wastes is still incomplete. Nevertheless, rubber pyrolysis is complete at 550 °C considering that further heating would only entails small changes in the yields. In the case of F3 minor changes in the yields occur at temperatures higher than 550 °C. The amount of gas produced during pyrolysis is higher in the case of F3 compared to that of the tyre crumbs (Fig. 2). An increase in temperature leads to an increase in the gas yields from 1.4 to 4.8 wt% for TC3 while in the case of F3 the values obtained showed a rise from 6.2 to 10.3 wt%.

3.2. Pyrolysis oil composition

Considering that a final temperature of 400 °C is not high enough to bring about the decomposition of the two wastes, the oil composition was determined at 550 and 900 °C. A qualitative observation of the FTIR spectra corresponding to the oil at 550 and 900 °C (Fig. 3) indicates the presence of aromatic groups, alkanes, alkenes, and compounds containing sulfur, nitrogen and oxygen functionalities. Bands 3 and 4 have enlarged to better observe the differences between the two wastes. A series of absorption bands were identified in the spectra and summarized in Table 2, the numbers correspond to the different bands identified in Fig. 3 [5,21–23]. (1) The bands between 3100 and 2990 cm^{-1} are assigned to the stretching of aromatic C–H. (2) The 2990–2795 cm^{-1} range are assigned to the stretching of aliphatic C–H. (3) The band at 2230 cm^{-1} assigned to symmetric stretching of $\text{C}\equiv\text{N}$ in saturated nitriles which has

been observed in the oil derived from the fibres. (4) The band corresponding to stretching of $\text{C}=\text{O}$ in ester type bond, which has been observed only in the oil from the fibres. (5) The band corresponding to carbonyl/carboxyl $\text{C}=\text{O}$ bond. The band corresponding to aromatic $\text{C}=\text{C}$ (6) has been detected and together with the band (1) confirms the presence of aromatic compounds. The band at 1455 cm^{-1} assigned to compounds containing sulfur has been observed in the oil from both wastes (7). The band observed at 1377 cm^{-1} , assigned to C–H in $-\text{CH}_3$ was observed in the oils from both residues (8), in the case of the fibres some contribution of the vibration of N–C in amines can be considered. The range between 900 and 700 cm^{-1} (9) corresponds to the out-of-plane aromatic C–H vibration modes that reveal differences in the substitution patterns of the aromatic structures. Williams et al. [5] in his analysis the oil obtained from the pyrolysis of whole tyres observed similar spectra with bands that confirmed the presence of alkanes, ketones, aldehydes, aromatic and alkyl substituted aromatic compounds. A semiquantitative analysis of the spectra was carried out in order to establish the differences between the oil obtained from TC3 and F3. The $\text{Hal} = \text{Aal}/\text{Aar}$ index can be calculated as the ratio between the area corresponding to the band (2) and the area of the band (1). The values obtained were 8.9 and 13.8 for TC3 and 15.8 and 12.4 for F3 at both temperatures, indicating the high contribution of the structures containing aliphatic hydrogen to the composition of the oils. Another index that was calculated was the ratio of the area in the range between 1775 and 1565 cm^{-1} to the area under band 6. This index reflects the presence of oxygen functionalities. The values obtained were much higher for the oil of F3 (5.6) than for that of TC3 (3.0) and no significant variations were observed as the temperature was increased. The presence of oxygen in the raw materials (Table 1) suggests that oxygenated hydrocarbons such as aldehydes, ketones, and carboxylic acids, may be present in the reaction products [5].

The soluble fraction in dichloromethane obtained from the oil at 550 and 900 °C was analyzed by GC–FID–MS to determine the variation in composition resulting from the increase in temperature. A comparison of the profiles of the tars obtained at these temperatures indicates that they are qualitatively similar. Fig. 4 shows gas chromatograms of the oil obtained at 550 °C from the two wastes. The chromatograms evidence the great complexity of the oils and the difficulties involved in identifying the compounds. Some authors have tackled this problem by concentrating only on one fraction of the oil [11,24,25], whereas other authors

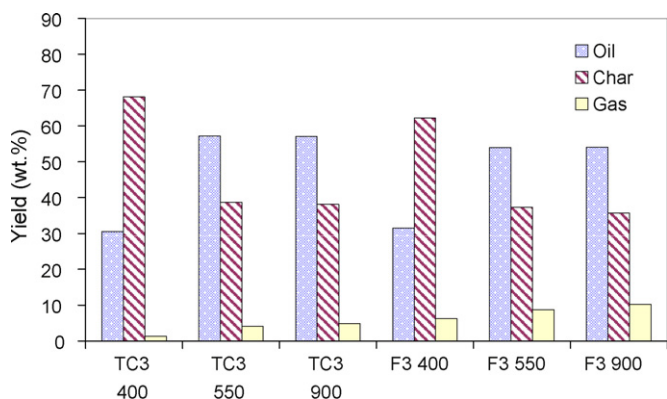


Fig. 2. Oil, char and gas yields obtained at 400, 550 and 900 °C.

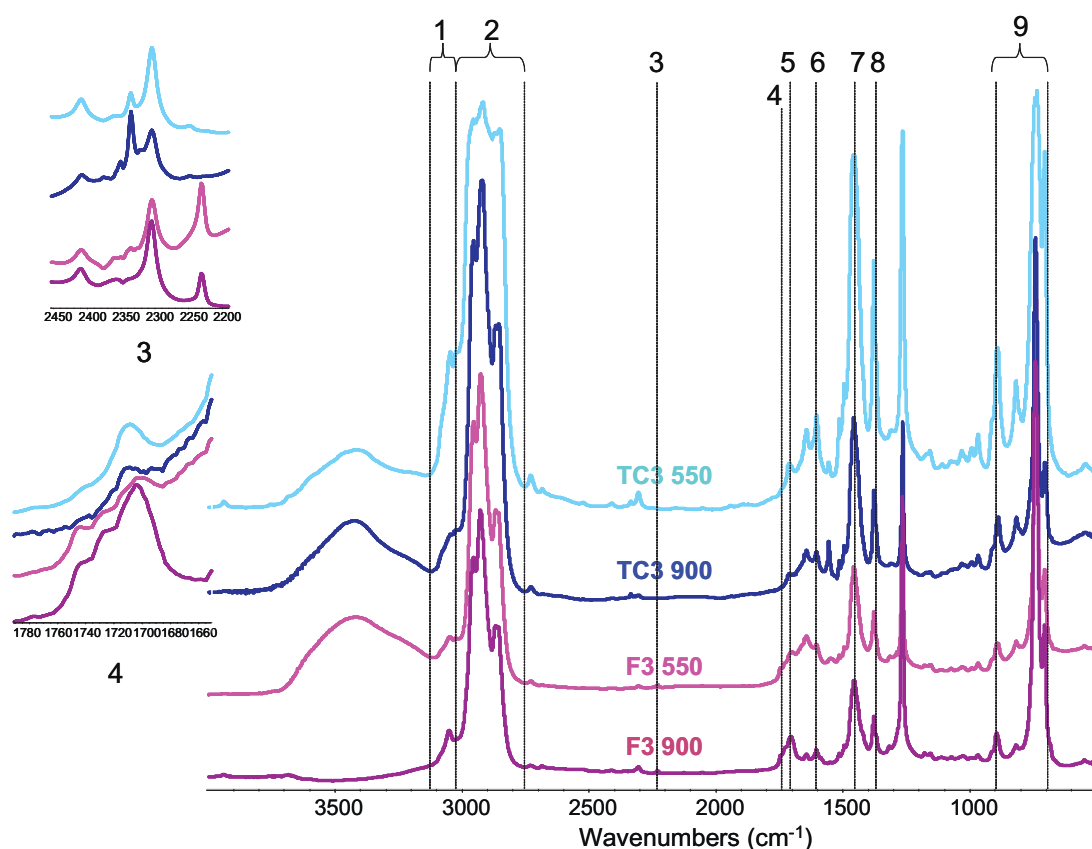


Fig. 3. FTIR of the tars obtained at 550 °C and 900 °C.

[26,27] have studied the whole oil. Our aim at this stage was to obtain a general idea of the composition of the oils, although efforts are being made to improve the identification of the compounds present in the oil and to establish the differences between oils produced from TC3 and F3. The main compounds identified by means of GC–MS were: cyclopentanone (peak 1) dimethylcyclohexene (peak 2), ethylbenzene (peak 3), xylene (peak 4), styrene (peak 5), ethylmethylbenzene (peak 6), methylstyrene (peak 7) benzonitrile (peak 8), limonene (peak 9), terpinolene (peak 10), methylbenzonitrile (peak 11), benzoic acid (peak 12) benzothiazol (peak 13), caprolactama (peak 14), methylnaftalene (peak 15) dimethylnaphthalene (peak 16), pentadecene (peak 17) trimethylnaphthalene (peak 18), heptadecene (peak 19), N-hexylbenzamide (peak 20), hexadecanitrile (peak 21), heptadecanitrile (peak 22). The most abundant compound in the oil derived from TC3 and F3 was limonene ($C_{10}H_{16}$), which is a cyclic terpene that contains two units of isoprene and owes its presence in the oil to the decomposition of rubber. The area percentage of the peak corresponding to limonene is similar in the oils obtained from TC3 and F3 at the two temperatures employed. F3 is a very heterogeneous material

containing a high weight percentage of rubber. Consequently the percentage of limonene can be expected to be high in the oil from both TC3 and F3. The values, expressed as percentages present in the pyrolysis oil from TC3 lie in the range between 14% and 16%. In the case of F3 the range is wider due to its heterogeneity and values between 12.5% and 16% were obtained.

The values reported in the literature tend to decrease with the temperature with maximum values being achieved at temperatures of around 300–400 °C [24,27]. As a consequence of the decomposition of benzothiazyl disulfide used as accelerator, benzothiazol was produced in the oil obtained from TC3 and F3.

Aromatic compounds present in the oil originate from the decomposition of the polymers that constitute rubber and fibres. A general mechanism for the aromatization of alkene compounds and the formation of aromatics with the increase in the amount of permanent light gases like CH_4 and H_2 has been described by other authors [24,27–30]. The amount of aromatics depends on the conditions in the reactor and on the possibility of secondary reactions [31,32]. In the present research work no significant difference was found between the compositions of the oils obtained at the two

Table 2
Assignment of main IRTF bands.

Band	Frequency range (cm^{-1})	Functional groups	Class of compounds	Sample
1	3115–3020	C–H stretching	Aromatic compounds	F3, TC3
2	3020–2750	C–H stretching	Aliphatic compounds	F3, TC3
3	2230	C≡N symmetric stretching	Saturated nitriles	F3
4	1746, 1725	C=O stretching	Ester	F3
5	1704	C=O	Carbonyl/carboxyl	F3, TC3
6	1600	C=C stretching	Aromatic compounds	F3, TC3
7	1455	Scissoring vibration of CH_2 affected by S atoms	$-CH_2-S-CH_2-$	F3, TC3
8	1377	N–B–N stretching; B = benzenoid moieties C–H in CH_3	Amine $-CH_3$	F3, TC3
9	890–705	C–H out of plane	Aromatic compounds	F3, TC3

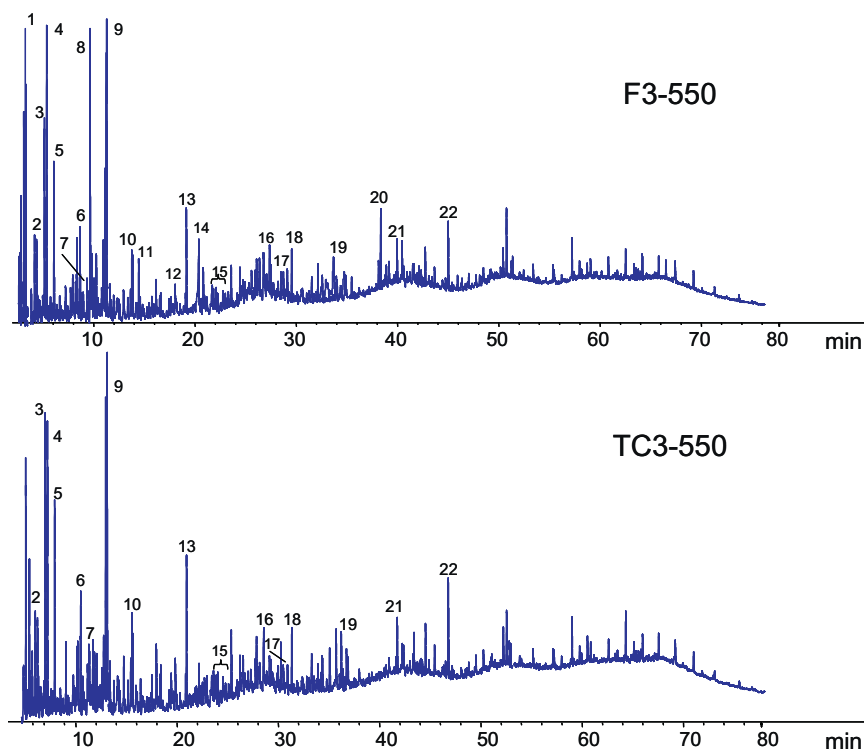


Fig. 4. GC-FID chromatogram of the pyrolysis oil obtained at 550 °C.

temperatures due to the fact that the configuration of the reactor minimizes the possibility of secondary reactions. Some authors [24,27] observed the presence of high molecular weight polyaromatic compounds that were not present in the oil recovered in the present work.

The contribution of the fibres to the composition of the oil is clearly reflected in the presence of compounds that proceed from the thermal decomposition of the polymers that make up the fibres, such as cyclopentanone, caprolactam, benzonitrile, methylbenzonitrile, benzoic acid and N-hexylbenzamide that are not present in the oil from the rubber granules. Some of these compounds were also found by other authors when pyrolysing whole tyres [27]. Polyamides decompose to produce caprolactam and cyclopentanone [33]. Whereas the thermal degradation of polyester produces CO_2 and CO which modify the composition of the gas, together with volatile aromatics such as toluene and benzoic acid [34].

3.3. Chromatographic analysis of the gas

The gases collected during the pyrolysis experiments were analyzed by gas chromatography using a TCD detector. H_2 was evaluated by difference due to the difficulties associated with its quantification [35]. Table 3 shows the composition of the gas evolved during the pyrolysis of the tyre crumbs and the fibres at 550 and 900 °C. The amount of methane increases with increasing pyrolysis temperature, especially in the case of the rubber granules. The amount of C3 (propane and propene) does not vary with the rise in temperature. The behavior of C2 (ethane and ethene) is different for the two wastes: whereas it increases with temperature in the case of the tyre granules, it does not show any great variation in the case of the fibres. The amount of CO_x ($\text{CO} + \text{CO}_2$) in the gas originating from the fibres was higher than that measured for the rubber granules, due to the decomposition of the polymers that constitute the tyre cord. In the case of the rubber granules some authors have suggested that the increase in CO_x is due to the decomposition of

the inorganic compounds present in the tyres [36,37]. Sulfidric acid was also detected in the samples from tyre crumbs. Sulfidric acid originates from the decomposition of sulfur links. It can be seen that the amount of H_2S does not vary with an increase in pyrolysis temperature, indicating that the vulcanized structure of the rubber has already decomposed at 550 °C. From the point of view of practical application, the presence of H_2S will make it necessary to apply some kind of desulfurization procedure before the gas can be used. The C4 components of the gas (butane, butane and iso-butylene) originate from the depolymerization of styrene-butadiene rubber. Their diminution with temperature is attributed to the occurrence of reactions that lead to an increase in the amount of lighter hydrocarbons and hydrogen. This is especially evident in the case of TC3. C4 (butane, butane and iso-butylene) generates mainly propene, ethane, methane and hydrogen [38]. The main reactions that occur during pyrolysis are the following:

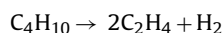
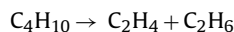
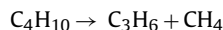


Table 3

Composition of the gas evolved during the pyrolysis.

	TC3-550	TC3-900	F3-550	F3-900
C1	9.9	24.1	6.0	7.7
C2	5.9	10.3	10.6	9.1
C3	5.3	6.2	3.2	3.2
C4	38.1	24.8	28.0	25.6
N_2	21.0	10.8	1.1	0.0
CO_x	9.0	13.0	48.4	45.8
H_2S	2.9	2.5	0.0	0.0
H_2	7.9	8.4	2.7	8.6
GCV ($\text{MJ}/\text{N m}^3$)	65.6	57.5	50.9	48.1

GVC: gross calorific value.

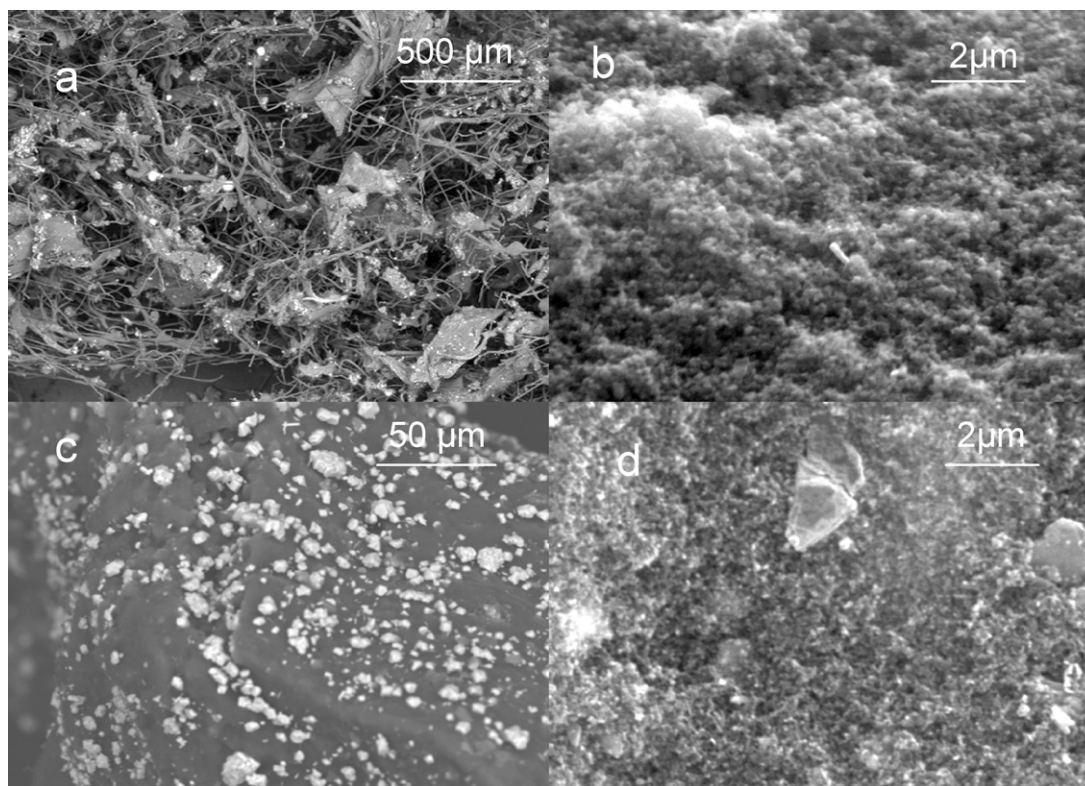
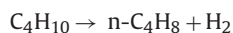
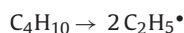


Fig. 5. SEM micrographs of the chars obtained at 900 °C from the fibres (a and b) and the tyre crumbs (c and d).



A free radical decomposition mechanism is involved in the pyrolysis of butane similar to those involved in from the pyrolysis of ethane, and propane. Two main reactions occur in the initiation step:



These reactions generate other free radicals due to numerous propagation reactions. Among the newly formed free radicals are H^\bullet , CH_3^\bullet , $\text{C}_4\text{H}_9^\bullet$.

Gross calorific values (GCV) were calculated taking into account the composition of the gas for each temperature and type of waste (Table 3). For both types of waste (TC3 and F3) an increase in temperature involves a decrease in the calorific value of the gas produced because the amount of longer chain hydrocarbons decreases in favor of the lighter hydrocarbons and hydrogen. It was also observed that at both temperatures the gas obtained from the pyrolysis of TC3 has a higher calorific value than that of F3. Bearing in mind that natural gas has a gross calorific value of 43,000 kJ/N m³, it follows that the gas produced from the pyrolysis of the wastes studied here could be used as fuel. In the literature calorific values in the range of 30–40 MJ/N m³ can be found [5,10] while values in the range of 60–76.7 MJ/N m³ are reported for gases produced between 500 and 700 °C [37,39]. The differences between these values and ours can be ascribed to the different pyrolysis conditions and to the fact that our gas samples correspond to the whole process, whereas other authors report on samples taken at certain temperatures during the process.

3.4. Characterization of the chars

The char that formed during the pyrolysis of the two wastes was found to contain carbon black mixed with a solid residue from the pyrolysis of the polymers. The main drawbacks of this char are its high ash content, the presence of char from the polymers and large particle size [5]. Nevertheless it could be used as reinforcement for rubber articles of low technical character. On the other hand, active carbons can also be produced from scrap tyres for use as adsorbents of various pollutants [15]. Sulfur content of the chars obtained in the present work is 2.68 wt% for TC3 and 2.34 wt% for F3. The ash content is lower for the chars from fibres (around 15 wt%) than for the chars from tyre crumbs (around 17 wt%). The ash values obtained were similar to those reported by Ariyadejwanich et al. [40] although values lower [41,42] and higher [39,43] than those obtained in the present work were found in the literature. Commercial carbon blacks present very low ash content, consequently, the carbon blacks from tyre pyrolysis need to be demineralized in order to be used [44].

The SEM micrographs in Fig. 5 show the topography of the chars obtained at 900 °C. A general view of char F3-900 is presented in Fig. 5a. It is composed of a mixture of carbonized fibres, the char derived from the rubber and mineral matter. Fig. 5b shows a micrograph taken at high magnification ($\times 10,000$) to illustrate the presence of carbon black in the char from the fibres. In both cases the mineral matter appears to be dispersed over the surface of the char (Fig. 5c). The char from the pyrolysis of the rubber granules is formed by the carbon black present in the original tyres and some residues derived from the pyrolysis of the rubber since most of the rubber components have volatilized during the heating. The presence of carbon black is apparent in the chars from both wastes, as illustrated in Fig. 5b and d.

Surface area is one of the most important indicators of the adsorption capacity of porous materials, while the BET model is the

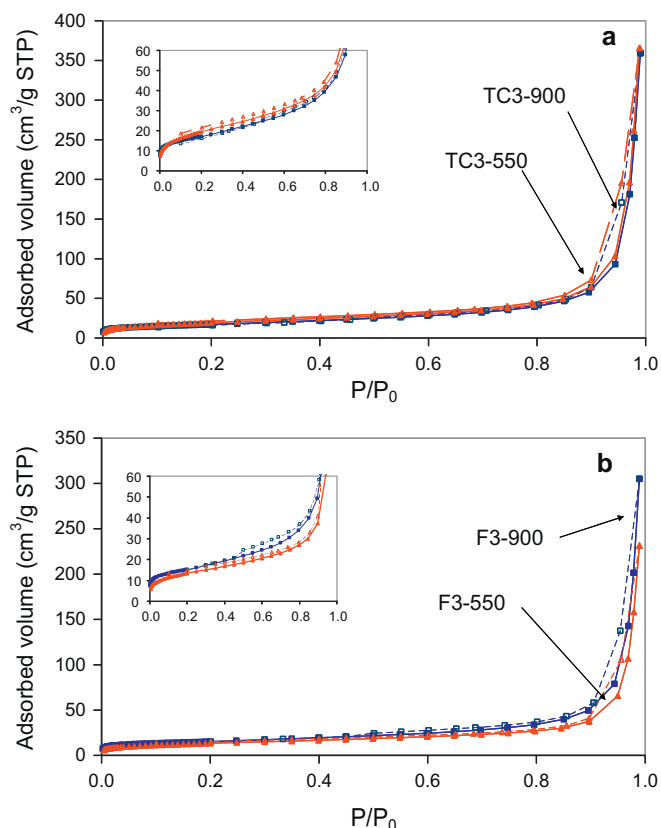


Fig. 6. N_2 isotherms of the chars from TC3 (a) and F3 at 500 and 900 °C. Open symbols correspond to desorption.

generally accepted method for evaluating it. Fig. 6a and b displays the adsorption/desorption N_2 isotherms of the 900 °C and 550 °C chars obtained from TC3 and F3. The isotherms are of type IV. All of them have a hysteresis loop that is characteristic of mesoporous materials [45,46]. The shape of the N_2 isotherms is similar to those recorded by other authors [47], but with a greater degree of hysteresis and less microporosity development. In the case of the TC3, N_2 uptake does not show any variation with the temperature of char preparation. For F3 the amount of N_2 adsorbed increases slightly with the rise in pyrolysis temperature, indicating that an increase in temperature produces a modification of the porous texture of the chars obtained from the F3.

Table 4 shows the porous structure parameters calculated from the N_2 adsorption isotherms. The total pore volume (V_T) was calculated for relative pressure values of around 0.97. To evaluate the volume of mesoporosity it was assumed that the microporosity volume can be calculated by applying the Dubinin–Raduskevich equation to the N_2 adsorption data up to relative pressures of 0.015. Mesopore volume was also calculated by applying the DFT method to the N_2 isotherm adsorption values. The values in parenthesis represent the percentage of mesopores with respect to the total pore volume. The BET surface areas do not show any great variations with the increase in temperature for either of the wastes.

Table 4
Textural characteristics of the chars.

	TC3-550	TC3-900	F3-550	F3-900
S_{BET} (m^2/g)	68	61	48	55
V_T (cm^3/g)	0.30	0.28	0.17	0.22
V_{meso} (cm^3/g)	0.27 (90%)	0.26 (93%)	0.15 (88%)	0.20 (91%)
$V_{mesoDFT}$ (cm^3/g)	0.24	0.25	0.12	0.19

Values in parenthesis represent the percentage of mesopores.

Values of the same order of magnitude were found in the literature for unactivated chars. Thus, Suuberg and Aarna [47] obtained chars with a surface area in the 54–87 m^2/g range while Kaminsky and Mennerich [7] recorded areas between 76 and 85 for chars produced between 500 and 600 °C. Koreňová et al. [43] reported different areas for chars obtained from tread and sidewall, the latter showing values similar to those of this work. Chaala et al. [44] who also employed sidewall obtained chars with a surface area of 43 m^2/g , which is similar to the area reported for the char from F3. Other authors however found that increasing the temperature led to an increase in the surface area [48]. The tyre crumbs show a slightly greater surface area and total pore volume than the fibres at both temperatures. The surface areas of the chars obtained in the present work correspond to those of semireinforcing and nonreinforcing carbon blacks [41]. In agreement with the results of other authors [47,49–51] the contribution of mesoporosity to the total pore volume was found to be very important in these types of char. The char TC3-550 presented a surface area and mesopore volume similar to that observed by other authors [40,42,52]. Increasing the temperature did not produce an increase in surface area, although a slight increase in mesopore volume was observed in the case of F3-900. Chars pyrolyzed at 550 °C and activated by a post-pyrolysis oxygenation process in mild conditions [40] gave similar textural properties to those of F3 (the oxygen content was similar in both cases). However, an increase in activation temperature produced an increase in surface area and mesopore volume [53].

The micropore volume calculated by subjecting the nitrogen isotherm data to a DR micropore analysis gives a micropore volume estimate of 0.02 cm^3/g for F3-550, F3-900 and TC3-900, while for TC3-550 a value of 0.03 cm^3/g is obtained, similar to the value recorded by Suuberg and Aarna [47] (0.027 cm^3/g). However this is lower than that reported by González et al. [50] (0.05 cm^3/g).

The mesoporosity volume calculated by the two methods explained in Section 2 (Table 4) is very similar for all four chars (those produced from TC3 and F3 at both temperatures) and constitutes a percentage of more than 88% of the total pore volume. However, the mesopore volume proved to be slightly higher in the case of the chars from TC3 than in the char derived from the fibres at both temperatures.

In the case of TC3 a rise in temperature does not produce a variation in mesopore volume, 0.27 vs 0.26 cm^3/g . Nevertheless in the case of F3 an increase in temperature produces an increase in mesopore volume from 0.15 to 0.20 cm^3/g . The char derived from F3 at 550 °C will contain, apart from carbon black and mineral matter, some particles derived from the polymers that constitute the reinforcement. Further heating of F3 to 900 °C produces a char with porous characteristics similar to those of TC3-900 (Table 4).

4. Conclusion

The GCV of the gas produced from the pyrolysis of TC3 and F3 is high enough to justify using the gas to fuel the process itself, although it is higher in the gas from TC3 than in that from F3, the most significant difference being the higher percentage of CO_x in the case of F3. The liquid obtained from the pyrolysis of TC3 and F3 has a very complex composition including a large amount of limonene. Compounds such as cyclopentanone, caprolactam, benzonitrile, methylbenzonitrile, N-hexylbenzamide and benzoic acid, derived from the thermal decomposition of the polymers that compose F3, were detected in the oil from F3. The chars obtained from TC3 and F3 have low BET surface areas in the 48 and 68 m^2/g range. Consequently, these need to be activated prior to being used as activated carbon. Their high ash content is clearly a drawback, and so a demineralization process is needed to recover the carbon black present in the char. In summary, the characteristics of the products

derived from the pyrolysis of F3 are of a similar quality to that of TC3, although an increase in the pyrolysis temperature has a greater influence on the products of F3 pyrolysis than on those of TC3. Consequently, a higher pyrolysis temperature is needed to ensure the complete decomposition of the constituents of F3.

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