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

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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 77K and under CO_2 at 273K. The chars were also examined by scanning electron microscopy (SEM). The oils were subjected to Fourier spectrosocopy (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.

Keywords: Coal, scrap tyres, carbonization, chars, pyrolysis oil.

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 hydropyrolysis 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. Figure 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:

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

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

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

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:

$$d_p\,(nm) = \frac{1244}{P(MPa)} \qquad (3)$$

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 (VT) 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 (VT) 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 precedure 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:

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

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

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

2.4. FTIR spectroscopy of the oils obtained in the two ovens.

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 measured at a resolution of 4 cm^{-1} to obtain the spectra.

3. RESULTS AND DISCUSSION

The reinforcing fibre (RF) is a very heterogeneous material and so, in order to use representative samples, it was separated into two parts: the cord or fibre (F) and the microfibre (MF) which is a fluff with some fine rubber attached to it. The separation of RF gave rise to 54 wt% of F and 46 wt% of MF. These percentages were used in all the experiments.

Table 1 shows the volatile matter, ash and elemental composition of the raw materials used. The two wastes present a higher volatile matter and ash contents than the coal. Consequently it was though that blending these wastes with the coal would produce an increase in the char yield together with a decrease in the ash content. A comparison of the composition of F and MF shows that F contains a larger amount of rubber than the microfibre. Also noticeable are the high oxygen and low carbon contents in MF which is in agreement with its low C/H atomic ratio. The highest sulphur content corresponds to the tyre crumbs.

3.1. Pyrolysis experiments

Pyrolysis experiments with the two wastes and the coal were carried out in the two types of oven: a rotary oven and a fixed bed oven. Blends of each of the wastes with the coal were prepared in a proportion of 1:1 and pyrolyzed. The yields of the three products obtained are displayed in Table 2. TC gave a char yield of 41 wt.% in the rotary oven compared to 38 wt.% in the fixed bed oven, which is higher than that obtained for RF. The differences in the case of RF and the coal are not as great. Other authors [5,14,15,16] have reported char yields which are similar to those found in the present research work in the 38 wt.% and 42.3 wt.% range depending on the final temperature and the configuration of the oven. The coal produced mainly char as a result of the pyrolysis and the values obtained in both ovens are very similar (65 wt.%

RO vs. 66 wt.% FB). In the case of the blends, the char yield for the blend containing TC is also higher in the RO than in the FB oven (55 wt.% vs 52 wt.%).

The yields calculated by applying the additivity law are presented in Table 2 in parenthesis. In the case of the RF:coal blend pyrolyzed in the FB oven the experimental and calculated yields are identical. Only the blend that contains TC presents slightly higher experimental values than the calculated char yield. Blending TC and RF with the coal char yield increased by 14 % and 14 % in the case of TC and 17 % and 18 % in the case of RF, after pyrolysis in the RO and the FB respectively.

A considerable difference can also be observed in the oil and gas yields (Table 1). The oil yield is always greater in the fixed bed oven than in the rotary oven, unlike the gas yield. In order to confirm these results extra carbonization tests were carried out in the rotary oven and then in a set-up similar to that designed to collect oils from the FB (Figure 1). The results obtained confirm the previous results, since no oil was collected in the ice-cooled trap. The differences in the oil and gas yields in 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 size and shape. It is in this hot zone where the non-condensed oil gave, on the one hand, a larger amount of non-condensable gases and on the other, a more condensed oil because of secondary reactions. Table 3 shows the results reported in the literature for oil yields during the pyrolysis of tyre crumbs. Low yields in the 23 and 33 wt.% range [19,20,21] together with other values in the 53 and 59 wt.% range were obtained. The factors responsible for these differences have been reported in the literature [19,20,21] to be related to the final temperature, the size and type of reactor, heating rate, the efficiency of heat transfer and the residence time of the gas in the hot zone.

The possibility that synergism would occur between the components of the blends was thought to be likely firstly because polymers in RF melt during heating and secondly because movement of the sample during heating in the rotary oven could favour blending of the components. In addition thermal decomposition of the precursors and blends had been studied in a previous work [**22**] and it was shown that there was a common temperature range of precursor decomposition.

Nevertheless, the mass balances carried out show that there was no systematic trend towards a higher char yield in either oven. Moreover a comparison of the experimental and calculated yield values revealed no synergistic improvement from the use of a rotary oven.

3.2. Characteristics of the chars

The results of the ash content and elemental analysis of the chars are shown in Table 4. The ash content of the TC and RF chars increases with respect to that of the initial materials due to their high volatile matter content (Table 1). It can be seen that the ash from the TC char has the highest value. Blending the two wastes with coal produces a decrease in ash and sulphur and an increase in carbon content. In general, the ash content is higher in the chars prepared in the FB reactor. The highest carbon content in the chars from single components corresponds to the char from the coal followed by the char from RF and TC. Consequently the RF/Coal blend has the second highest C content. The char from TC presents the largest C/H atomic ratio due to its low H content.

The carbonization of blends of coal with the two tyre wastes produces char with similar elemental compositions in both ovens. The porous characteristics, as determined by means of He true density, Hg apparent density and Hg porosimetry are presented in Table 5. There is no apparent trend towards a higher pore volume or porosity in either of the ovens. Nevertheless it can be seen that in the case of the chars from the blends, the porosity is greater in RO than in FB, especially in the TC/Coal blend. The TC char presents the highest porosity.

Hg porosimetry is the technique most widely used to assess macroporosity (pore size greater than 50 nm) in carbon materials [23]. Hg does not wet the carbon surface and the pressure needed to introduce Hg into the pores is related to the size of the pores by means of the Washburn equation. This relationship allows the pore size distribution to be determined. Figure 2 shows the pore size distribution corresponding to the chars from TC, RF and the coal, which was obtained by means of Hg porosimetry. The macropore volume for all three samples is higher in the chars from FB than in those from RO. The mesopore volume of the char from the coal is very low while that of TC is very high with values reaching 0.424 and 0.474 cm^3/g for the RO and the FB ovens respectively. In the case of RF the pore size distribution of the char varies depending on the oven. In the RO oven the mesopore volume is larger than both the macropore and micropore volume but for the chars produced in the FB oven the trend is Vmacro>Vmeso>Vmicro. The pore size distribution of the char from the coal is similar in both ovens. It is mainly macroporous, the amount of micropores being approximately half that of the macropores. The introduction of coal blended with the two wastes produces very important changes in the pore size distribution of the chars.

The pore size distribution corresponding to the blends of the two wastes with coal (Figure 3) was studied taking into account the pore volume of the chars from the individual materials. The differences observed between the pore sizes obtained in the two ovens are very low, although the chars from the blends produced in FB show a higher percentage of mesopores and a lower percentage of micropores. The char from the coal is predominantly macroporous, whereas the char from TC has a mesoporosity of approximately 50%. Char RF shows similar macro and mesoporosities. The inclusion of coal produces an increase in the macropore volume to values of around 37 % in the case of TC/Coal and to 51% in the case of the RF/Coal blend. The TC/Coal blend presents a Vmacro value very similar to its Vmicro value but the presence of coal in the blend halves the Vmeso present in the char from TC.

The pore size distribution of the chars from the blends was calculated by applying the additivity law. The experimental and calculated values are similar with the exception of the experimental Vmicro value corresponding to the char from TC/Coal which is higher than the calculated one.

The N_2 adsorption isotherms obtained were type IV with a hysteresis loop which denotes the presence of mesopores. The isotherms for each of the five samples in the two ovens are very similar. The BET equation was applied to obtain the parameters presented in Table 6. The BET surface area, VT and Vmeso obtained for the chars prepared in the two ovens are all very similar. The S_{BET} obtained for the TC char is similar to that reported by other authors [3,15,24] ranging between 60 to 80 m^2/g for non-activated chars. RF has a slightly lower surface area than TC. On the other hand, the coal has a S_{BET} of <1 m^2/g. Consequently its addition to any of the two wastes halves the S_{BET} of the chars from the blends. It is apparent from the data presented in Table 6 that more that 90% of the VT corresponds to the mesopore size (i.e. between 2 and 50 nanometers). S_{BET} was calculated taking into account the surface area of the two components of the blends and the additivity law. The calculated results are very similar to the experimental ones, i.e. neither of the two ovens favours synergism.

The most widely used adsorptive is N_2 at 77K. However, to assess the porosity of chars or low activated carbons [**25,26**] the use of CO_2 as adsorptive would be preferable because the higher temperature used for CO_2 adsorption would facilitate the entrance of the gas into the narrow pores. Because the char from the coal has a S_{BET} lower than 1 m^2/g, the CO_2 adsorption isotherms were determined in order to obtain a better knowledge of the entire range of porosity present in the samples. Moreover, an analysis of the CO_2 adsorption isotherms at 273 K would be useful for quantifying the microporosity corresponding to pores with sizes lower than 0.7 nm [26]. Table 7 shows the adsorbed volume (W_0), the activation energy (E_0), the micropore size (L) and the surface area of the micropores (Smi). The chars prepared from the coal present the highest micropore volume (W_0) and accordingly the chars from the blends produce carbons with a higher W_0 than the chars from the tyre wastes. The chars obtained from the blends in the RO oven present W_0 and Smi values slightly higher than those corresponding to the chars produced in the FB. The micropore volume obtained from the N_2 isotherms (Table 6) is lower than that calculated from the CO_2 isotherms (Table

7) except for the char from TC. This is because the microporosity of the chars is too narrow for N_2 to penetrate at 77K [27]. In the case of the char from TC the reason is that it is mainly mesoporous.

In order to obtain a better appreciation of the characteristics of the blends, the chars were examined by means of scanning electron microscopy (SEM). Figure 4 shows the topography of the chars from the tyre and coal waste. TC is composed of elastomers, carbon black and other inorganic fillers. Therefore, in addition to carbon black, the char must contain some carbon originating from the rubber, even though the char yield of this rubber is low. Figure 4a shows the presence of solid material with different characteristics in the char from TC together with some mineral matter. The reinforcing fibres contain, apart from the polymers that constitute the fibres, a small amount of rubber which remains stuck to their surface due to difficulties encountered in the separation process. For this reason Figure 4b shows, apart from the fibres, other carbon material that is derived from the rubber. The presence of mineral matter in the fibres is also seen in Figure 4c which shows a close-up of the fibres. The general appearance of the char from the coal is illustrated in Figure 4d. Considering that no differences were observed in the textural characteristics of the chars obtained in the two ovens, Figure 5 only presents micrographs of the chars produced in the RO from the carbonization of the blends. Figure 5a shows char particles from the coal and TC. In agreement with the textural characterization results, it can be seen that no interaction occurred during the pyrolysis of the two components of the blends. The same applies to Figure 5b where particles corresponding to the coal, the rubber and the fibres are shown in the SEM micrograph.

3.3. Characteristics of the oils

The elemental analysis of the oils obtained from the two ovens is included in Table 8. The oils from RO have higher C, N and S contents but lower O contents. In addition, the C/H atomic ratio is higher in the case of the RO oils indicating a higher degree of condensation. From the results presented in Tables 4 and 8, the sulphur content of the FB chars appears to be higher than that of the chars prepared in the RO oven. In the reaction system sulphur comes mainly from TC or RF (see Table 1) and its presence in these materials is due to the vulcanization process. The reason for the differences in sulphur distribution between the char and tar in the two ovens may be related to the different configurations of the ovens and the more drastic conditions present in the RO oven with the possibility of secondary reactions.

In order to obtain a better knowledge of the composition of the oils, FTIR was used to identify the functional groups. It was also thought that a qualitative study of the spectra [28,29] could be useful for comparing the differences between them. The differences were attributed to the carbonization conditions in each oven. Figures 6 and 7 show the spectra corresponding to the oils obtained in the two ovens from TC, RF, the coal and the blends respectively. The 3120 and 2997 cm^{-1} wavenumber range which is assigned to the stretching of aromatic C-H shows a higher intensity in the oils from RO than in those from FB, while the band between 2997 and 2730 cm^{-1} corresponding to the stretching of aliphatic C-H reflects a lower intensity in the tars from RO. In the oils obtained from FB the band between 1770 and 1600 cm^{-1} which is assigned to C=O, indicates that various types of C=O groups (esters, ketones, aldehyde, carboxylic or a combination of these groups) have a higher intensity. The band at 1600 cm^{-1} which corresponds to aromatic C=C is present in the oils from both ovens. The bands at 1438 and 1377 cm^{-1} corresponding to bending vibrations of methylene and methyl groups indicate the length of the aliphatic chains. The range between 900 and 700 cm^{-1} is usually assigned to aromatic CH out-of-plane bending modes, indicating the presence of substituted aromatic rings. The tars from RO present bands in this region, whereas the tars from FB do not, the oil from the coal being an exception. The differences in the characteristics of the tars indicate that the reaction conditions in the RO are more severe. A longer reaction time in the hot zone of the reactor results in secondary reactions which lead to the appearance of larger aromatic compounds. The presence of a larger amount of oxygenated compounds in the tars from FB than in those from RO also confirms that the compounds in RO may start to react once they have formed. The results obtained from FTIR are in agreement with the higher C/H atomic ratio of the RO oils and the higher O content of the oils produced in the FB oven.

Tyre rubber is known to be composed of polyisoprene, styrene-butadiene and polybutadiene rubbers. 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 has been proposed by some authors [5,14].

The amount of aromatics depends on the conditions in the reactor and on the possibility of secondary reactions [30,31]. This is in agreement with the mass balances for both ovens and with the presence of more aromatic compounds in the RO together with a higher percentage of permanent gases. Short residence times in the hot zone of the reactor are considered to favour the formation of liquid products, since the pyrolysis gases and vapours condense before any further reaction breaks down the higher molecular weight species into gaseous products [14]. These conditions in the FB minimize the possibility of secondary reactions that give rise to larger amounts of less aromatic, less condensed oil and a higher amount of oxygenated functionalities.

Conclusions

The pyrolysis of blends of coal and two wastes from scrap tyres was carried out in two ovens of different configuration (i.e. a fixed bed and a rotary oven). Mass balances were calculated. It was found that, although the char yield obtained was similar, the oil and gas yields depended on the type of oven. RO promoted the production of gas while FB gave rise to a larger amount of oil. The chars obtained from RF and TC were found to be mainly mesoporous (especially that obtained from tyre crumbs) whereas the char from the coal contained a larger amount of macro and micropores, as determined by mercury porosimetry. N_2 and CO_2 isotherms revealed that the characteristics of the chars from the two ovens were similar. However, the oil produced in the rotary oven was more aromatic and contained a smaller amount of oxygenated compounds as a consequence of the longer residence time of the gas in the hot zone of the reactor.

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References

[1] Sienkiewicz M, Kucinska-Lipka J, Janik H, Balas A. Progress in used tyres management in the European Union: A review. Waste Manage 2012;32: 1742–1751.

[2] Cunliffe AM, Williams PT. Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires. Energ Fuel 1996; 13:166-175.

[3] Murillo R, Aylón E, Navarro MV, Callén MS, Aranda A, Mastral AM. The application of thermal processes to valorise waste tyre. Fuel Process Technol 2006; 87: 143-147.

[4] Fernández AM, Barriocanal C, Alvarez R. Pyrolysis of a waste from the grinding of scrap tyres. J Hazard Mater 2012; 203– 204:236– 243.

[5] Laresgoiti MF, Caballero BM, De Marco I, Torres A, Cabrero MA, Chomón MJ. Characterization of the liquid products obtained in tyre pyrolysis. J Anal Appl Pyrol 2004; 71: 917–934.

[6] Gonzalez JF, Encinar JM, Canito JL, Rodríguez JJ. Pyrolysis of automobile tyre waste.Influence of operating variables and kinetics study. J Anal Appl Pyrol 2001; 58-59:667-683.

[7] Williams PT, Besler S. Pyrolysis-thermogravimetric analysis of tyres and tyre components. Fuel Process Technol 1995; 74: 1277-1283.

[8] Seidelt S, Müller-Hagedorn M. Description of tire pyrolysis by thermal degradation behaviour of main components. J Anal Appl Pyrol 2006; 75:11-18.

[9] Purcell AH. Tire recycling: research trends and needs. Conserv Recycling 1978; 2:137- 143.

[10] Maderuelo-Sanz R, Nadal-Gisbert AV, Crespo-Amorós JE, Parres-García F. A novel sound absorber with recycled fibers coming from end of life tires (ELTs). Appl Acoustics 2012; 73: 402–408.

[11] Mastral AM, Murillo R, Callén MS, García T. Evidence of coal and tire interactions in coal–tire coprocessing for short residence times. Fuel Process Technol 2001; 69:127–140.

[12] Önenç S, Brebu M, Vasile C, Yanik J. Copyrolysis of scrap tires with oily wastes. J Anal Appl Pyrol 2012; 94:184-189.

[13] Stoeckli F. Characterization of microporous carbons by adsorption and immersion techniques. In: Patrick JW, editor. Porosity in carbons, London: Edward Arnold; 1995, p. 67-92.

[14] Cunliffe AM, Williams PT. Composition of oils derived from the batch pyrolysis of tyres. J Anal Appl Pyrol 1998; 44: 131-152.

[15] Kyari M, Cunliffe A, Williams PT. Characterization of oils, gases and char in relation to the pyrolysis of different brands of scrap automotive tires. Energ Fuel 2005; 19: 1165-1173.

[16] San Miguel G, Fowler GD. Pyrolysis of tire rubber: porosity and adsorption characteristic of the pyrolytic chars. Ind Eng Chem 1998; 37: 2430-2435.

[17] Kawakami S, Inoue K, Tanaka H, Sakai T. Pyrolysis process for scrap tyres. In: Jones JL, Radding SB, Editors. Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, Washington DC: American Chemical Society Publishers; 1980, p. 557-572.

[18] Williams PT, Besler S, Taylor DT. The pyrolysis of scrap automotive tyres. Fuel Process Technol 1990; 69: 1474-1482.

[19] Kaminsky W, Sinn H. Pyrolysis of plastic waste and scrap tyres using a fluidised bed process. In: Jones JL, Radding SB, Editors. Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, Washington DC: American Chemical Society Publishers; 1980, p. 423-439.

[20] Collin G. Pyrolytic recovery of raw materials from special wastes. In: Jones JL, Radding SB, Editors. Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, Washington DC: American Chemical Society Publishers; 1980, p. 479-484.

[21] Williams PT, Besler S, Taylor DT. The batch pyrolysis of tyre waste-fuel properties of the derived pyrolytic oil and overall plant economics. Proc Inst Mech Eng 1993; 207: 55-63.

[22] Acevedo B. Barriocanal C, Alvarez R. Proceedings of the 9th ICCS&T Conference. 2011 Oviedo.

[23] Porosity in carbons: Characterization and applications. Edited by JW Patrick. Eduard Arnold 1995.

[24] Ariyadejwanich P, Tanthapanichakoon W, Nakagawa K, Mukai SR, Tamon H. Praparation and characterization of mesoporous activated carbon from waste tires. Carbon 2003; 41: 157-164.

[25] Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A. Usefulness of CO2 adsorption at 273 K for the characterization of porous carbons. Carbon 2004;42: 1233–1242.

[26] Garrido J, Linares-Solano A, Martin-Martinez JM, Molina-Sabio M, Rodríguez-Reinoso F, Torregrosa R. Use of N_2 vs. CO_2 in the Characterization of Activated Carbons. Langmuir 1987; 3: 76-81.

[27] Rodríguez-Reinoso F, Garrido J, Martín-Martínez JM. Molina-Sabio M, Torregrosa R. The combined use of different approaches in the characterization of microporous carbons. Carbon 1989; 27: 23-32.

[28] Painter PC, Starsinic M, Squires E, Davis AA. Concerning the 1600 cm-1 region in the i.r. spectrum of coal. Fuel 1983; 62: 742-744.

[29] Smith B. Infrared Spectral Interpretation: a systematic approach. Boca Raton: CRC Press; 1998.

[30] Williams PT, Taylor DT. Aromatization of tyre pyrolysis oil to yield polycyclic aromatic hydrocarbons. Fuel 1993; 72: 1469-1474.

[31] Cypres R, Bettens B. Production of benzoles and active carbon from waste rubber and plastic materials by means of pyrolysis with simultaneous post-cracking. In: Ferrero GL, Maniatis K, Buekens A, Bridgwater AV, Editors. Pyrolysis and Gasification, London: Elsevier Applied Science; 1989, p. 209-229.

Table 1. Main characteristics of the raw materials.

	TC	F	MF	RF[d]	Coal
VM[a] (wt.% db[b])	65.5	66.5[e]	80.4[e]	72.9	36.2
Ash(wt.% db)	7.5	6.0[f]	3.0[f]	4.6	6.4
C (wt.% db)	78.5	77.6	57.2	68.2	78.6
H (wt.% db)	7.0	7.0	6.3	6.7	4.5
N (wt.% db)	1.3	0.4	2.0	1.1	2.0
S (wt.% db)	2.13	1.48	0.51	1.03	0.51
O (wt.% db)	3.9	7.8	31.2	18.6	8.2
C/H[c]	0.93	0.92	0.76	0.85	1.46

a: volatile matter, b: dry basis, c: atomic ratio, d: calculated from F and MF data considering 54 wt% of F and 46 wt% of MF, e: from thermogravimetric analysis.

Table 2. Yields obtained in the two ovens.

		Char (wt%db)	Oil (wt%db)	Gas (wt%bs)
TC	RO	41	28	31
	FB	38	58	4
RF	RO	29	34	37
	FB	30	56	14
Coal	RO	65	11	24
	FB	66	20	14
TC/Coal	RO	55 *(53)*	22 *(20)*	23 *(28)*
	FB	52 *(52)*	38 *(39)*	10 *(9)*
RF/Coal	RO	46 *(47)*	23 *(22)*	31 *(31)*
	FB	48 *(48)*	37 *(38)*	15 *(13)*

The values in parenthesis were calculated applying the additivity law.

Table 3. Data from the literature on the oil yields from the pyrolysis of tyres.

High oil yields		Low oil yields	
57% (850 °C)	Present work (FB)	24% (850 °C)	Present work (RO)
53.1% (600ºC)	Cunliffe y Williams [14]	27% (840ºC)	Kaminsky y Sinn [19]
53% (540-640ºC)	Kamakami [17]	23% (700ºC)	Collin [20]
58.8% (720ºC)	Williams [18]	32.5% (700-950 °C)	Williams [21]

Table 4. Elemental analysis and ash content of the chars.

		Ash (%wt.db)	C (%wt.db)	H (%wt.db)	N (%wt.db)	S (%wt.db)	O (%wt.db)	C/H[a]
TC	RO	17.2	77.4	0.4	0.4	2.28	3.1	16.13
	FB	20.4	73.9	0.4	0.4	2.54	3.5	15.40
RF	RO	13.1	79.0	0.8	1.2	1.72	4.8	9.49
	FB	11.9	82.1	1.0	1.0	1.74	2.5	6.18
Coal	RO	6.6	86.5	0.9	1.9	0.44	4.0	8.01
	FB	10.0	84.5	0.8	1.4	0.57	3.3	8.80
TC/Coal	RO	12.2	80.9	0.7	1.1	1.17	4.5	9.63
	FB	11.7	82.3	0.7	1.0	1.29	3.3	9.80
RF/Coal	RO	8.0	85.0	0.9	1.7	0.97	3.7	7.87
	FB	9.6	84.6	0.9	1.3	0.99	2.8	9.99

a: C/H atomic ratio.

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Table 5. True, apparent density, total pore volume and porosity of the chars.

		ρ_{Hg} (g/cm^3)	ρ_{He} (g/cm^3)	V_T (cm^3/g)	ε(%)
TC	RO	0.72	1.86	0.84	61.1
	FB	0.68	1.87	0.93	63.4
RF	RO	0.82	1.87	0.69	56.2
	FB	0.84	1.83	0.65	54.2
Coal	RO	1.07	1.80	0.38	40.8
	FB	0.98	1.74	0.45	43.8
TC/Coal	RO	0.84 (*0.94*)	1.84 (*1.82*)	0.65 (*0.56*)	54.2 (*48.5*)
	FB	0.92 (*0.89*)	1.79 (*1.78*)	0.53 (*0.60*)	48.9 (*50.0*)
RF/Coal	RO	1.00 (*0.96*)	1.81 (*1.82*)	0.45 (*0.52*)	44.7 (*45.4*)
	FB	1,03 (*0.94*)	1,80 (*1.77*)	0,41 (*0.51*)	42,6 (*47.1*)

ε: Porosity calculated with equation1. V_T calculated with equation 2.The values in parenthesis were calculated by applying the additivity law.

Table 6. Textural characteristics of the chars determined from the N_2 adsorption isotherm at 77 K.

		S_{BET}[a] m^2/g)	C[b]	r[c]	VT[d] (cm^3/g)	V_{meso}[e] (cm^3/g)	V_{meso}[f] DFT (cm^3/g)	V_{microD}[g] (cm^3/g)
TC	RO	57	118	0.99995	0.25	0.23	0.29	0.02
	FB	68	177	0.99998	0.27	0.25	0.27	0.02
RF	RO	43	147	0.99996	0.17	0.15	0.16	0.02
	FB	40	200	0.99999	0.14	0.12	0.12	0.02
TC/Coal	RO	26	137	0.99996	0.10	0.09	0.10	0.01
	FB	29	258	1.00000	0.12	0.11	0.11	0.01
RF/Coal	RO	11	186	0.99997	0.04	0.04	0.04	0.00
	FB	12	196	0.99997	0.05	0.05	0.05	0.00

a: Surface area obtained by applying the BET equation, b: BET constant, c: correlation coefficient, d: total pore volume at P/P0=0.97, e:mesopore volume, f: mesopore volume calculated from the DFT pore size distribution, g:micropore volume determined by applying the DR equation to the lower relative pressure zone of the isotherm.

Table 7. Textural characteristics of the chars obtained by applying the Dubinin-Raduskevich equation to the CO_2 adsorption isotherms.

		Wo[a] (cm^3/g)	Eo[b] (kJ/mol)	L[c] (nm)	Smi [d](m^2/g)
TC	RO	0.01	24.3	0.84	35
	FB	0.02	25.6	0.76	50
RF	RO	0.04	28.8	0.62	124
	FB	0.06	22.7	0.96	133
Coal	RO	0.17	25.9	0.75	448
	FB	0.13	29.2	0.61	437
TC/Coal	RO	0.11	23.2	0.92	250
	FB	0.09	25.3	0.77	242
RF/Coal	RO	0.14	26.0	0.74	383
	FB	0.12	27.9	0.65	360

a: Micropore volume, b: Activation energy, c: average width, d: micropore surface.

Table 8. Elemental analysis of the oils obtained in the two ovens.

		C (%wt.db)	H (%wt.db)	N (%wt.db)	S (%wt.db)	O (%wt.db)	C/H[a]
TC	RO	87.1	10.4	0.6	1.13	1.5	0.70
	FB	85.1	11.1	0.5	0.96	3.2	0.64
RF	RO	76.2	8.5	3.4	0.85	9.0	0.75
	FB	76.9	10.3	1.0	0.55	10.5	0.62
TC/Coal	RO	87.6	9.6	0.9	1.01	3.1	0.76
	FB	79.1	10.9	0.6	0.73	10.3	0.60
RF/Coal	RO	77.9	9.0	2.7	0.79	5.8	0.72
	FB	75.0	10.1	1.4	0.40	10.5	0.62

a: C/H atomic ratio.

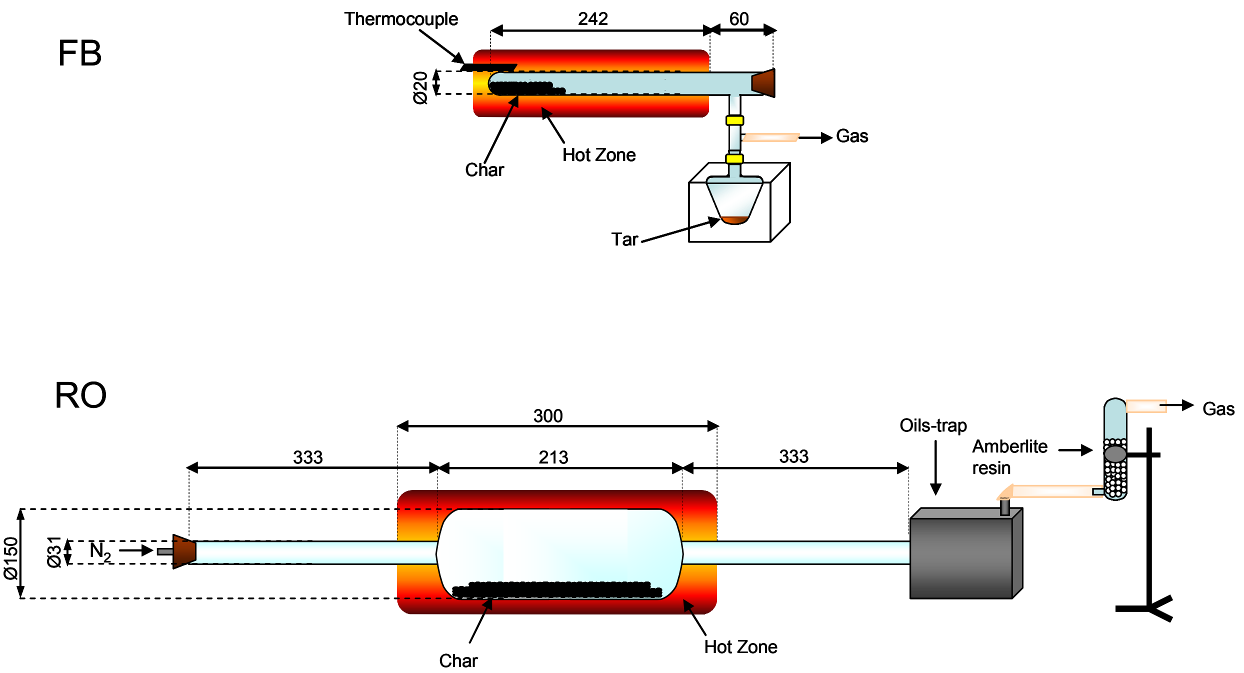

Figure 1. Diagram showing the configuration of the two ovens.

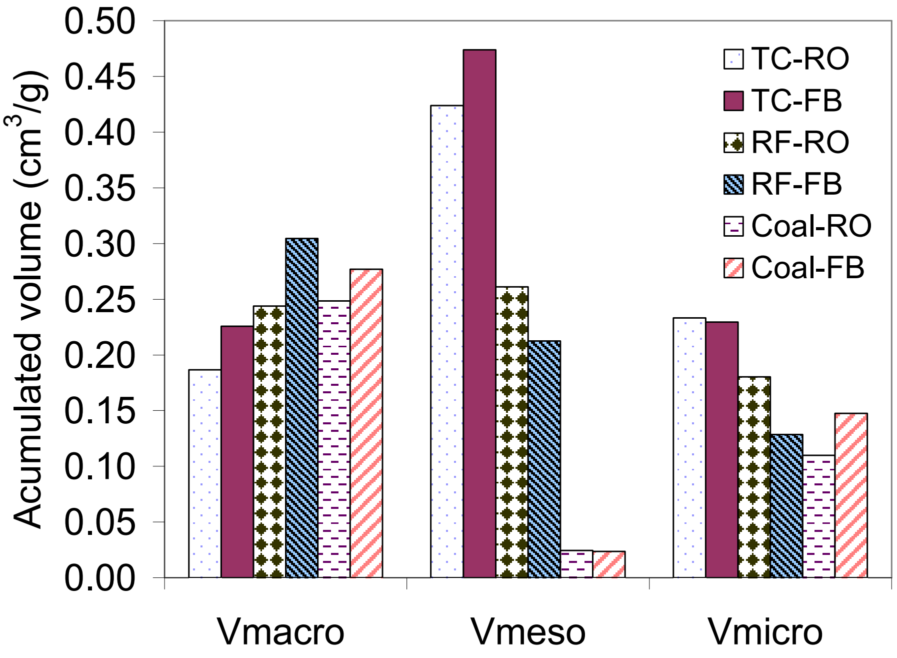

Figure 2. Pore size distribution of the TC, RF and coal chars obtained in the two ovens by means of Hg porosimetry. Vmacro:>50 nm, 50 nm<Vmeso<5.5 nm, Vmicro: <5.5 nm.

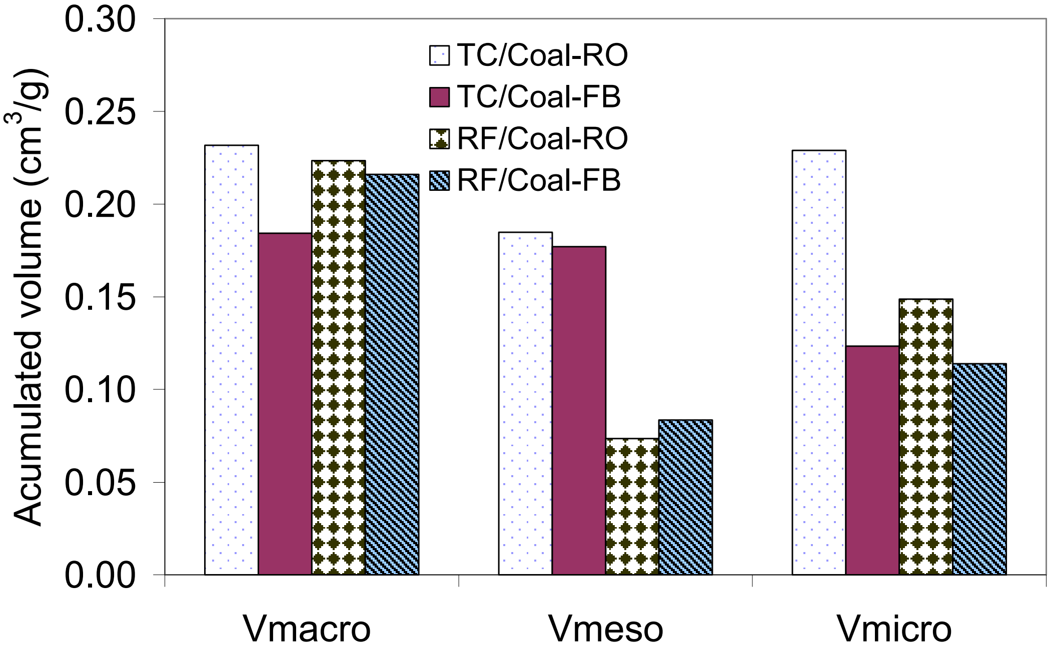

Figure 3. Pore size distribution of the chars from blends of tyre wastes and coal obtained in the two ovens by means of Hg porosimetry. Vmacro: >50 nm, 50 nm<Vmeso<5.5 nm, Vmicro: <5.5 nm.

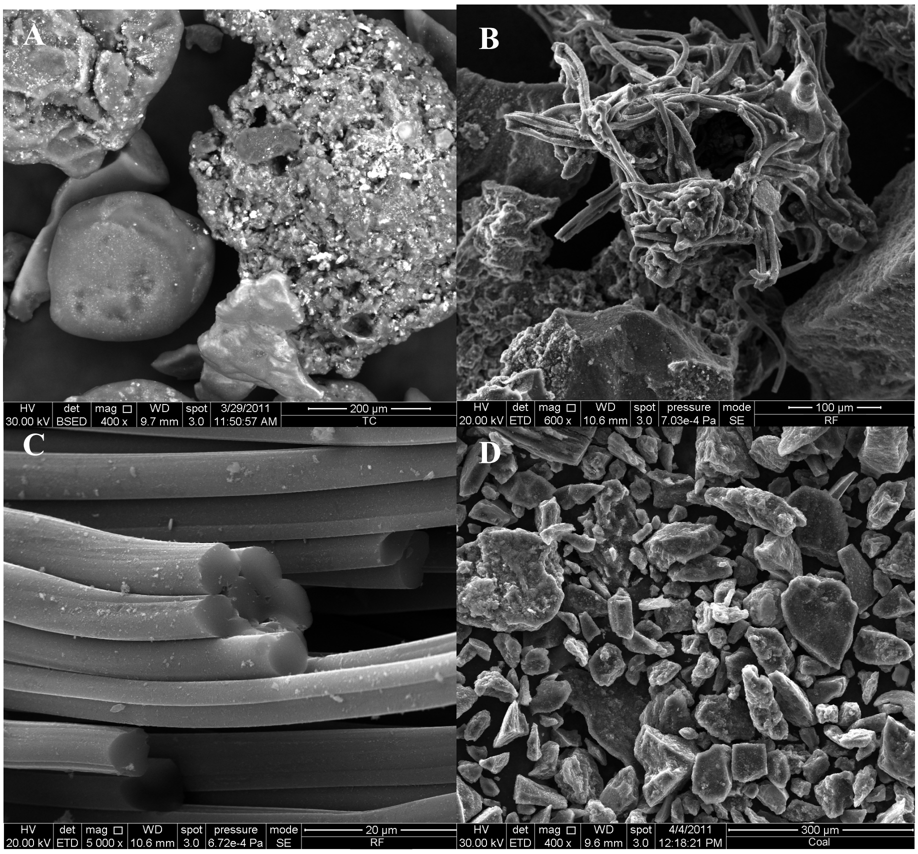

Figure 4. SEM micrographs corresponding to a) TC char, b) RF char c) Close-up of the fibres present in RF char, d) Coal Char.

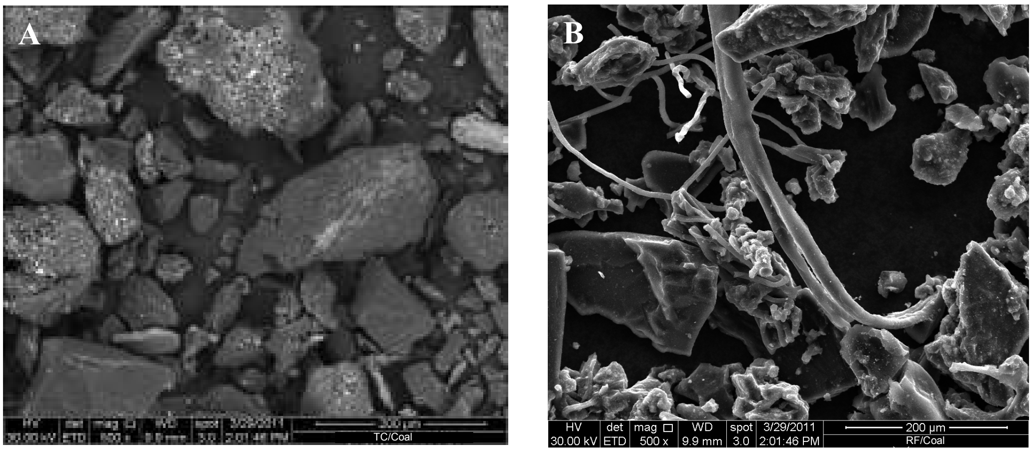

Figure 5. SEM micrographs. a) char from the TC/Coal blend, b) char from the RF/Coal blend.

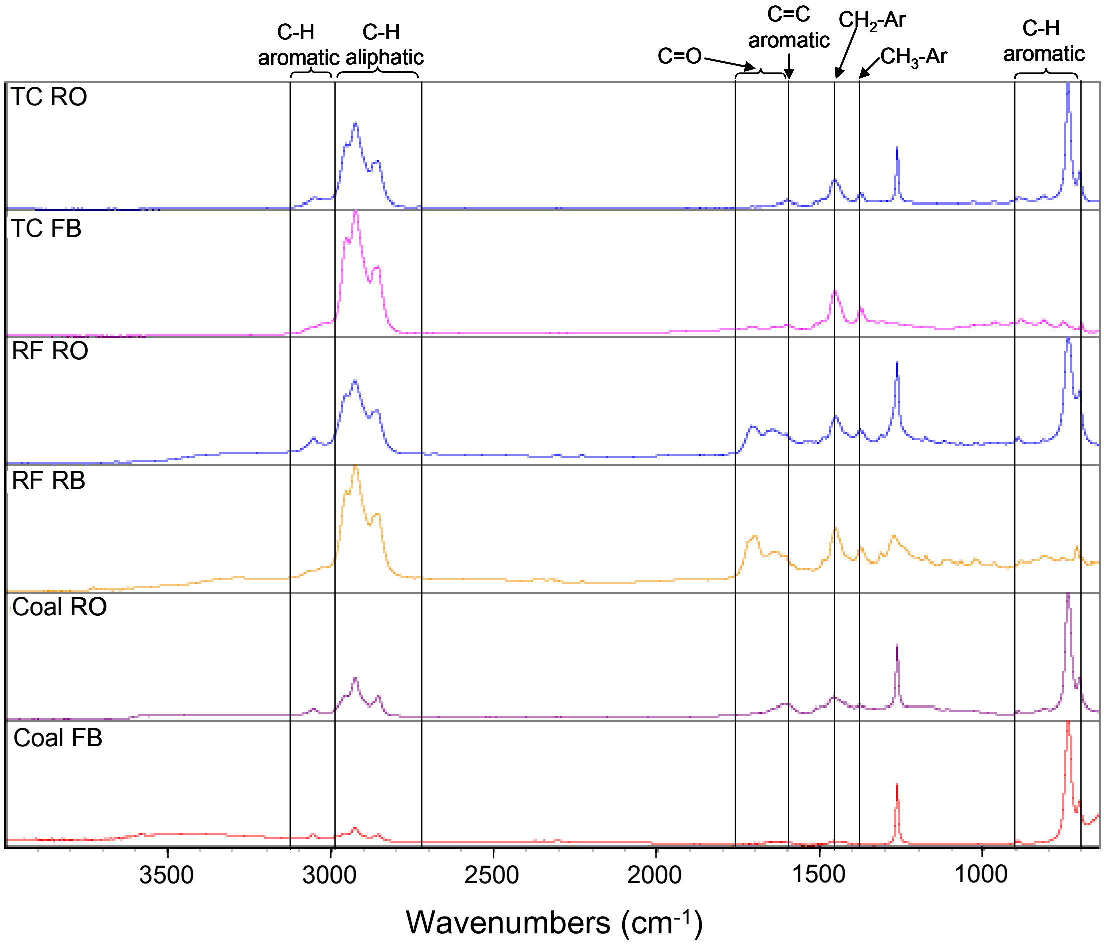

Figure 6. FTIR spectra of the oils obtained from pyrolysis in a rotary (RO) and fixed bed (FB) oven.

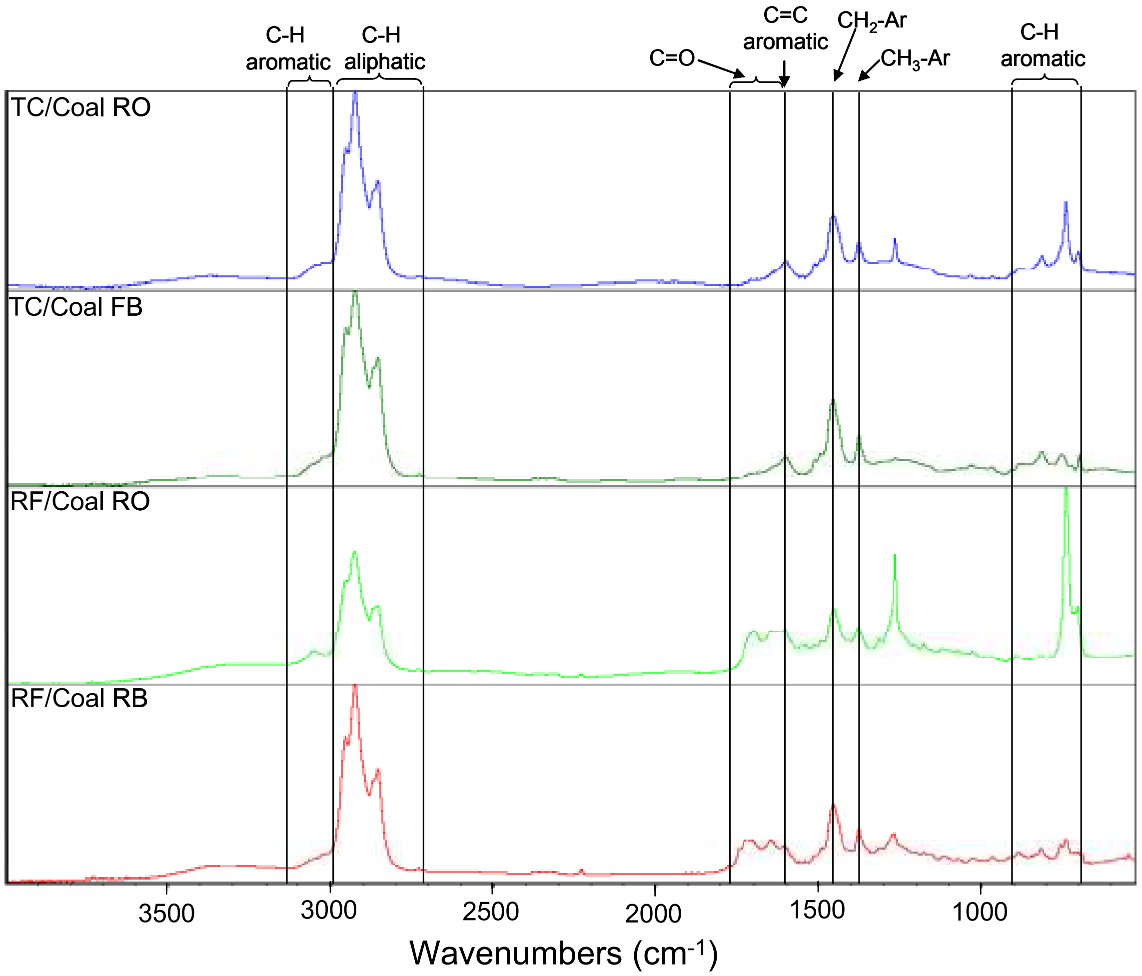

Figure 7. FTIR spectra of the oils obtained from the pyrolysis of the blends in a rotary (RO) and fixed bed (FB) oven.