

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

Beatriz Acevedo, Carmen Barriocanal*

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

*Corresponding author. Tel: +34 985 11 90 90; Fax:+34 985 29 76 62; e.mail address:
carmenbr@incar.csic.es

ABSTRACT

Two wastes from the tyre recycling industry -the fibres 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 sulphur 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.

Keywords: Pyrolysis oil, Scrap Tyres, Reinforcing Fibre, Coal, GC-MS, FTIR

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, pirolytic 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 fibre 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 fibre is usually recovered as a heterogeneous fluff made up of polymeric fibres 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 the co-pyrolysis of waste tyres with coal or 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/fibres (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 sulphur 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 cm⁻¹ to 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 minutes. 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 fibre 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 sulphur content corresponds to the bituminous waste and the tyre crumbs. The sulphur present in the tyres is due to the vulcanizing procedure that allows rubber to be converted into more durable materials. In this procedure sulphur 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. Figure 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 non-condensable gases and more condensed oil due to secondary reactions.

Blending RF and TC with coal produced in both ovens an increase in char together with a decrease in the oil and condensable products. On the other hand when RF was co-pyrolyzed with BW an increase in char and condensable products occurred.

The results of the elemental analysis together with the calorific values of the oils obtained in the two ovens are shown in Table 3. The oils produced in the rotary oven contain a higher percentage of carbon, nitrogen and sulphur while those from the fixed bed have higher percentages of hydrogen and oxygen. As a consequence the C/H atomic ratio is higher in the oils from the RO indicating a higher degree of condensation in these products. The nitrogen and oxygen contents of the oils from RF, RF/Coal and RF/BW are higher in the oils of both ovens than in those from TC. In a previous research work it was shown that RF is composed mainly of polyethylene terephthalate (PET) and polyamide [3]. The decomposition of polyamide produces nitrogen-enriched compounds whereas PET produces oxygenated compounds [3,21].

The high calorific value (HHV) of fuels is related to their elemental composition and more specifically the percentage of carbon they contain [22]. In the present research work the HHV is generally higher in the oils produced in the rotary oven. At the same time they contain a higher percentage of carbon. The oil from TC has a

higher HHV than the oil from the reinforcing fibre. Blending TC with coal yields an oil with a slightly lower HHV, but co-pyrolysis of RF with the bituminous waste increases the HHV of the oils due to the increase in carbon content. The oils produced from the pyrolysis of tyre wastes and those from their co-pyrolysis with coal and a bituminous waste are comparable to the HHVs of other fuels [20,23-26]. A common limiting factor of fuel oils is their sulphur content. For marine diesel oil the maximum limit is 2 wt.% according to the ISO 8217 standard. In the case of medium fuel oil for use in furnaces and boilers the maximum is 3 wt.%. The oils produced in the present research work have sulphur contents lower than 1.13 wt.%.

3.2. FTIR analysis of pyrolysis oils

Infrared spectroscopy is a very useful technique for identifying functional groups and types of bonds in a molecule. This technique allows not only a qualitative analysis but also a semi-quantitative analysis based on area of the absorption bands appearing at specific wavenumbers in the spectra. All of the oils obtained in the fixed and the rotary oven were analysed. In the case of the rotary oven, both oils OT and AMB were analysed.

According to the FTIR spectra these oils contain a variety of aromatic compounds with aliphatic chains, aliphatic compounds, and oxygenated functional groups, such as phenolic, hydroxyl or carbonyl groups. This study focussed on the bands which correspond to various oxygenated and nitrogenated functionalities together with C-H stretching in aromatic and aliphatic compounds and C=C bonds in aromatic compounds [3, 9, 20, 27-29].

The FTIR spectra for wavenumbers between 3500 and 2500 cm^{-1} are shown in Figure 2, while those for the 1800-1400 cm^{-1} range appear in Figure 3. In the oils from the rotary oven (RO) a wide band is observed at 3300 cm^{-1} which is absent in the oils from the FB (Figure 2) indicating the presence of OH functionalities in the RO oils. This band is more pronounced in the oils derived from RF that contains a higher percentage of oxygen. The band between 3136 and 2997 cm^{-1} corresponding to

aromatic C-H stretching is larger in the oils from RO and especially in the oil obtained from co-pyrolysis with the bituminous waste (BW). This indicates the greater aromatic character of the oils derived from RO. Co-pyrolysis with low-rank coal produces an increase in the bands corresponding to aliphatic C-H stretching (range 1997-1765 cm^{-1}). Previous research works have shown that the condensable liquids derived from low rank coals (i.e. volatile matter in the 30-35 wt.% db range) show a clear series of n-alkanes ranging from C_{11} to C_{28} together with polar compounds like phenols [16].

At 2230 cm^{-1} (Figure 3) a small band is visible in the oils produced from RF and their blends with coal and BW which corresponds to a saturated nitrile $\text{C}\equiv\text{N}$ [3,27].

Figure 3 shows that in the 1770 and 1650 cm^{-1} range which is assigned to oxygenated compounds the absorption is higher for the oils produced in FB. The oil from RF/coal co-pyrolysis presents the greatest absorption band in the range corresponding to the oxygenated compounds irrespective of the oven considered. This result is attributed to the higher oxygen contents of RF and the coal (see Table 2). The band at 1600 cm^{-1} indicates the presence of the aromatic $\text{C}=\text{C}$ bond which is present in all the spectra together with those at 1455 and 1375 cm^{-1} corresponding to bending vibrations in methyl and methylene groups [6, 9,27].

For semiquantitative purposes various indices can be calculated using the integrated area (A) of different absorption bands of the FTIR spectra. Although various indices derived from FTIR spectra have been used to evaluate the chemical characteristics of fuels [29-31], only two described in Table 1 have been employed in the present research work: 1. Ar/AI which gives an indication of the degree of aromaticity and 2. the index which indicates the ratio of oxygenated functional groups in the oils. The parameter A_{ar}/A_{al} , is calculated from the ratio of the area in the 3100-2990 cm^{-1} region corresponding to aromatic C-H versus the area in the 2990-2795 cm^{-1} region, corresponding to aliphatic C-H (CH , CH_2 and CH_3). This index was calculated to estimate the degree of aromatization in the pyrolysis oil.

As the reaction time increases, the methylene groups decrease because of the removal of methylene cross-links in the macromolecular structure and to some extent due to the decomposition of the aliphatic side chains. This results in the formation of terminal CH₃ groups and aromatic C-H bonds with ring closure reactions, all of which leads to the growth of aromatic clusters.

Figure 4 shows the values of the indices for the oils produced in the two furnaces of different configuration. It is clear in all cases that the aromaticity of the oils from RO is higher than that of the oils produced in the fixed bed reactor. This is in accordance with their higher C/H atomic ratio (Table 3). Special attention should be paid to the aromaticity of the oils produced from co-pyrolysis with BW. In a previous paper [32] the composition of two bituminous wastes similar to the one used here were studied and the aromaticity indices obtained there were 0.69 and 0.55 indicating the highly aromatic character of the wastes. The aromaticity values in this study for the oil derived from the co-pyrolysis of RF/BW were 0.32 and 0.25 in the rotary oven and the fixed bed respectively. Therefore co-pyrolysis with BW produces an increase in the aromatic character of the pyrolysis oils. The presence of compounds with oxygenated functionalities can be studied using the index calculated as the ratio of the area in the 1770-1650 cm⁻¹ range versus the area of the band at 1600 cm⁻¹ which corresponds to the stretching of the C=C bond in aromatic compounds. The oxygenated compounds are more abundant in the oils generated in the fixed bed. This result is in agreement with the higher oxygen content of the oils from the fixed bed furnace (Table 3). The reason for the higher oxygen content is to be found in the configuration of the oven. While in FB the oils are collected as they are produced, in RO the oils are allowed to undergo secondary reactions with the consequent decrease in the more reactive compounds and increase in aromatic compounds.

In the case of the two wastes, the aromatic compounds present in the oil originate from the decomposition of the polymers that constitute the 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 [23,24,33,34].

3.3 *Chromatographic analysis of the pyrolysis oil*

Figures 5 and 6 show the chromatograms corresponding to the oils from the co-pyrolysis of RF with BW and RF with coal respectively. Each figure includes the chromatograms of the oil recovered from the FB, the amberlite resin (AMB) from the rotary oven (RO) and from the oil trap (OT) of the rotary oven (RO). Peak identification has been included in the caption. It appears that all the compounds present in the FB oil are also present in the RO oil either in the amberlite resin (AMB) or in the oil trap (OT). A great variety of compounds have been identified ranging from cyclopentanone to polyaromatic hydrocarbons such as anthracene, pyrene or perylene. In the case of the blend with coal (Figure 6) the aliphatic series up to C30 has been identified.

Quantitative chromatographic analysis of the pyrolysis oils has been carried out and the results are shown in Table 4 classified according to the type of compounds. Aromatics as a function of the number of aromatic rings (benzene and indane/indene, naphthalene and fluorene, phenanthrene and fluoranthene, pyrene and perylene), terpenes, oxygen, nitrogen and sulphur containing compounds and aliphatics. Only the oil from co-pyrolysis with BW contains significant amounts of fluorene, phenanthrene, fluoranthene and pyrene. Benzene derivatives are the only aromatic compounds that are more abundant in the fixed bed than in the rotary oven. Previous studies also found these types of compounds to be present in the pyrolysis oils from tyre crumbs [6, 9, 16,35]. In the present study the influence of including coal and a bituminous waste can be observed together with the type of furnace use. The fixed bed furnace produces a higher amount of benzene derivatives and limonene while in the rotary oven there are greater proportions of indane, indene and polyaromatic compounds with 2, 3 and 4 benzene rings. These differences are due to the different residence time of the decomposition products in the hot zone of the reactor which is longer in the RO than in the FB resulting in secondary reactions like that of Diels-Alder and condensation. As a

consequence of this the amount of aromatics and permanent gases is increased and there is a reduction in aliphatic compounds [9,17, 25-28]. As explained in section 3.1 the mass balance indicates that the production of gas is higher in RO than in FB. The distribution of aliphatics in both ovens is also different in that cyclic aliphatics are more abundant in the FB, whereas the RO produces a greater proportion of non-cyclic aliphatics. This result is also due to the existence of secondary reactions in the RO.

Limonene is employed in formulation of industrial solvents, resins, and adhesives and as a dispersing agent for pigment. It is also employed as feedstock for the production of various kinds of terpenoid alcohol fragrances. It is also used as a way for avoiding the toxicity of conventional industrial solvents [36-38]. The production of limonene is specially high in the FB reactor with TC producing the highest amount of limonene in the pyrolysis oil. The reinforcing fibre also produces a considerable percentage of limonene in the FB reactor because of the rubber present in its composition. Limonene is formed from the isoprene and butadiene present in the decomposition of rubber [36,39-41]. Benzene derivatives, as in the case of limonene, are more abundant in the oils from TC and TC/coal because they are formed from styrene which is derived from the SBR (styrene-butadiene rubber) contained in rubber [33].

The amount of oxygen-containing compounds is greater in the case of oils produced in the FB which is in agreement with the results of the elemental analysis and the FTIR. The exception is the oils produced from RF and their blends with coal. It needs to be considered in this case that a high amount of benzoic acid is produced and this produces a peak whose quantification might lead to errors. The oxygenated compounds present in the oils from RF and their blends include: acids such as benzoic acid, ketones like cyclopentanone, cyclohexanone and their derivatives, esters such as methyl hexacosanoate, phenols and ethers.

Nitrogen-containing compounds are more abundant in the oil from RO and especially in the oil derived from RF and their blends with coal and BW. These

compounds are derived from the decomposition of the polyethylene terephthalate and polyamides that make up the reinforcing fibre [3]. This result is in agreement with the higher oxygen and nitrogen contents of the oils (Table 3). The nitrogen-containing aromatic compounds that have been identified include: benzonitrile, methylbenzonitrile, benzenedicarbonitrile, benzamide, N-hexylbenzamide. The aliphatic ones include: caprolactam, hexadecanonitrile and heptadecanonitrile [3, 42]. The most abundant sulphur compounds present in the oils are: benzotiazole and alkylated thiophenes [38].

The coal used in the co-pyrolysis experiments produces an increase in the non-cyclic aliphatic content, while co-pyrolysis with bituminous waste leads to a considerable increase in the aromatic compounds in both ovens.

The environmental protection agency (EPA) from USA has identified 16 PAHs as potential carcinogenic and mutagenic agents for humans [43]. Out of the list so far considered only the oil from co-pyrolysis with BW contains a high proportion of these types of compound, 53.21 % in RO and 51.63 in FB, the rest of the oils present percentages lower than 5% of this type of compounds. The following compounds of those 16 PAHs classified as dangerous by the EPA were identified in the RF/BW oil: naphthalene, acenaphthylene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, crisene, benzo[k]fluoranthene, benzo[a]pyrene.

In order to facilitate comparison between the compositions of the oils produced in both ovens various indices have been calculated (Table 5) on the basis of the percentages of various types of compounds present in the oils. According to the results from FTIR the aliphatic/aromatic compound ratio is always higher in the case of the FB oven. In addition the presence of the coal produces an increase in this ratio when it is co-pyrolyzed with TC and RF in both ovens. The presence of the bituminous waste produces a dramatic reduction in the aliphatic compounds in the oil produced in FB and RO. The condensation index calculated as the naphthalene to benzene ratio is

consistently higher in the oils from RO in agreement with the C/H ratio and aromaticity index from FTIR analysis. The alicyclic/aromatics ratio is also consistently higher in the FB oils as one would expect in view of the more drastic pyrolysis conditions of RO.

4. Conclusions

The mass balance of the carbonizations depends on the type of furnace used. The amount of oils was lower in the rotary oven because here secondary reactions occurred (condensation and Diels-Alder) which diminished the percentage of oils and thereby increased the amount of gas. In addition the higher residence time of the volatile products gave rise to a decrease in the more reactive compounds. As a consequence of this the oil produced in the RO from the two tyre wastes and their blends with coal and bituminous waste was more aromatic and had a higher C/H ratio and lower oxygen content. In contrast the oil from the fixed bed furnace presented a higher aliphatic/aromatic compound ratio, BTX and an abundance of limonene.

Tyre crumbs produced a greater amount of limonene and BTX, whereas the reinforcing fibre produced a larger amount of oxygenated and nitrogenated compounds such as ketones, acids, nitriles and amides. Blending with coal and with a bituminous waste increased the percentage of linear aliphatics and produced even more aromatic oil respectively. The bituminous waste caused a drastic reduction in the aliphatic compounds in the oil produced in both ovens.

Acknowledgements

The research leading to these results has received funding from the Spanish MICINN project reference CTM2009-10227. BA. thanks the Government of the Principado de Asturias for the award of a predoctoral grant with funding from PCTI-Asturias.

References

- [1] European Tyre & Rubber Manufacturing Association, <<http://www.etrma.org/uploads/Modules/Documentsmanager/brochure-elt-2011-final.pdf>>, 11/03/2013.
- [2] Antoniou N, Zabaniotou A. Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery. *Renew. Sust. Energ. Rev.* 2013;20: 539-558.
- [3] Fernández AM, Barriocanal C, Alvarez R. Pyrolysis of a waste from the grinding of scrap tyres. *J. Hazard. Mater.* 2012;203– 204:236– 243.
- [4] ÖnenÇ S, Brebu M, Vasile C, Yanik J. Copyrolysis of scrap tires with oily wastes. *J. Anal. Appl. Pyrolysis* 2012; 94:184-189.
- [5] 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.
- [6] Kyari M, Cunliffe A, Williams PT. Characterization of oils, gases and char in relation to the pyrolysis of different brands of scrap automotive tires. *Energy Fuels* 2005;19:1165-1173.
- [7] Amari T, Themelis NJ, Wernick IK. Resource recovery from used rubber tires. *Resour. Policy* 1999;25:179-188.
- [8] Mastral AM, Murillo R, Perez-Surio MJ, Callén MS. Coal Hydrocprocessing with Tires and tire components. *Energy Fuels* 1996;10:941-947.
- [9] Williams PT, Besler S, Taylor DT. The pyrolysis of scrap automotive tyres. *Fuel* 1990;69:1474-1482.
- [10] Parres F, Crespo-Amorós JE, Nadal-Gisbert A. Characterization of fibers obtained from shredded tires. *J. Appl. Polym. Sci.* 2009;113:2136-2142.
- [11] Acevedo B, Barriocanal C, Álvarez R. Pyrolysis of blends of coal and tyre wastes in a fixed bed reactor and a rotary oven. *Fuel* 2013;113:817-825.

- [12] Callén M, Hall S, Mastral AM, García T, Ross A, Bartle KD. PAH presence in oils and tars from coal-tyre coprocessing. *Fuel Process. Technol.* 2000; 62:53-63.
- [13] Mastral AM, Callén S, García T, Navarro MV. Aromatization of oils from coal-tyre cothermolysis II. PAH content study as a function of the process variables. *Fuel Process Technol.* 2000;68:45-55.
- [14] van Krevelen DW. *Coal. Typology- Chemistry – Physics- Constitution.* Elsevier, Amsterdam, 1981.
- [15] Solomon PR, Fletcher TH, Pugmire RJ. Progress in coal pyrolysis. *Fuel* 1993; 72:587-597.
- [16] Casal MD, Díez MA, Alvarez R, Barriocanal C. Primary tar from different coking coal ranks. *Int. J. Coal Geol.* 2008;76:237–242.
- [17] Snape CE, Ladner WR, Bartlet KD. Fate of aliphatic groups in low-rank coals during extraction and pyrolysis processes. *Fuel* 1985; 64:1394-1400.
- [18] Martínez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tyre pyrolysis—A review. *Renew. Sust. Energ. Rev.* 2013;23:179–213.
- [19] Meier D, Faix O. State of the art of applied fase pyrolysis of lignocellulosic materials –a review. *Bioresourc. Technol.* 68 (1999) 71–77.
- [20] Januszewicz K, Klein M, Klugmann-radziemska E. Gaseous products from scrap tires pyrolysis, *Ecol. Chem. Eng. S.* 2012;19: 451- 460.
- [21] Ohtani H, Nagaya T, Sugimura Y, Tsuge S. Studies on thermal degradation of aliphatic polyamides by pyrolysis-glass capillary gas chromatograpy. *J. Anal. Appl. Pyrol.* 1982;4:117-131.
- [22] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 2002; 81:051-1063.
- [23] 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;71:917–34.

- [24] Cunliffe AM, Williams PT. Composition of oils derived from the batch pyrolysis of tyres. *J. Anal. Appl. Pyrol.* 1998;44:131–52.
- [25] López FA, Centeno TA, Alguacil FJ, Lobato B, Urien A. The GRAUTHERMIC-Tyres process for the recycling of granulated scrap tyres. *J. Anal. Appl. Pyrol.* 2013;103:207-215.
- [26] Banar M, Akyildiz V, Özkan A, Çokaygil Z, Onay Ö. Characterization of pyrolytic oil obtained from pyrolysis of TDF (Tire Derived Fuel). *Energ. Convers. Manag.* 2012;62:22-30.
- [27] Smith B. *Infrared Spectral Interpretation: A Systematic Approach*, CRC Press, Boca Raton, 1998.
- [28] Petersen HI, Rosenberg P, Nytoft HP. Oxygen groups in coals and alginite-rich kerogen revisited. *Int. J. Coal Geol.* 2008;74:93–113.
- [29] Chen Y, Mastalerz M, Schimmelmann A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *Int. J. Coal Geol.* 2012;104: 22–33.
- [30] Ibarra JV, Muñoz E, Moliner R. FTIR study of the evolution of coal structure during the coalification process. *Org. Geochem.* 1996;24:725-735.
- [31] Iglesias MJ, Jiménez A, Laggoun-Defarge F, Suarez-Ruiz I. FTIR Study of Pure Vitrains and Associated Coals. *Energy Fuels* 1995;9:458-466.
- [32] Fernández AM, Barriocanal C, Díez MA, Alvarez R. Evaluation of bituminous wastes as coal fluidity enhancers. *Fuel* 2012;101: 45-52.
- [33] Kwon E, Castaldi MJ. Fundamental understanding of the thermal degradation mechanisms of waste tires and their air pollutant generation in a N₂ Atmosphere. *Environ. Sci. Technol.* 2009;43 5996–6002.
- [34] Kwon E, Castaldi MJ. Investigation of mechanisms of polycyclic aromatic hydrocarbons (PAHs) initiated from the thermal degradation of styrene butadiene rubber (SBR) in N₂ atmosphere. *Environ. Sci. Technol.* 2008; 42:2175–2180.

- [35] Cao Q, Jin L, Bao W, Lv Y. Investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire. *Fuel Processing Technology* 2009;90:337-342.
- [36] Pakdel H, Roy C, Aubin H, Jean G, Coulombe S. Formation of dl-limonene in used tire vacuum pyrolysis oils. *Environ. Sci. Technol.* 1991;25:1646-1649.
- [37] Roy C, Darmstadt H, Benallal B, Amen-Chen C. Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber. *Fuel Process Technol.* 1997;50: 87-103.
- [38] Williams PT, Bottrill RP. Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil. *Fuel* 1995;74:736-742.
- [39] Unapumnuk K, Lu M, Keener T. C. Carbon distribution from the pyrolysis of tire-derived fuels. *Ind. Eng.Chem.Res.* 2006;45:8757-8764.
- [40] Mastral AM, Murillo R, Callén MS, García T, Snape CE. Influence of process variables on oils from tire pyrolysis and hydrolysis in a swept fixed bed reactor. *Energy Fuels* 2000; 14:739-744.
- [41] Stanciulescu M, Ikura M. Limonene ethers from tire pyrolysis oil Part 1: Batch experiments. *J. Anal. Appl. Pyrolysis* 2006;75:217–225.
- [42] Mirmiran S, Pakdel H, Roy C. Characterization of used tire vacuum pyrolysis oil: Nitrogenous compounds from the naphtha fraction. *J.Anal. Appl.Pyrol.* 1995;22: 205-215.
- [43] Heidi K, Peter G. Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Reg. Toxicol. Pharmacol.* 2007;47:288-295.

Table 1. Indices derived from the FTIR spectra.

Semi-quantitative index		Band region (cm ⁻¹)
Aromaticity (Ar/Al)	CHar stretching / CHal stretching	(3136-2997) / (2997-2765)
Ratio of oxygenated groups	Oxygenated groups / C=C stretching	(1770-1650) / 1600

Table 2. Proximate and elemental analysis of the raw materials used.

	TC	RF	Coal	BW
VM ^a (wt.% db ^b)	65.5	72.9 ^d	36.2	68.2 ^d
Ash(wt.% db)	7.5	4.6 ^d	6.4	0.2 ^d
C (wt.% db)	78.5	68.2	78.6	86.7
H (wt.% db)	7.0	6.7	4.5	5.1
N (wt.% db)	1.3	1.1	2.0	4.4
S (wt.% db)	2.13	1.03	0.51	2.39
O (wt.% db)	3.9	18.6	8.2	2.3
C/H ^c	0.93	0.85	1.46	1.39

a: volatile matter, b: dry basis, c: atomic ratio, d: from thermogravimetric analysis.

Table 3. Elemental analysis and calorific value of the oils obtained in the two ovens of different configuration.

		C (%wt.db)	H (%wt.db)	N (%wt.db)	S (%wt.db)	O (%wt.db)	C/H ^b	HHV ^c (MJ/kg)	LHV ^d (MJ/kg)
TC	RO	87.1	10.4	0.6	1.13	1.5	0.70	42.1	40.0
	FB	85.1	11.1	0.5	0.96	3.2	0.64	42.7	40.4
RF	RO	76.2	8.5	3.4	0.85	9.0	0.75	37.4	35.7
	FB	76.9	10.3	1.0	0.55	10.5	0.62	34.1	32.0
TC/Coal	RO	87.6	9.6	0.9	1.01	3.1	0.76	41.7	39.7
	FB	79.1	10.9	0.6	0.73	10.3	0.60	38.6	36.4
RF/Coal	RO	77.9	9.0	2.7	0.79	5.8	0.72	36.2	34.3
	FB	75.0	10.1	1.4	0.40	10.5	0.62	27.6	25.6
RF/BW	RO	84.0	6.7	3.4	0.86	5.1 ^a	1.04	37.6	36.2
	FB	82.7	7.6	2.3	1.02	6.4 ^a	0.90	38.4	36.8

a: calculated by difference. b: atomic ratio. c: High Heating Value. d: Low Heating Value.

Table 4. Composition of the oils determined by gas chromatography.

Compounds (%)	TC		RF		TC/Coal		RF/Coal		RF/BW	
	RO	FB	RO	FB	RO	FB	RO	FB	RO	FB
Benzene + derivatives	11.57	21.15	5.47	8.98	8.83	22.21	1.03	15.99	2.92	4.92
Indane / indene + derivatives	9.74	3.85	1.58	0.00	9.37	3.34	0.38	0.00	0.53	1.04
Naphthalene + derivatives	23.18	2.13	7.32	0.31	16.35	2.85	2.75	1.39	32.51	28.58
Fluorene + derivatives	0.01	0.00	0.00	0.00	0.06	0.00	0.45	0.00	14.08	13.86
Phenanthrene/Anthracene + derivatives	2.32	0.46	0.00	0.00	0.00	0.00	0.00	0.00	12.02	13.79
Fluoranthene + derivatives	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.92	3.73
Pyrene + derivatives	0.00	0.00	0.00	0.00	1.34	0.00	0.00	0.00	3.78	2.20
Perylene + derivatives	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.00
Limonene + Terpene	5.12	21.58	3.57	14.70	3.50	14.20	0.53	13.96	0.39	1.12
Oxygenated compounds	0.56	6.63	28.03	16.60	2.94	7.36	26.37	12.82	9.03	11.41
Nitrogenated compounds	4.55	3.11	31.89	22.29	0.00	0.95	18.36	11.09	9.56	8.88
Sulphur compounds	1.60	0.82	0.71	1.40	1.40	0.70	0.68	0.24	0.50	0.54
Alicyclic	1.32	7.12	1.14	16.28	0.29	1.28	0.57	11.28	0.30	1.22
Non-cyclic Aliphatics	10.23	4.27	3.96	1.05	21.00	18.99	23.18	13.90	0.00	0.00

Table 5. Indices calculated from the chromatographic analysis.

	TC		RF		TC/Coal		RF/Coal		RF/BW	
	RO	FB	RO	FB	RO	FB	RO	FB	RO	FB
Aliphatic / Aromatic	0.43	1.50	0.94	1.48	0.62	1.42	1.09	1.65	0.01	0.04
Condensation index (Naphthalene/ Benzene)	2.00	0.10	1.33	0.03	1.85	0.13	2.70	0.09	11.11	5.88
Alicyclic / Aromatics	0.13	1.01	0.11	0.94	0.09	0.52	0.03	0.83	0.01	0.03

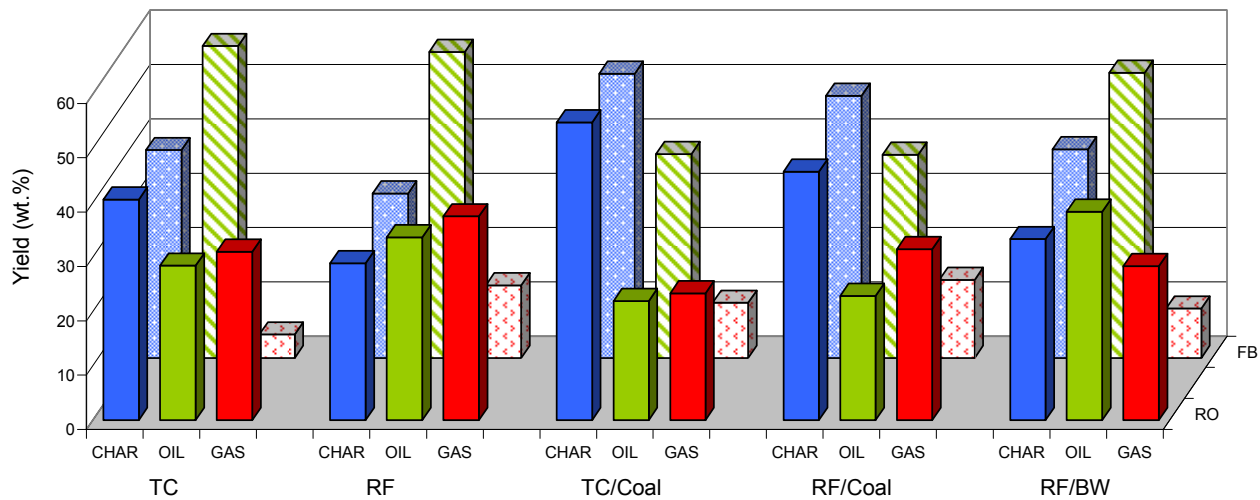


Figure 1. Mass Balance in the two ovens

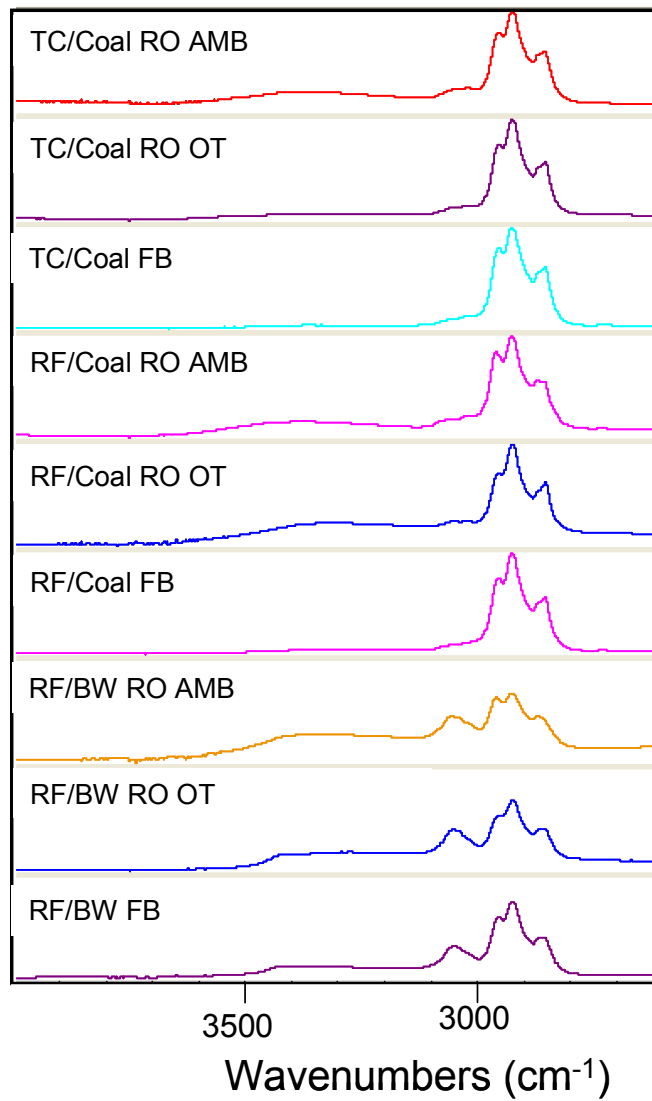


Figure 2. FTIR spectra of the oils obtained from the pyrolysis of the blends in a rotary (RO) and fixed bed (FB) oven. Wavenumbers: 3500-2500cm⁻¹

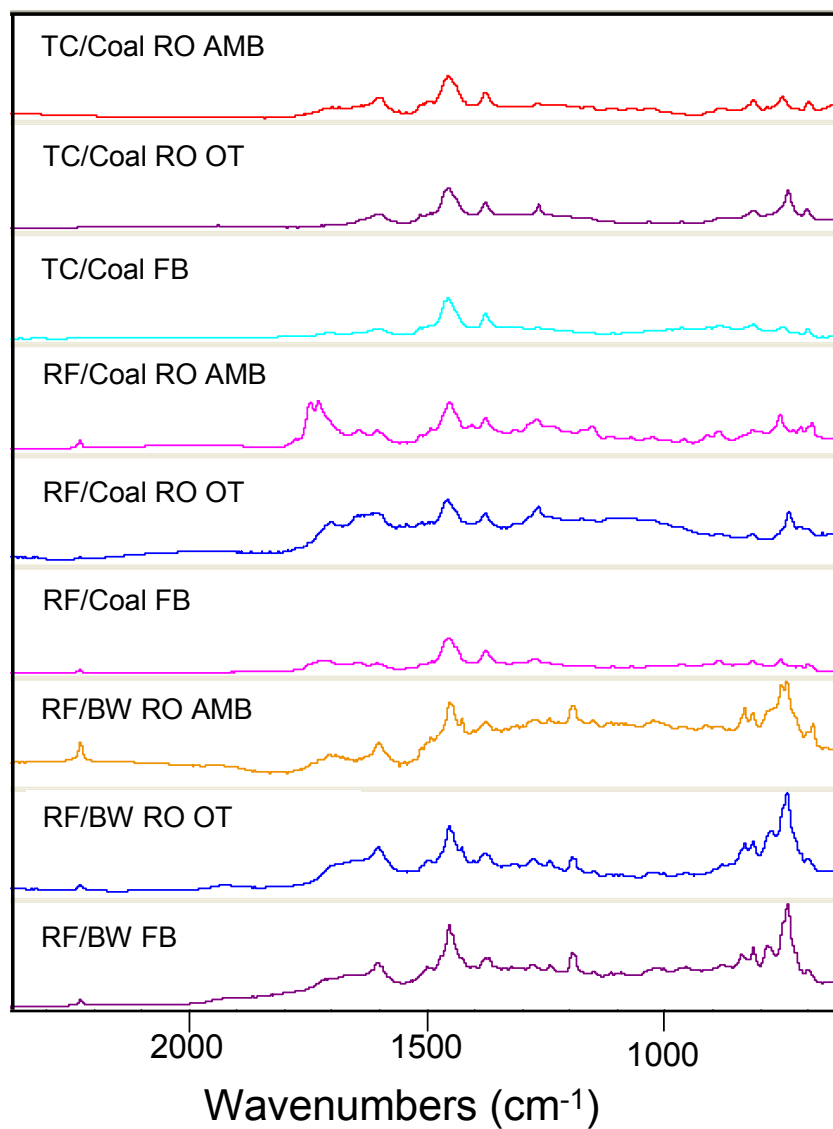


Figure 3. FTIR spectra of the oils obtained from the pyrolysis of the blends in a rotary (RO) and fixed bed (FB) oven. Wavenumbers: 1800-1400cm⁻¹

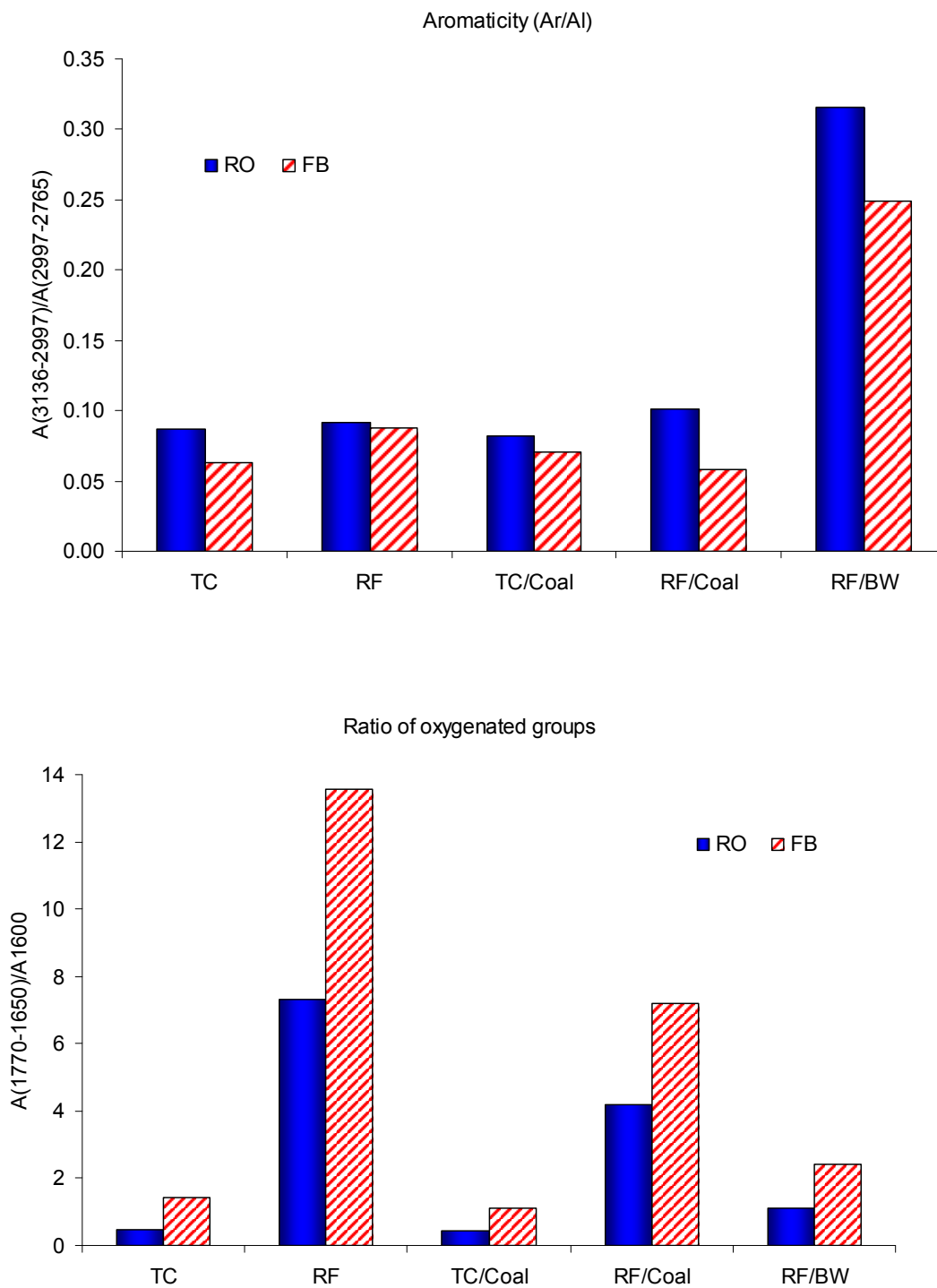


Figure 4. Semi-quantitative ratios derived from the FTIR spectra of the oils obtained from the pyrolysis of the blends in a rotary (RO) and fixed bed (FB) oven.

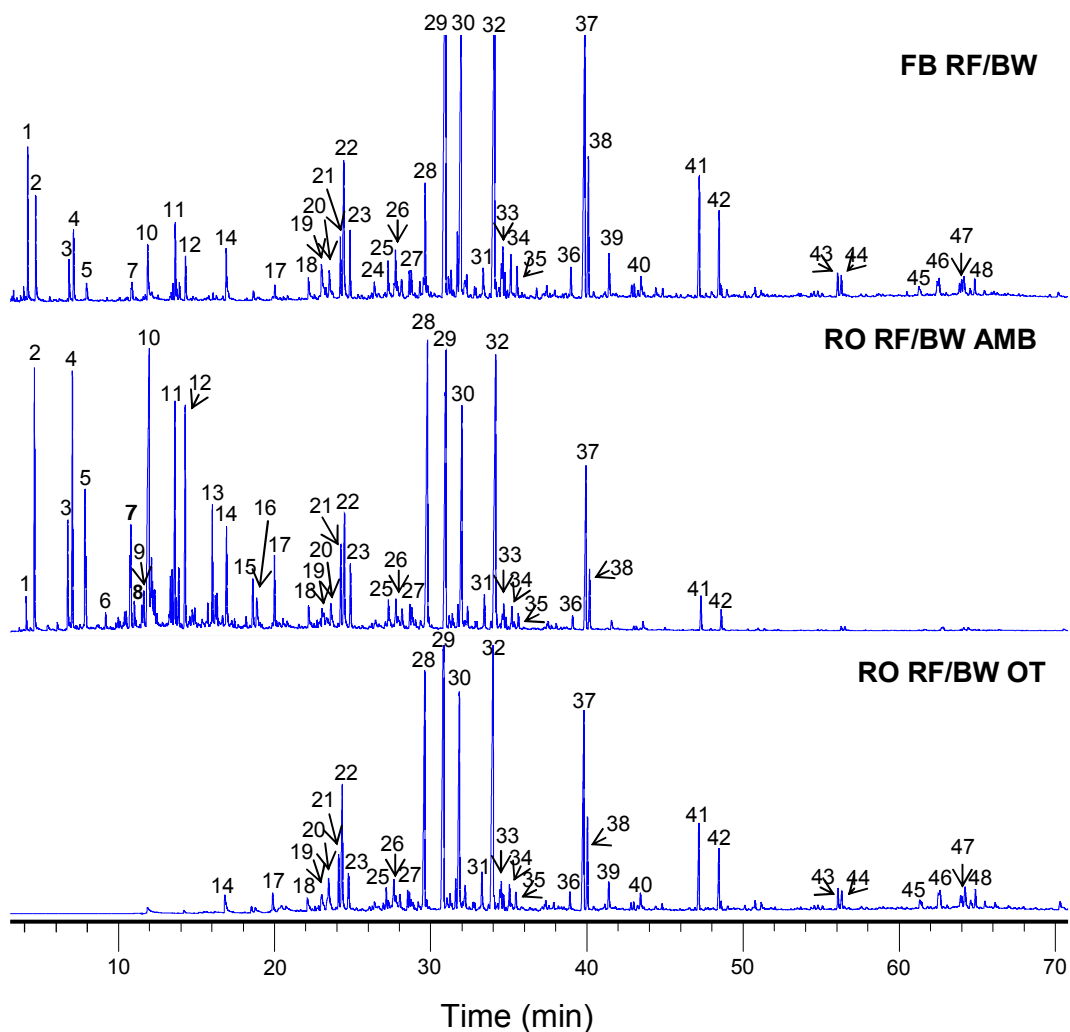


Figure 5. GC-FID chromatogram of the 1:1 RF/BW blend.

Peak Identification: 1. Cyclopentanone, 2. Dimethylcyclohexene, 3. Ethylbenzene, 4. p-Xylene, 5. Styrene, 6. Methyl ethylbenzene, 7. Ethylmethylbenzene, 8. Trimethylbenzene, 9. α -Methylstyrene, 10. Benzonitrile, 11. Limonene, 12. Indene, 13. Ethenylethylbenzene, 14. Methylbenzonitrile, 15. Methylindene, 16. Methylindene, 17. Naphthalene, 18. Isoquinoline, 19. Quinoline, 20. benzenedicarbonitrile, 21. methylnaphthalene, 22. Indole, 23. Methylnaphthalene, 24. Methylquinoline, 25. Biphenyl, 26. Ethylnaphthalene, 27. Dimethylnaphthalene, 28. Acenaphthylene, 29. Acenaphthene, 30. Dibenzofurane, 31. Fenalene, 32. Fluorene, 33. Methylfluorene, 34. Methyl dibenzofurane, 35. Methyl dibenzofurane, 36. Dibenzothiophene, 37. Phenanthrene, 38. Anthracene, 39. Carbazole, 40. Cyclopenta [d, e, f] Phenanthrene, 41. Fluoranthene, 42. Pyrene, 43. Benzo (a) anthracene, 44. Crysene, 45. Quinindoline, 46. Benzo (k) fluoranthene, 47. Benzo (a) pyrene, 48. Perylene.

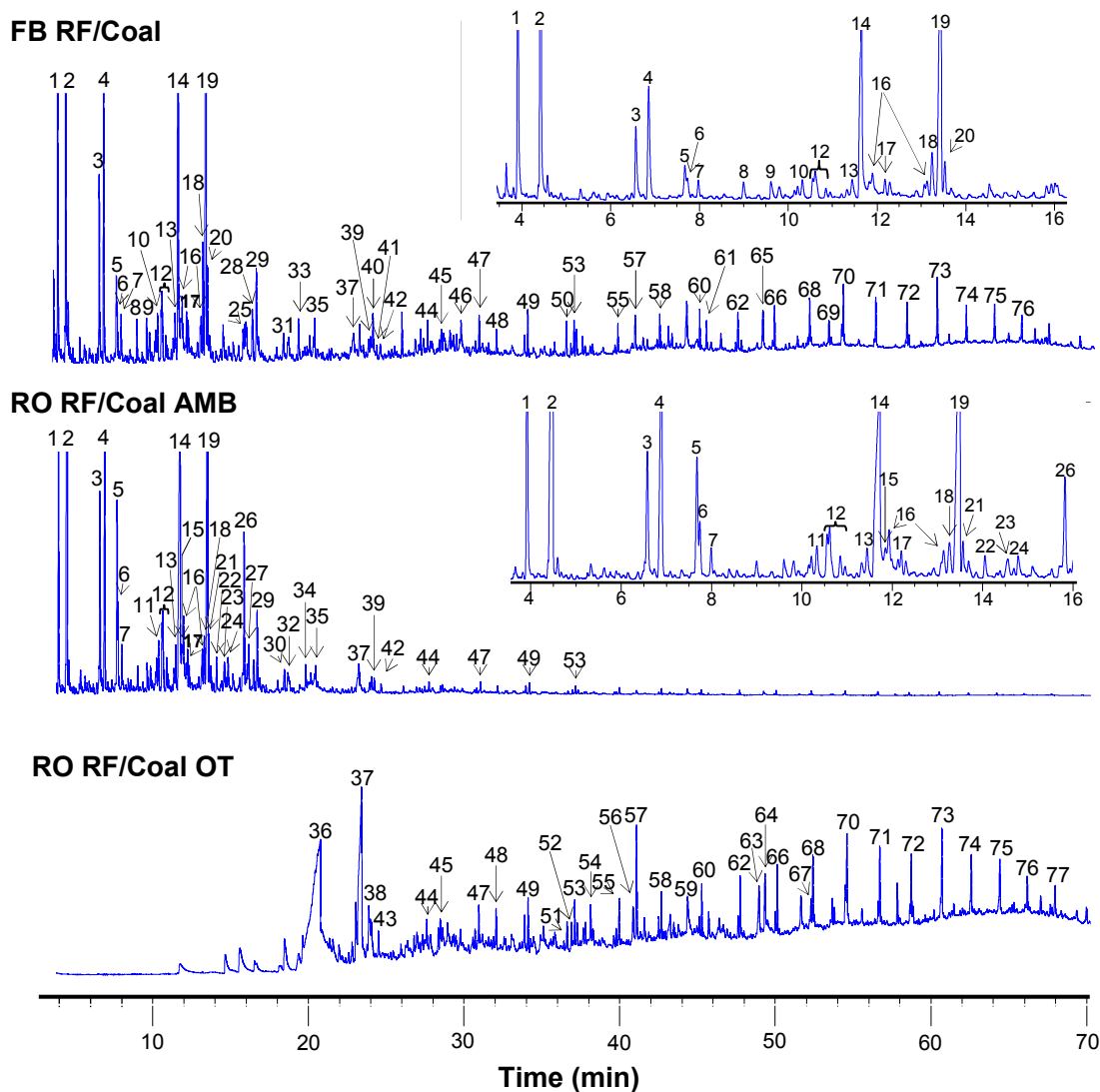


Figure 6. GC-FID chromatogram of the 1:1 RF/Coal blend.
 Peak identification: 1.Cyclopentanone, 2. Dimethylcyclohexene, 3. Ethylbenzene, 4. Dimethylbenzene, 5. Styrene, 6. Xylene, 7. C9, 8. Methylethylbenzene, 9. Ethylcyclopentanone, 10. Limonene, 11. Isopropylidnamethylvinylcyclobutane, 12. Ethylmethylbenzene, 13. Methylethenylbenzene, 14. Benzonitrile, 15. Phenol, 16. Trimethylbenzene, 17. C10, 18. Methyl (methylethyl) benzene, 19. Limonene, 20. Pentylcyclohexanone, 21. Methylheptenone, 22. Indene, 23. Hexahydronaphthalene, 24. Acetophenone, 25. Methylphenol, 26. Ethenyl (ethyl) benzene, 27. Ethenyl (ethyl) benzene, 28. C11, 29. Methylbenzonitrile, 30. Methylindene, 31. Methylpropenylbenzene, 32. Dimethylphenol, 33. Ethyl ester benzoic acid, 34. Naphthalene, 35. C12, 36. Benzoic acid, 37. Caprolactam, 38. Benzenedicarbonitrile, 39. Methylnaphthalene, 40. Tridecene, 41. C13, 42. Methylnaphthalene, 43. Methylbenzoic acid, 44. C14, 45. Dimethylnaphthalene, 46. Gamma-curcumene, 47. C15, 48. Trimethylnaphthalene, 49. C16, 50. Bromomethylcyclohexane, 51. Thiophene methanediol, 52. Methylfluorene, 53. C17, 54. Methylbenzamide, 55. C18, 56. Phenylpropanone, 57. Hexylbenzamide, 58. C19, 59. Methylpropiophenone, 60. C20, 61. Heptenone, 62. C21, 63. Indole acetaldehyde, 64. Hexenyl methoxymethyl cyclohexadienol, 65. Diphenyl dimethyl pentanone, 66. C22, 67. Tricosene, 68. C23, 69. Chlorohexilcyclohexanone, 70. C24, 71. C25, 72. C26, 73. C27, 74. C28, 75. C29, 76.C30.