

DISTILLATION OF GRANULATED SCRAP TIRES IN A PILOT PLANT

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ABSTRACT

This paper reports the pyrolytic treatment of granulated scrap tires (GST) in a pilot distillation unit at moderate temperature (550°C) and atmospheric pressure, to produce oil, char and gas products. Tire-derived oil is a complex mixture of organic C₅–C₂₄ compounds, including a very large proportion of aromatic compounds. This oil has a high gross calorific value (~43 MJ kg⁻¹) and N and S contents of 0.4% and 0.6% respectively, falling within the specifications of certain heating fuels. The distillation gas is composed of hydrocarbons; methane and n-butane are the most abundant, investing the distillation gas with a very high gross calorific value (~68 MJ Nm⁻³). This gas is transformed into electric power by a co-generation turbine. The distillation char is mostly made of carbon but with significant inorganic impurities (~12 wt%). The quality of the solid residue of the process is comparable to that of some commercial chars. The quantity of residual solids, and the qualities of the gas, liquid and solid fractions, are similar to those obtained by conventional pyrolytic treatments of waste tires. However, the simplicity of the proposed technology and its low investment costs make it a very attractive alternative.

Keywords: *Scrap tires, Distillation, Tire-derived oil, Char, Recycling*

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1. Introduction

More than $3.4 \cdot 10^6$ tonnes of end-of-life tires (ELTs) are generated annually in the European Union (EU), some 10% of these in Spain [1]. The disposal of ELTs in landfills is banned in the EU (Directive 1993/31/EC); their disposal is therefore mainly managed via: i) integrated management systems (IMS) run by non-profit companies (a system used in 18 countries); ii) the free market (e.g., in the United Kingdom, Ireland, Germany, Switzerland, Austria, Bulgaria and Croatia), and iii) a system of taxes paid by the manufacturers (Denmark, Slovenia and Slovakia). In 2009, 19% of the tires generated in Europe were retreaded, 6% were disposed of in holding facilities, 37% were used in energy-generating processes, and 38% were used in the manufacture of other materials. Alternative fates for ELTs, including their retreading [2], devulcanization [3], their use in the steel industry [4], the manufacturing of rubber-modified asphalt [5], their use as road bases [6], and their use as fillers for the tread and sidewalls of new tires [7], have been the subject of study for years. Ground rubber products are also used for athletic and recreational materials, such as running tracks and playground surfaces [8]. Currently, there is much interest in using these materials for energy generation. Tire-derived fuels (TDF) are used as substitutes of fossil fuels in the concrete industry [9-11] and in combustion processes for the generation of electric power, e.g., by boilers in the paper manufacturing industry, by industrial boilers and by power stations etc. [12]. In Europe, nearly 40% of ELTs are used as TDF, whereas in USA and Japan this percentage reaches 53% and 70% respectively [13].

The pyrolysis (thermal degradation in the absence of oxygen) of tires produces pyrolytic oil, gas and char. The quality and quantity of these fractions depend greatly on the raw material as well as on the temperature and the design of the reactor in which the pyrolysis takes place. At temperatures of around 500-550°C, the major product is a liquid consisting of various hydrocarbons, whereas above 650-700°C the primary

product is a gas, a consequence of the further cracking of the liquid fraction.

Different technologies have been used in tire pyrolysis such as fixed bed reactors [14,15], rotary kilns [16,17], circulating fluid beds [18], bubbling fluid beds [19], vacuum moving beds [20] and conical spouted bed reactors [21]. Recent research trends have involved thermal plasma pyrolysis, pyrolysis in the presence of catalysts (zeolites) [22] and hydrogenative pyrolysis [23].

The use of tire-derived oil provides an opportunity to minimize the use of diesel fuel [24-26]. Tire-derived char may also participate successfully in co-combustion processes in pulverized coal power plants [27]. Zabaniotou and Stavropoulos [28] describe the gasification of tire char with steam and CO₂ to produce fuel gases. Gasification also results in the production of tire based-activated carbons with micropore volumes over 40% of the total pore volume and BET surface areas of around 1000 m²g⁻¹ [29-31]. Tire-derived activated carbons have been successfully used to adsorb phenols, basic dyes, metals, butane and natural gas, etc. [32-34].

The present work describes a novel distillation technology for generating energy from granulated scrap tires (GST). This involves a pyrolytic process at 550°C and at atmospheric pressure, characterized by a long residence time for the GST in the reactor. A portion of the volatile products are condensed at a temperature below 5°C (oil). The non-condensable fraction – gas – is mainly composed of low molecular weight hydrocarbons, H₂ and CO. This is injected into a generator to produce electric power. The distillation step was studied in a 18 kg h⁻¹ capacity pilot unit.

2. Materials and Methods

2.1. Characterization of materials

The GST used in this work (GABA-Barcelona, Spain) was exclusively

composed of the elastomers and rubber types found in car and truck tires. Tires generally contain either natural rubber or synthetic rubber (styrene butadiene rubber or butadiene rubber), elastomers, char, hydrocarbon oils, zinc oxide, sulfur, sulfur compounds, and other chemicals such as stabilizers, anti-oxidants and anti-ozonants, etc. In the present study, rubber particles (fluff [textile] <2 wt%, steel <0.1 wt%) with a diameter of 6 mm and a length of 12 mm (density 1113 kg m⁻³) were used as the raw material for distillation. Proximate and elemental analyses (performed using a LECO TGA 701 analyzer and LECO CHNS 923 analyzer respectively) and the determination of the gross calorific value (GCV) of the GST particles (performed using a GCV IKAWEEME C4000 automatic bomb calorimeter) were undertaken using a representative sample frozen in liquid nitrogen before grinding. Table 1 shows the raw GST used has a composition similar to that reported in the literature [24, 35-41].

The GST particles were also subjected to thermogravimetric analysis (DTA/TG) using a SETARAM Sensys Evolution apparatus in: (1) a nitrogen atmosphere (100 ml min⁻¹, 5°C min⁻¹) to quantify the volatile components (mainly rubbers and minor components such as accelerators and extender oils, etc.) and (2) an oxygen atmosphere (100 ml min⁻¹, 5°C min⁻¹) to estimate the non-volatile fraction (essentially composed of char). Table 2 shows the results of the DTA/TG experiments.

2.2. Distillation experiments

The proposed distillation plant consists of six vertical, tubular, stainless steel reactors (length 1510 mm; wall thickness 6 mm; external diameter 154 mm) operated at batch scale. Each reactor has a capacity of 12 kg GST and is fed through a PN-16 3" type valve. The distillation gas flows out by natural convection and is cooled in two successive condensers (water- and cryogenically-cooled respectively) to recover the oil. The condensers are composed of a number of stainless steel tubes. The upper and lower part of each condenser is equipped with a small expansion chamber for the expansion of

gases and the collection of condensed oil. The gas temperature at the entrance of the first condenser is near 250°C, and at about 100°C at the exit. The gas reaches the second condenser at 45°C. Gas condensation is enhanced by a cryogenic cooling system to guarantee a gas temperature below 5°C in the second condenser. The condensed oils are collected in a deposit equipped with a level-maintaining valve and a pump.

At the bottom of the reactor there is a system to heat the tubes via propane gas. Each tube has three thermocouples, one at the bottom, one in the middle, and one at the top. These, like the rest of the monitoring systems, are connected to a central control unit. When the temperature of the reactor reaches 550°C, the burners switch off. Whenever the temperature falls they automatically switch on again. The pilot installation has an automated control system that records the temperature measured by the thermocouples. Each batch of GST (12 kg per tube) is heated for 4 h at 550°C (consumption 0.15 kg propane per kg GST). This temperature was chosen after running a number of DTA/TG assays and preliminary testing of the pilot installation.

The cold gas is cleaned by a three filter system (water, a 1M $\text{Pb}(\text{CO}_3)_2$ solution, and activated carbon). The clean gas passes through a flowmeter to measure the volume and is conducted to a TOTEM[®] electric co-generation turbine (Total Energy Module) consisting of a distillation gas-fed 903 cm³ engine coupled to an engine/alternator. Both are asynchronous. The module has an electronic coupling system that diverts the electricity produced into the Spanish electric grid.

After completing the distillation process (the endpoint is determined when the rotameter inside the tubing detects total absence of distillation gas), the reactors were cooled for 4 h, opened, and the distillation solids (char) removed by aspiration. The oil was taken from the deposit by using a pump and filtered under pressure. The yields (by weight) of the oil and char fractions were then determined; the difference between the

sum of these weights and the weight of the GST equals the weight of the gas. Figure 1 show a flowsheet of the process.

2.3. Characterization of liquids

The elemental composition of the liquid (oil) fraction was determined using an automated LECO CHNS 923 analyzer. Its GCV was determined using an IKAWEEME C4000 automatic bomb calorimeter. The oil was also analyzed by GC/MS using an AGILENT 7890A gas chromatograph equipped with an AGILENT MS 5975C mass selective detector. The capillary column was HP-5MS (5% diphenyl, 95% dimethyl siloxane).

The flashpoint of the liquid fraction was estimated using a STANHOPE-SETA Setaflash 3 apparatus and a closed cup system (ASTM D1655). Kinematic viscosity was determined at 40°C using a THERMO SCIENTIFIC Haake 1 plus viscosimeter.

An automatic distillation test using a PAC Optidis apparatus was carried out following the ASTM D86 method at atmospheric pressure on a pooled sample of the oils obtained in different runs at 550°C. This test was performed from room temperature up to the temperature at which no more distillation products were collected.

2.4. Characterization of the distillation gas

The distillation gas was collected in Tedlar bags and analyzed by gas chromatography using a HEWLETT-PACKARD 5890 chromatograph equipped with a Porapak N and Molecular Sieve multicolumn system, a thermal conductivity detector and a flame ionisation detector. The carrier gas (0.39 MPa) was He (99.999% pure).

2.5. Characterization of distillation solids (distillation char)

The proximate and elemental compositions and the GCV of the distillation char

(DC) was determined as for the liquids.

The porous characteristics of the solid were estimated from the analysis of the N₂ isotherm at 77K using a Beckman Coulter SA1100 analyzer, employing the BET equation [42] and Dubinin's theorem [43]. Textural data were cross-checked by immersion calorimetry [44] involving CH₂Cl₂ and C₆H₆.

The crystalline phases in the solid were characterized by X-ray diffraction (XRD) using a Bruker XRD Mod. D8 Discover diffractometer (Cu_{kα} radiation, 0.03 2θ° step-widths, counting time 5 s per step).

Morphological studies were performed using a Hitachi model S-2100 scanning electron microscope (SEM). A field emission microscope (Jeol JSM 6500 F) equipped with an energy dispersive analyzer (Link Oxford Inca, EDAX unit) was used to determine the composition of the samples.

The DC ashes were analyzed by atomic absorption/emission spectroscopy using a Shimadzu AA-6300 apparatus, employing a deuterium lamp for background correction (BGC-D2). Zn, Cu, Fe, Ti, Al, Ca, Mg and Si concentrations were estimated by atomic absorption; K and Na were evaluated by atomic emission.

3. Results and Discussion

3.1. TG experiments

Figure 2 shows the behavior of GST at different temperatures under the N₂ and oxygen atmospheres. With the former, the derived TG (DTG) curve showed three consecutive effects in the range 290-600°C characteristic of the thermal decomposition of the GST [45,46]: i) the elimination of oil and lubricants (299 °C), ii) the breakdown of the natural rubber (378.4°C) and iii) the degradation of styrene-butadiene and polybutadiene (450.5°C). The small signal at 871.5°C may be due to the formation of ZnO. An extra peak appeared at 480°C in the oxygen atmosphere conditions,

corresponding to the combustion of the carbon black in the GST.

According to TG analysis, GSTs are composed of 63.5 wt% natural rubber and elastomers, 2.5 wt% oils, 31.5 wt% carbon black, and 2.5 wt% inorganic fillers [47].

3.2. Distillation

Preliminary work showed 550°C to be the best temperature for the distillation process. The distillation experiments produced fraction yields similar to those reported for tire pyrolysis by other authors using different techniques [27, 36, 48-53]. The solid fraction made up some 40 wt% (with respect to the raw material), whereas the oil and gas accounted for 46.1 wt% and 13.9 wt% respectively. The solid yield was somewhat higher than the theoretical value estimated by TG analysis (34%). It has been reported [47] that a certain amount of char or coke-like material is formed in the pyrolysis of many polymeric materials due to secondary repolymerisation reactions.

3.2.1. Tire-derived oil

Table 2 shows the chemical composition of the oil obtained from each condensers, and that of the total mixture. The first condenser collected 84% of the total weight of the oil; the second collected the remaining 16%. The chemical composition of the oils from each condenser varied slightly, as a consequence of the different cooling temperatures of the distillation gases. The oil from condenser 1 had larger quantities of C, N and S and higher viscosity than that collected by the second one. The H/C atomic ratio for the oil from condenser 1 was 1.84, whereas that from condenser 2 corresponded to 1.34. This indicates a greater proportion of aromatic compounds, mainly naphthalene and its derivatives, in oil from condenser 1.

As reported for other tire-derived oils [12,24], the present oil mix from both condensers had carbon and hydrogen contents of 85 wt% and 11 wt% respectively

(Table 2). These values are rather similar to those of refined petroleum fuels. The nitrogen content (0.44 wt%) is similar to that of a heavy fuel oil, whereas the sulfur quantity (0.58 wt%) is much lower than the 0.8-1.4 wt% found in oils derived from conventional tire pyrolysis [24]. The H/C atomic ratio of around 1.6 indicates that this distillation oil is a mixture of aromatic and aliphatic compounds, as confirmed by CG/MS analysis (see below).

Figure 3 shows that about 24% of the oil distills at below $\approx 170^{\circ}\text{C}$, which falls within the boiling point range of light naphtha (initial boiling point 160°C). Around 16% of the components correspond to heavy naphtha, distilling in the range $160\text{-}200^{\circ}\text{C}$. Finally, $\approx 43\%$ of oil is a middle distillate ($200\text{-}350^{\circ}\text{C}$). Laresgoiti et al. [54] report a similar pattern when using a similar technique to the present, with contributions of 20% naphtha, 10% heavy naphtha and 35% minor middle distillate fraction. Figure 3 also shows that, compared to commercial diesel, the present oil has a higher proportion of light components (vapor temperature $< 260^{\circ}\text{C}$). This is an advantage since it can be better atomized, with combustion initiating at a lower temperature. However, the large amount of heavy products (vapor temperature $> 287^{\circ}\text{C}$) reduces its potential due to legal/environmental restrictions.

The flash point of the oil (20°C) is well below the 75°C and 79°C limits set for diesel fuel and light fuel oil respectively. Such a low value is not surprising since the product corresponds to an unrefined oil made of a mixture of components with a wide distillation range.

The calorific value of 43.2 MJ kg^{-1} falls into the $41\text{-}43\text{ MJ kg}^{-1}$ range obtained for other oils produced by conventional pyrolysis technologies [55]. Finally, the density (0.9 kg m^{-3}) and the kinematic viscosity of the oil at 40°C (2.82 cSt) (Table 2) are similar to those of diesel fuel.

Figure 3 shows that oil is suitable for certain industrial uses. One possibility could be to mix this liquid fraction with diesel oil. The legislation of the Catalonian Autonomous Community (NE Spain) allows adding tire-derived oil to diesel fuel to the extent of 4% by weight (DOGC 2166/1996. Decreto 34/1996). Another possibility could be to feed tire-derived liquids with other feedstock from wastes into refinery units, such as those for fluid catalytic cracking (FCC), thermal cracking or coking [56].

The compounds tentatively identified in the GC/MS chromatogram, and the subsequent comparison of the relative areas under each peak, clearly show the predominantly aromatic nature of the oil. Table 3 summarizes the major fractions of volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), and hetero-N and -S containing PAHs. Note that a very low proportion of aliphatics ($\approx 10\%$) was detected.

The high proportion of aromatic compounds in the oil is partly attributed to the raw polymeric material (styrene butadiene rubber and poly-isoprene rubber), and partly to recombination reactions involving aliphatic and aromatic free radicals; the cyclation of aliphatic chains also increases the aromatic content of the resulting liquid.

As expected, the distilled oil is a very complex mixture of organic C_5 – C_{24} compounds. In agreement with the GC/MS data for similar materials, the most abundant products (peak areas around or greater than 1%) were benzene and its derivatives (ethylbenzene, ethylmethylbenzenes, methylethenylbenzenes), naphthalene and its alkyl derivatives, and limonene, toluene, o-m-p-xylene, indene, phenanthrene, biphenyl, benzothiazol, cyclohexenes, cyclobutane, pentanes and octanes [57,58].

Table 3 shows a relatively important contribution of VOCs ($\approx 48\%$), the major constituents being benzene, limonene, toluene and o-m-p-xylene. The formation of PAHs (29%) can be attributed to reactions between aromatic compounds and olefines, followed by cyclation of the olefinic branch and subsequent dehydrogenation [54,58].

The major PAH constituents are naphthalene, indene, phenanthrene, fluorene, biphenyl and their alkylated derivatives.

Table 3 also shows the presence of nitrogenated compounds [48]. Their origin may be nitrile rubber (acrylonitrile butadiene rubber) and/or styrene butadiene rubber (the main component of tire rubber). Finally, a significant amount of benzothiazol, an accelerator typically used in rubber formulations, was also detected (Table 3)

3.2.2. *Tire distillation gas*

The gas fraction produced by distillation at 550°C is made up of C₁-C₄ hydrocarbons, H₂, CO and CO₂ (Table 4). Hydrocarbons are generated from the rupture (depolymerization) of styrene butadiene rubber [58] and from secondary cracking reactions, which are favored by high temperature. Among the hydrocarbons, methane and n-butane are the most abundant (Table 4). Similar results are reported by Dung et al. [59], although other authors report isobutylene [52] and 1,3-butadiene [55] as major products.

The CO_x components derive from oxygenated organic compounds (stearic acid, extender oils, etc.) and even from inorganic components such as metal oxides, CaCO₃, etc. [51,54].

The gas obtained is much richer in H₂ than those produced by conventional pyrolysis quoted in the literature. Berrueco et al. [52] reported H₂ contents of between 2.6 and 17.8 vol.% for gases from tire pyrolysis at temperatures between 400°C and 700°C, the maximum being achieved at 550°C. Similarly, Galvagno et al. [37] reported maximum hydrogen production to be at around 600°C

The volume of gas generated by the present distillation at 550°C accounted for 0.63 Nm³ kg⁻¹ of the GST, and returned GCV figures as high as 68.7 MJ Nm⁻³ (46.5 MJ kg⁻¹). This clearly exceeds the standard values of 30-43 MJ m⁻³ [24,36,54]. The

difference is attributed to the greater concentrations of methane and n-butane in the present gas.

The use of this gas in the co-generation turbine produced 440 kWh electricity/t GST. The electric yield of the turbine was 71%.

3.2.3. Distillation char

With a composition similar to materials derived from pyrolysis [60-62], the solid residue (i.e., the DC) of GST distillation at 550°C was mostly made of carbon with a significant quantity (12%) of inorganic impurities. Around 60 wt% of the sulfur in the starting GST was retained in the DC, which may significantly limit its further use [63].

Zn was present in an amount similar to that found in other tire-pyrolysis residues [41]. The XRD spectrum (Fig. 4) highlights the presence of ZnO (zincite) and ZnS (wurtzite) in the carbon matrix [64,65]. The cubic and hexagonal crystals of the latter were also revealed by SEM images (Fig. 5). No elemental S was detected in the solid as it is mostly retained as PbS in the gas filter with Pb(NO₃)₂ solution.

Table 6 shows the ash to have a very diverse composition resulting from components of the tires and the sand used as an inert material to enhance the spouted bed regime.

The GCV of the solid residue is similar to that of the chars obtained when using conventional pyrolysis technologies.

The N₂ isotherm for the DC is characterized by very little gas adsorption at low relative pressures (p/p_o). The rapid increase in the volume adsorbed at $p/p_o > 0.8$ shows that the porosity of DC corresponds to macropores and large cavities (Fig. 6) with a total volume (estimated at $p/p_o = 0.98$) of approximately $0.4 \text{ cm}^3 \text{ g}^{-1}$. The analysis of the isotherm using Dubinin's theory confirms the absence of significant microporosity ($E_o \sim 12-13 \text{ kJ mol}^{-1}$). Additionally, the low enthalpy values calculated for immersion in

CH_2Cl_2 (13 J g^{-1}) and C_6H_6 (6 J g^{-1}) confirm this poor microporosity.

The BET-surface area of $64 \text{ m}^2 \text{ g}^{-1}$ is within the values for commercial chars [66,67], surpassing those of carbon blacks used in tire manufacturing, e.g., N 550 ($43 \text{ m}^2 \text{ g}^{-1}$), N 660 ($36 \text{ m}^2 \text{ g}^{-1}$) or N 774 ($28 \text{ m}^2 \text{ g}^{-1}$) [55].

4. Conclusions

This paper shows that the treatment of GST at 550°C and at atmospheric pressure provides a distillation technique with a high potential for making products of value from such waste. The yields of the gas (14%), liquid (46%) and solid (40%) fractions are similar to those obtained by pyrolysis in nitrogen, but the simplicity and low investment costs of the present distillation technology make it very attractive.

The use of small tire granules (6-12 mm) improves heat transfer and, hence, the conversion achieved. In addition, the absence of steel and fluff increases the homogeneity of the feed-stock, further improving heat efficiency and affording a more consistent product composition. The long residence time, relatively small particles and moderate distillation temperature all facilitate good tire conversion and high char devolatilization.

The oil derived from GST distillation is a very complex mixture of aromatic and aliphatic compounds. Its density and kinematic viscosity are similar to those of diesel fuel, although it contains a higher proportion of light components (vapor temperature $<200^\circ\text{C}$). However, it also has a greater proportion of heavy products with vapor temperatures of $>300^\circ\text{C}$ than found in commercial diesel fuel. It also has relatively high contents of VOCs ($\approx 48\%$) and PAHs (29%). Hetero-N- and -S-containing PAHs (5%) are also present, whereas the proportion of aliphatics ($\approx 10\%$) is rather low. Its heating value of 43.2 MJ kg^{-1} falls into the range observed for the liquid fraction obtained by conventional pyrolytic technologies.

The gas fraction obtained in GST distillation is composed of C₁-C₄ hydrocarbons (the major products), H₂, CO and CO₂; it is much richer in H₂ (22%) than that produced by conventional tire pyrolysis. The high concentrations of methane and n-butane provide a high heating value - 68.7 MJ Nm⁻³ - clearly exceeding the 30-43 MJ m⁻³ range reported in the literature for the gas fraction produced by conventional tire pyrolysis.

The quality of the solid residue of GST distillation is similar to that of some commercial chars. It is mainly composed of carbon (86.3 wt%), its heat value is around 30 MJ kg⁻¹, and the BET-surface area achieves 64 m² g⁻¹. However, the presence of 3 wt% sulfur may limit the uses of such residue.

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References

- [1] European Tyre & Rubber Manufacturers Association, ETRMA. 2009. www.etrma.org
- [2] J.O'Connell, A.D. Roberts, F.R. Block, K.A. Grosch, Quality control and performance of retreaded tyres, in: I.Gaballah, J.Hager, R. Solozabal (Eds.), Global Symposium on Recycling, Waste Treatment and Clean Technology, San Sebastián, 1999, pp. 401-407.
- [3] M. Alexandre-Franco, C. Fernández-Gonzalez, M. Alfaro-Dominguez, M. Latasa, J.M. Palacios, V. Gómez-Serrano, Devulcanization and demineralization of used tire rubber by thermal chemical methods: A study by X-ray diffraction, *Energ. Fuel.* 24 (2010) 3401-3409.
- [4] M. Zaharia, V. Sahajwalla B.C. Kim, R. Khanna, N. Saha-Chaudhury, P. O'Kane, J. Dicker C. Skidmore, D. Knights, Recycling of rubber tires in electric arc furnace steel making: Simultaneous combustion of metallurgical coke and rubber tyres blends, *Energ. Fuel.* 23 (2009) 2467-2474.
- [5] F. Hernández-Olivares, B. Witoszek-Schultz, M. Alonso-Fernández, C. Benito-Moro, Rubber-modified hot-mix asphalt pavement by dry process more options, *Int. J. Pavement Eng.* 10 (2009) 277-288.
- [6] J. Gallego, L. de los Santos Granados. Mezclas bituminosas fabricadas con betunes de alto contenido de caucho. Aplicaciones al recrecimiento de un pavimento rígido en la A-7, *Revista de Obras Públicas* 150 (2003) 7-26.
- [7] D.A. Baeta, J. A. Zattera, M.G. Oliveira, P.J. Oliveira, The use of styrene-butadiene rubber waste as a potential filler in nitrile rubber: Order of addition and size of waste particles, *Braz. J. Chem. Eng.* 26 (2009) 23-31.
- [8] T. Amari, N.J. Themelis, I.K. Wernick, Resource recovery from used rubber tires, *Resour. Policy* 25 (1999) 179-188.
- [9] L.H. Chou, C.K. Lu, J.R. Chang, M.T. Lee, Use of waste rubber as concrete additive, *Waste Manage. Res.* 25 (2007) 68-76.
- [10] M.A.Trezza, A.N. Scian, Scrap tire ashes in Portland cement production, *Mat. Res.* 2 (2009) 489-494.

- [11] J.A. Conesa, A. Gálvez, F. Mateos, I. Martín-Gullón, R. Font, Organic and inorganic pollutants from cement kiln stack feeding alternative fuels, *J. Hazard. Mater.* 158 (2008) 585-592
- [12] S. Singh, W. Nimmo, B.M. Gibbs, P.T. Williams, Waste tyre rubber as a secondary fuel for power plants more options, *Fuel* 88 (2009) 2473-2480.
- [13] European Tyre & Rubber Manufacturers Association, ETRMA. 2010. www.etrma.org
- [14] J.A. Conesa, I. Martín-Gullón, R. Font, J. Jauhainen, Complete study of the pyrolysis and gasification of scrap tires in a pilot plant reactor, *Environ. Sci. Technol.* 38 (2004) 3189-3194.
- [15] M.R. Islam, H. Haniu, M.R.A. Beg, Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: Product yields, compositions and related properties, *Fuel* 87 (2008) 3112-3122.
- [16] S.Q. Li, Q. Yao, Y. Chi, J.H. Yan, K.F. Cen, Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor, *Ind. Eng. Chem. Res.* 43 (2004) 5133-5145.
- [17] E. Aylon, A. Fernández-Colino, M.V. Navarro, R. Murillo, T. García, A.M. Mastral, Waste tire pyrolysis: Comparison between fixed bed reactor and moving bed reactor, *Ind. Eng. Chem. Res.* 47 (2008) 4029-4033.
- [18] X. Dai, X. Yin, C. Wu, W. Zhang, Y. Chen, Pyrolysis of waste tires in a circulating fluidized-bed reactor, *Energy* 26 (2001) 385-399.
- [19] W. Kaminsky, C. Mennerich, Z. Zhang, Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed, *J. Anal. Appl. Pyrol.* 85 (2009) 334-337.
- [20] C. Roy, A. Chaala, H. Darmstadt. The vacuum pyrolysis of used tires: End-uses for oil and carbon black products, *J. Anal. Appl. Pyrol.* 51 (1999) 201-221.
- [21] M. Olazar, M. Amutio, R. Aguado, J. Bilbao, Influence of tire formulation on the products of continuous pyrolysis in a conical spouted bed reactor, *Energ. Fuel.* 23 (2009) 5423-5431.
- [22] B. Shen, C. Wu, R. Wang, B. Guo, C. Liang, Pyrolysis of scrap tyres with zeolite USY, *J. Hazard. Mater.* 137 (2006) 1065-1073.
- [23] F. Murena, E. Garufi, R. B. Smith, F. Gioia, Hydrogenative pyrolysis of waste

- tires, *J. Hazard. Mater.* 50 (1996) 79-98
- [24] S. Murugan, M.C. Ramaswamy, G. Nagarajan, The use of tyre pyrolysis oil in diesel engines. *Waste Manage.* 28 (2008) 2743-2749.
- [25] S. Murugan, M.C. Ramaswamy, G. Nagarajan, Assessment of pyrolysis oil as an energy source for diesel engines, *Fuel Process. Technol.* 90 (2009) 67-74.
- [26] S.Galvagno, G. Casciaro, S. Casu, M. Martino, M. Mingazzini, C. Russo, S. Portofino, Steam gasification of tyre waste, poplar, and refuse-derived fuel: A comparative analysis, *Waste Manage.* 29 (2009) 678-689.
- [27] A. Napoli, Y. Soudais, D. Lecomte, S. Castillo. Scrap tyre pyrolysis: Are the effluents valuable products?, *J. Anal. Appl. Pyrol.* 40-41 (1997) 373-382.
- [28] A.A. Zabaniotou, G. Stavropoulos, Pyrolysis of used automobile tires and residual char utilization, *J. Anal. Appl. Pyrol.* 70 (2003) 711-722.
- [29] E.L.K. Mui, D.C.K. Ko, G. McKay, Production of active carbons from waste tyres – a review, *Carbon* 42 (2004) 2789–2805.
- [30] M.Betancur, J. Daniel Martínez, R.Murillo, Production of activated carbon by waste tire thermochemical degradation with CO₂, *J. Hazard. Mater.* 168 (2009) 882-887.
- [31] D.C.K Ko, E.L.K. Mui, K.S.T Lau, G. McKay, Production of activated carbons from waste tire – process design and economical analysis, *Waste Manage.* 24 (2004) 875-888.
- [32] F. Heras, N. Alonso, M.A. Gilarranz, J.J. Rodriguez, Activation of waste tire char upon cyclic oxygen chemisorption-desorption, *Ind. Eng. Chem. Res.* 48 (2009) 4664-4670.
- [33] G. López, M. Olazar, M. Artetxea, M. Amutioa, G. Elordia, J. Bilbao, Steam activation of pyrolytic tyre char at different temperatures, *J. Anal. Appl. Pyrol.* 85 (2009) 539-543.
- [34] E.L.K. Mui, W.H. Cheung, G. McKay, Tyre char preparation from waste tyre rubber for dye removal from effluents, *J. Hazard. Mater.* 175 (2010) 151-158
- [35] M.F. Laresgoiti, I. De Marco, A. Torres, B. Caballero, M.A. Cabrero, M.J. Chomón, Chromatographic analysis of the gases obtained in tyre pyrolysis, *J. Anal. Appl. Pyrol.* 55 (2000) 43-54.

- [36] S. Ucar, S. Karagoz, A.R. Ozkan, J. Yanik, Evaluation of two different scrap tires as hydrocarbon source by pyrolysis, *Fuel* 84 (2005) 1884-1892.
- [37] S. Galvagno, S. Casu, T. Casabianca, A. Calabrese, G. Cornacchia, Pyrolysis process for the treatment of scrap tyres: preliminary experimental results, *Waste Manage.* 22 (2002) 917-923.
- [38] A.M. Fernández, M.A. Díez, R. Álvarez, C. Barriocanal, Pyrolysis of tyre wastes, in: F.A. López, F.Puertas, F.J. Alguacil, A. Guerrero (Eds.), *Advances in Materials Recycling and Eco-Energy*, CSIC, Madrid, 2009, pp.5-8.
- [39] E. Grieco, M. Bernardi, G. Baldi, Styrene-butadiene rubber pyrolysis: Products, kinetics, modelling, *J. Anal. Appl. Pyrol.* 82 (2008) 304-311.
- [40] M.A. Karel, M.H. Blumenthal, Air regulatory impacts of the use of tire-derived fuel, *Environ. Prog.* 20 (2001) 80-86.
- [41] A. Donatelli, P. Iovane, A. Molino, High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Experimental and numerical investigations, *Fuel* 89 (2010) 2721-2728
- [42] S. Brunauer, P.H. Emmett, E.Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309-319.
- [43] M.M. Dubinin, Fundamentals of theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures, *Carbon* 27 (1989) 457-467.
- [44] T.A. Centeno, F. Stoeckli, The assessment of surface areas in porous carbons by two model-independent techniques, the DR equation and DFT, *Carbon* 48 (2010) 2478-2486.
- [45] S. Galvano, S. Casu, M. Martino, E. Di Palma, S. Portofino, Thermal and kinetics study of tyre waste pyrolysis via TG-FTIR-MS analysis, *J. Therm. Anal. Calorim.* 88 (2007) 507-514.
- [46] J.H. Chen, K.S. Chen, L.Y. Tong, On the pyrolysis kinetics of scrap automotive tires, *J. Hazard. Mater.* 84 (2001) 43-55
- [47] I. de Marco Rodriguez, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomón, B.Caballero, Pyrolysis of scrap tyres, *Fuel Process. Technol.* 72 (2001) 9-22.
- [48] M.A. Cunliffe, P.T. Williams, Composition of oils derived from the batch

- pyrolysis of tyres, *J. Anal. Appl. Pyrolysis* 44 (1998) 131–152.
- [49] C. Roy, J. Unsworth, Pilot plant demonstration of used tyres vacuum pyrolysis, in: G.L. Ferrero, K. Maniatis, A. Buekens, A.V. Bridgwater (Eds.), *Pyrolysis and Gasification*, Elsevier Applied Science, London, 1989, pp. 180-189.
- [50] A. Lucchesi, G. Maschio, Semi-active carbon and aromatics produced by pyrolysis of scrap tires, *Resour. Conserv. Recy.* 6 (1983) 85-90.
- [51] F. González, J.M. Encinar, J.L. Canito, J.J. Rodríguez, Pyrolysis of automobile tires wastes. Influence of operating variable and kinetic study, *J. Anal. Appl. Pyrol.* 58–59 (2001) 667–683.
- [52] C. Berrueco, E. Esperanza, F.J. Mastral, J. Ceamanos, P. García-Bacaicoa, Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained, *J. Anal. Appl. Pyrol.* 74 (2005) 245-253.
- [53] J.M. Bouvier, F. Charbel, M. Gelus, Gas-solid pyrolysis of tire wastes. Kinetics and material balances of batch pyrolysis of used tires, *Resour. Conserv. Recy.* 15 (1987) 205-214.
- [54] M.F. Laresgoiti, B.M. Caballero, I. de Marco, A. Torres, M.A.Cabrero, M.J.Chomón, Characterization of the liquid products obtained in tyre pyrolysis, *J. Anal. Appl. Pyrol.* 71 (2004) 917–934.
- [55] M. Olazar, R. Aguado, M. Arabiourrutia, G. Lopez, A. Barona, J. Bilbao, Catalyst effect on the composition of tire pyrolysis products, *Energ. Fuel.* 22 (2008) 2909–2916.
- [56] M. Arabiourrutia, G. Lopez, G. Elordi, M. Olazar, R. Aguado, J. Bilbao, Product distribution obtained in the pyrolysis of tyres in a conical spouted bed reactor, *Int. J. Chem. Reactor Eng.* 62 (2007) 5271-5275.
- [57] E. Kwon, M.J. Castaldi, An investigation of the thermal degradation mechanisms of a waste tire through chemical analysis including hydrocarbons, benzene derivatives, and Polycyclic Aromatic Hydrocarbons (PAHs) at high temperature. Proceedings of NAWTEC16. May 19-21, 2008, Philadelphia, Pennsylvania, USA (paper NAWTEC16-1914).
- [58] E. Kwon, M.J. Castaldi, Fundamental understanding of the thermal degradation mechanisms of waste tires and their air pollutant generation in a N₂ atmosphere, *Environ. Sci. Technol.* 43 (2009) 5996-6002.

- [59] N.A. Dung, R. Klaewkla S. Wongkasemjit, S. Jitkarnka, Light olefins and light oil production from catalytic pyrolysis of waste tire, *J. Anal. Appl. Pyrol.* 86 (2009) 281-286.
- [60] C. Díez, O. Martínez, L.F. Calvo, J. Cara, A. Morán, Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered, *Waste Manage.* 24 (2004) 463-469.
- [61] R. Helleur, N. Popovic, M. Ikura, M. Stanciulescu, D. Liu, Characterization and potential applications of pyrolytic char from ablative pyrolysis of used tires, *J. Anal. Appl. Pyrol.* 58 (2001) 813-824.
- [62] H. Darmstadt, C. Roy, S. Kaliaguine, ESCA characterization of commercial carbon blacks and of carbon blacks from vacuum pyrolysis of used tires, *Carbon* 32 (1994) 1399-1406.
- [63] G. San Miguel, G.D. Fowler, C.J. Sollars. A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber. *Carbon* 41 (2003) 1009-1016.
- [64] H. Darmstadt, C. Roy, S. Kaliagljine, Characterization of pyrolytic carbon blacks from commercial tire pyrolysis plants, *Carbon* 33 (1995)1449-1455.
- [65] R. Murillo, A. Aranda, E. Aylon, M.S. Callen, A.M. Mastral, Process for the separation of gas products from waste tire pyrolysis, *Ind. Eng. Chem. Res.* 45 (2006) 1734-1738.
- [66] H.F. Stoeckli, D. Huguenin, A. Laederach, On the characterization of carbon blacks by various techniques, *Carbon* 32 (1994) 1359-1362.
- [67] H.F. Stoeckli, A. Laederach, On the characterization of industrial carbon blacks by physico-chemical and by empirical parameters, *Carbon* 34 (1996) 135-137.

Figures

Figure 1. Flow diagram of the proposed distillation process.

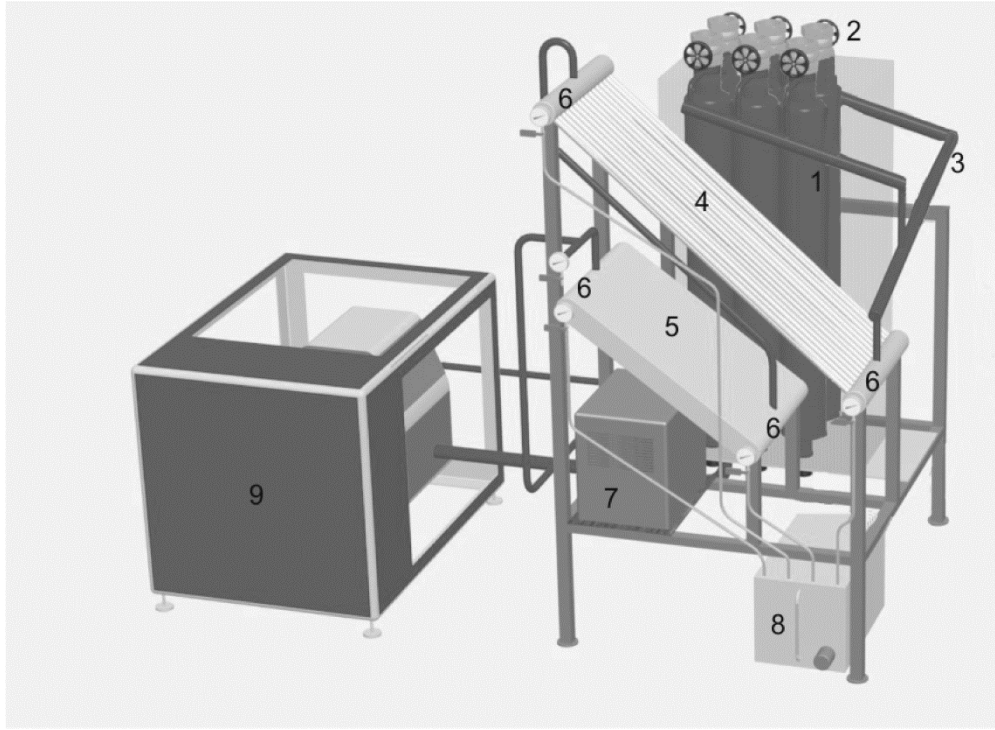


Figure 2. TG and DTG curves for GST under thermal degradation in N_2 and O_2 atmospheres.

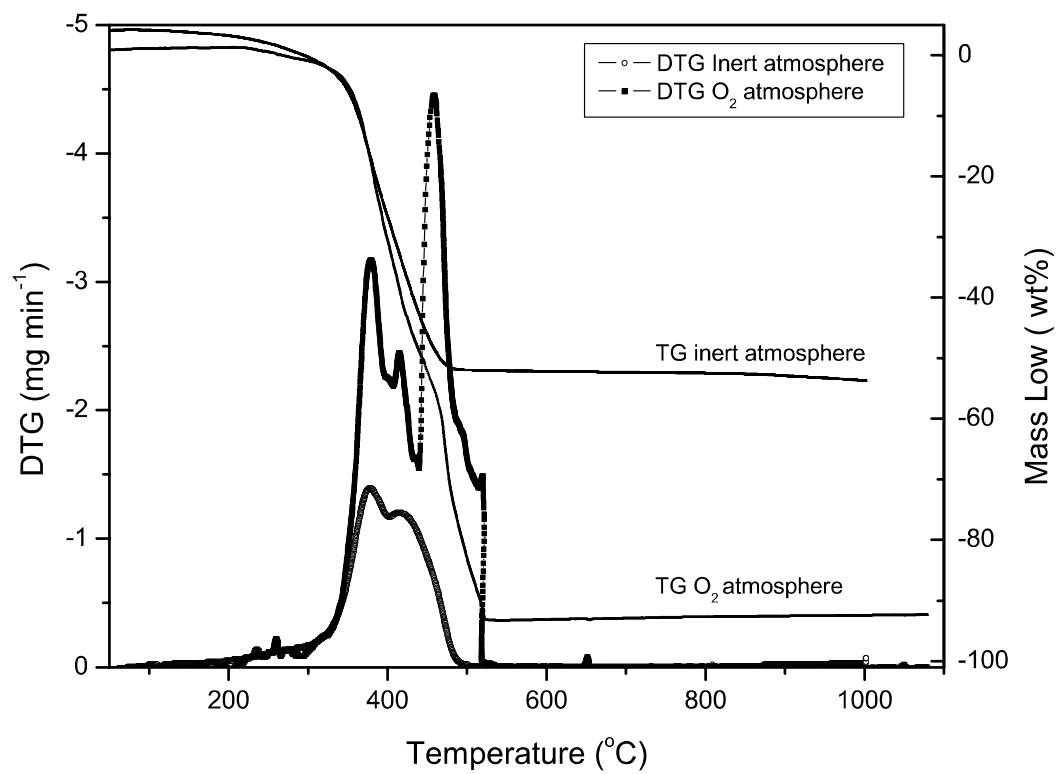


Figure 3. Distillation data from the tyre-derived oil, automotive diesel oil and gasoline.

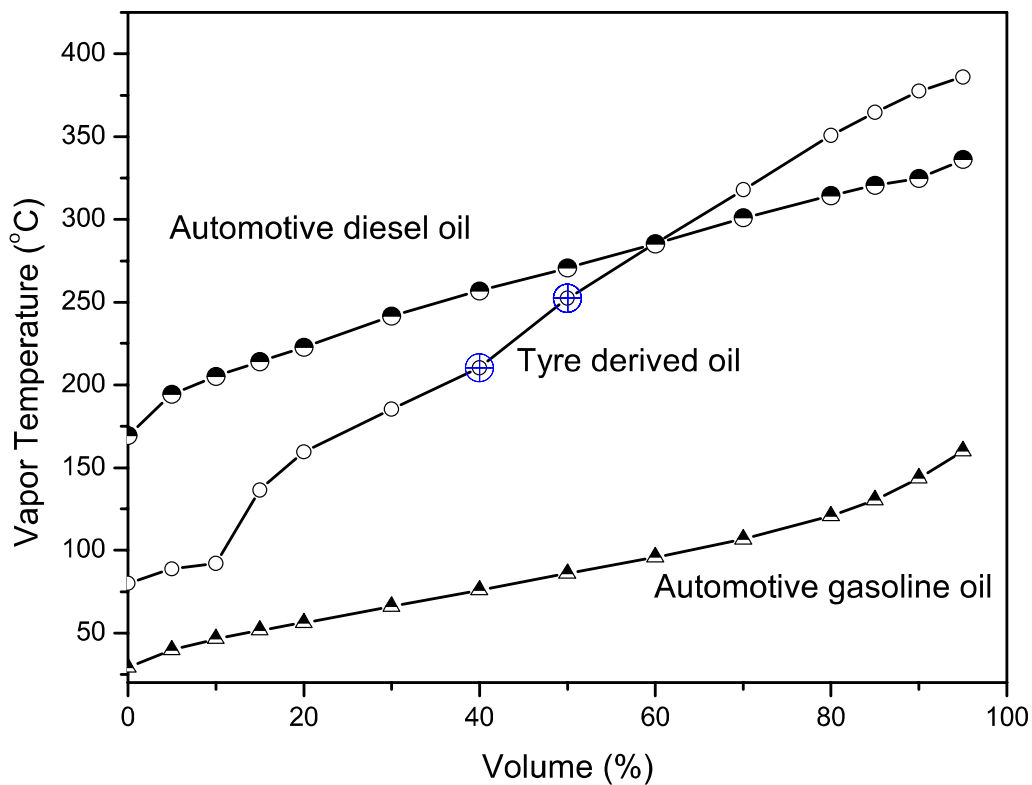


Figure 4. X-ray diffraction patterns for the char obtained by the distillation of GST at 550°C. (C = Carbon, W = Wurtzite (ZnS), Z= Zincite (ZnO))

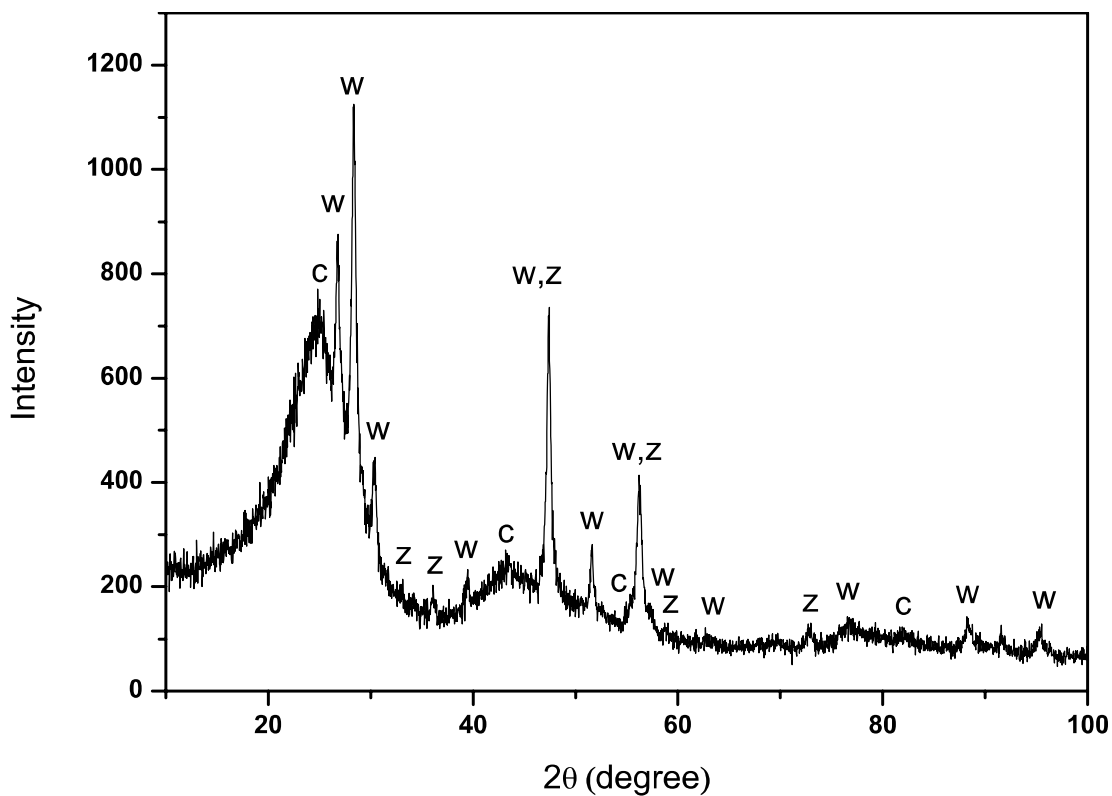


Figure 5. SEM image of char showing the hexagonal crystalline structure of ZnS.

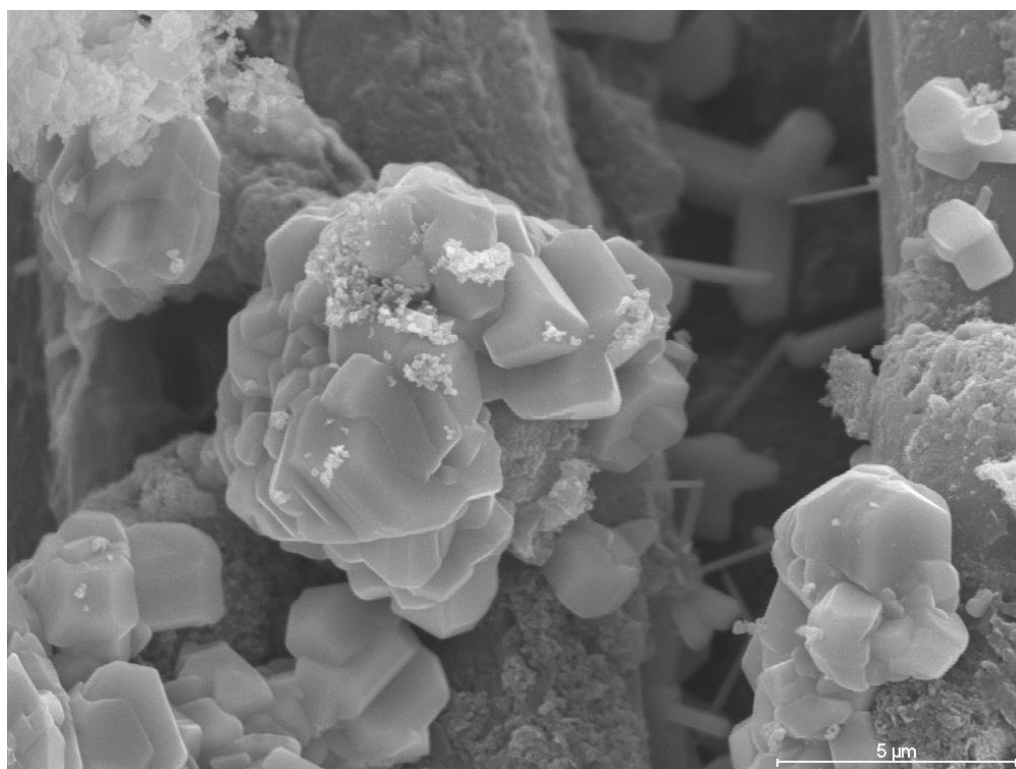
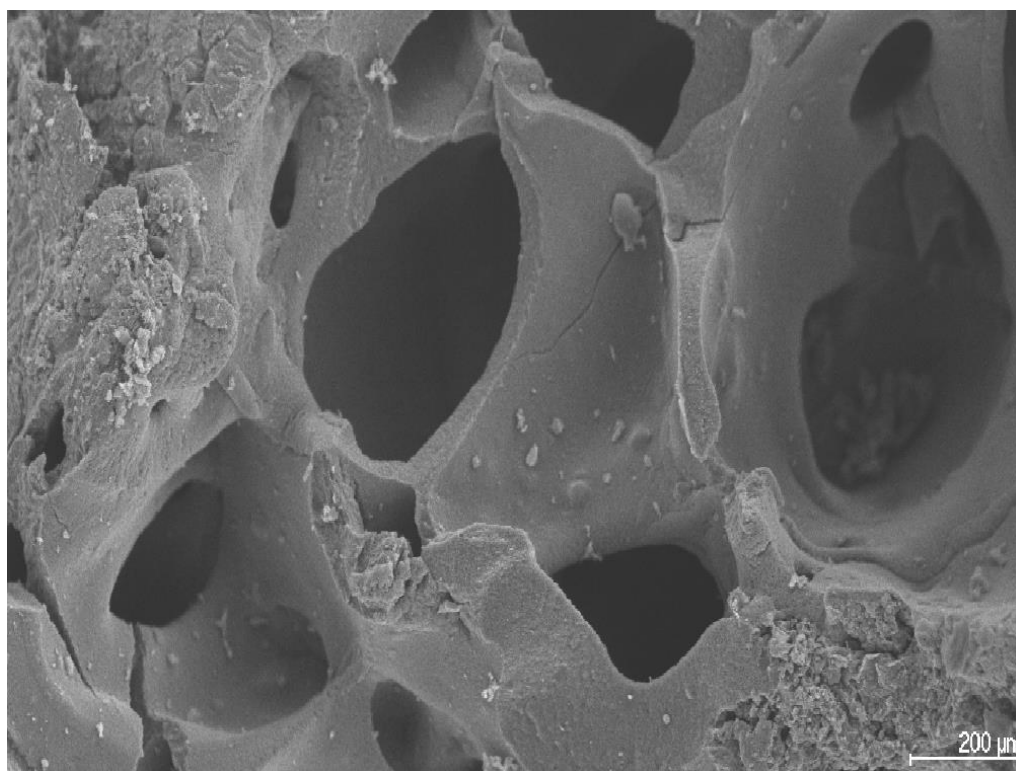


Figure 6. SEM image of macropores in the char.



Tables

Table 1. Proximate and elemental analysis of the GST used in this work and comparison with values quoted in the literature. († granulated scrap tires)

	Present paper [†]	Murugan <i>et al.</i> [29]	Laresgoiti <i>et al.</i> [41]	Ucar <i>et al.</i> [42]	Galvagno <i>et al.</i> [43]	Fernández <i>et al.</i> [†] [44]	Grieco <i>et al.</i> [45]	Karell <i>et al.</i> [46]	Donatelli <i>et al.</i> [†] [47]
Proximate analysis (% w/w _{dry})									
Moisture (% w/w)	0.4	0		1.4	1.2	-	-	0.6	0.8
Volatile matter	66.0	67.1		67.0	61.3	63.0	-	66.6	61.8
Ash	4.9	4.8		5.1	5.2	9.3	11.1	4.8	4.4
Fixed carbon	29.1	28.1		27.9	33.5	27.7	-	28.6	33.8
Elemental analysis (wt.%)									
C	86.0	83.5	85.4	83.2	85.2	87.6	90.7	88.1	89.1
H	8.4	13.1	6.7	7.7	7.3	7.6	7.5	7.4	7.6
N	0.5	0.2	0.3	1.5	0.4	0.3	0	0.2	0.4
S	1.9	0.7	1.7	1.4	2.3	2.0	1.3	1.3	2.4
O (by diff.)	3.2	2.5	4.7	6.2	0.5	3.1	0.5	2.2	0.4
GCV (MJ kg ⁻¹)	38.3	-	31.8	33.4	38.6	-	-	37.9	37.1

Table 2. Composition and physical properties of the liquid fraction obtained by distillation of GST at 550°C.

Condenser	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	GCV (MJkg ⁻¹)	Density at 20 °C (kgm ⁻³)	Viscosity at 40 °C (cSt)	Flash point (°C)
1	88.8	9.95	0.44	0.70	42.22	0.90	2.99	20
2	79.6	11.7	0.16	0.44	43.35	0.89	1.87	<20
Total oil	85.4	11.4	0.40	0.60	43.27	0.90	2.81	20

Table 3. Tentative characterization of the oil (pooled from condensers 1 and 2) obtained by GST distillation at 550°C (quantitative estimation based on the relative areas under each peak).

Compounds	% PCT
PAH's	
Fluorene	0.6±0.5
Anthracene and pheanthrene	2.2± 1.2
Indane	1.7±0.3
Indene	7.7±0.5
Naphthalene and derivatives	15.8±2.1
Biphenil	1.1±0.6
TOTAL PAH's	28.9±3.4
VOCs	16.6±0.4
Benzene and derivatives	0.7±0.4
Estirene	0.6±0.02
Cumene	12.2±2.9
Limonene	n.d
Phenol	5.2±0.2
o,m,p-xilenes	12.2±0.8
Toluene and derivatives	47.5±3.9
TOTAL VOCs	
Hetero-N and S	
Benzothiazol	1.4±0.3
Thiophene and benzo-thiophene	0.8±0.7
Heptadecan-1-nitrile	1.1±0.4
Dimethyl quinoline	0.8±0.1
1,4-benzendiamine	1.0±0.4
TOTAL Hetero-N and S	5.2±0.4
Aliphatics	
Pentadecane, heptadecane and octane	2.8±0.2
Cyclobutane and Cyclohexenes	6.8±2.8
TOTAL Aliphatics	9.7±2.9

Table 4. Composition and GCV of the distillation gas.

Gas	Vol. %
H ₂	22.27
O ₂	0.73
N ₂	1.86
CO	1.98
CO ₂	2.54
Total COx	4.51
CH ₄	21.32
Total C1	21.32
C ₂ H ₄ (ethene)	2.32
C ₂ H ₆ (ethane)	4.19
Total C2	6.50
C ₃ H ₆ (propene)	2.80
C ₃ H ₈ (propane)	2.63
Total C3	5.43
C ₄ H ₈ (2-butene)	0.44
nC ₄ H ₁₀ (n-butane)	33.60
isoC ₄ H ₁₀ (i-butane)	1.35
Total C4	35.39
C5 and C6	< 2
H ₂ S	n.d.
NH ₃	n.d.
GCV (MJ kg ⁻¹)	46.5
(MJ Nm ⁻³)	68.7

Table 5. Chemical composition and properties of the char obtained.

Property (% w/w _{dry})	Present paper	Olazar <i>et al.</i> [62] (Thermal Pyrolysis)	Olazar <i>et al.</i> [62] (Pyrolysis with Zeolites)	Ucar <i>et al.</i> [42] (Pyrolysis in a fixed bed reactor)	Lopez <i>et al.</i> [39] (Pyrolysis in a CSBR) ^a
Moisture (% w/w)	0.4	-	-	-	-
Volatile matter	1.8	-	-	-	-
Ash	12.5	14.8	-	13.5 -14.8	-
Fixed carbon	91.3	-	-	82.6-84.3	-
C (wt.%)	86.3	83.0	83.0-89.0	-	86.2 – 87.2
H (wt.%)	0.3	1.3	0.5	-	0.7 – 1.3
N (wt.%)	0.3	0.3	< 0.1	-	0.3 – 0.7
S (wt.%)	2.8	2.7	1.8 – 2.1	2.0-2.3	2.1 – 3.6
O (wt.%) [by diff.]	1.2	-	-	-	-
Zn (wt.%)	2.8	3.8	3.4-4.4	-	-
GCV (MJ kg ⁻¹)	29.7	29.3	29.1	33.4-34.2	-
S _{BET} (m ² g ⁻¹)	64	83	83-89	56.5-66.0	61.1 – 77.9
Total pore volume (cm ³ g ⁻¹)	0.4	-	-	-	-

^a Conical spouted bed reactor.

Table 6. Composition of the ash (expressed by wt% of oxides) in the char.

Component	Content (wt.%)
Na ₂ O	8.6
MgO	0.9
Al ₂ O ₃	2.8
SiO ₂	52.0
P ₂ O ₅	0.5
K ₂ O	0.7
CaO	4.6
TiO ₂	0.4
CuO	0.04
ZnO	27.0
Fe ₂ O ₃	0.8