

Article

Influence of Specific Power on the Solid and Liquid Products Obtained in the Microwave-Assisted Pyrolysis of End-of-Life Tires

María Teresa Martín ^{1,2,*} , Juan Luis Aguirre ^{1,2,*} , Juan Baena-González ^{1,2} , Sergio González ^{1,2}, Roberto Pérez-Aparicio ³ and Leticia Saiz-Rodríguez ³

¹ Cátedra de Medio Ambiente, Facultad de Ciencias, Universidad de Alcalá, 28871 Alcalá de Henares, Spain; juan.baena@uah.es (J.B.-G.); sergio.gonzalez@uah.es (S.G.)

² Environment and Bioproducts Group, Facultad de Ciencias, Universidad de Alcalá, 28871 Alcalá de Henares, Spain

³ Sistema Colectivo de Gestión de Neumáticos Fuera de Uso (SIGNUS), 28033 Madrid, Spain; rperez@signus.es (R.P.-A.); lsaiz@signus.es (L.S.-R.)

* Correspondence: maite.martin@edu.uah.es (M.T.M.); juanl.aguirre@uah.es (J.L.A.); Tel.: +34-918-854-924 (J.L.A.)

Abstract: In this work, chemical recycling as an alternative to conventional end-of-life treatments was studied. Two different types of end-of-life tires (ELT), truck tires and mix tires (50:50 mixture of passenger car and truck tires), were pyrolyzed in a batch microwave reactor. The influence of specific power (10, 20, and 30 W/g) on mass distribution was analyzed. The maximum liquid yield was attained at 10 W/g, while the maximum gas yield is obtained at 30 W/g. Liquid fractions were characterized by gas chromatography/quadrupole mass spectrometry (GC/qMS) to identify the main components, and major compounds were quantified. In all samples, limonene (3.76 ± 0.31 – 6.80 ± 2.37 wt. %) and BTEX (3.83 ± 0.20 – 1.19 ± 2.80 wt. %) were the main components. Major limonene concentration is obtained in oil produced from truck ELT while higher yields of aromatic compounds are obtained from mix ELT. The maximum BTEX concentration is obtained at 10 W/g being toluene the main compound with a concentration of 2.07 ± 0.42 and 4.63 ± 1.29 for truck and mix ELT, respectively. The separation and purification of these compounds will confer important value to these fractions. Higher yields of the solid fraction are produced when mix tires are pyrolyzed due to the higher concentration of ash in this type of ELT. Recovered carbon black was characterized by measuring the surface area.

Keywords: end-of-life tires; microwave-assisted pyrolysis; specific power; limonene; aromatics compounds



Citation: Martín, M.T.; Aguirre, J.L.; Baena-González, J.; González, S.; Pérez-Aparicio, R.; Saiz-Rodríguez, L. Influence of Specific Power on the Solid and Liquid Products Obtained in the Microwave-Assisted Pyrolysis of End-of-Life Tires. *Energies* **2022**, *15*, 2128. <https://doi.org/10.3390/en15062128>

Academic Editor: Gabriele Di Giacomo

Received: 30 January 2022

Accepted: 11 March 2022

Published: 14 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The recycling and recovery of end-of-life tires (ELT) is very important for the application of the Circular Economy model, as it allows a waste (ELT) to be transformed into a source of material and energy resources. Over the last few years, many efforts have been made in order to find more sustainable products and processes that minimize the consumption of resources. There are many advantages in using materials from ELT, in particular rubber, and there are numerous well-consolidated applications in different market niches, reflecting the increasing growth of ELT as a source of materials of technological and industrial interest. However, it is not enough and any development or innovative recovery process are needed to broaden the opportunities for the ELT rubber. Rubber is not the only component of ELT rubber, and the presence of other substances such as carbon black could also be a source of material resources [1,2].

Currently, the main ways of treating ELTs are crushing and/or mechanical granulation, at both environmental and cryogenic conditions, or energy recovery [3]. These recovery

and recycling procedures have some limitations and are not sufficient to manage the large amount of ELT generated annually. Therefore, chemical recycling would be a promising alternative to open new recovery opportunities, and obtain products with potential applications as raw materials for the chemical industry or in the synthesis of new materials. In this context, pyrolysis is postulated to be one of the most advantageous techniques for the chemical recycling of tires [4]. Pyrolysis is a thermochemical process that, in the total or partial absence of oxygen, causes the cracking of polymeric chains, resulting in a liquid fraction, a gas phase, and a solid fraction [5].

The liquid fraction consists of a mixture of C6–C24 hydrocarbons, where aromatic, aliphatic, and some oxygenated, nitrogenous, and sulfur compounds predominate [6,7]. This fraction could be an important source for obtaining high value-added chemical compounds, such as aromatic hydrocarbons, BTEX (mixture of benzene, toluene, ethylbenzene, and xylene), or limonene [8,9]. In addition, due to its high heating value of 41–44 MJ/kg [10], it could be used as fuel. To improve its properties as a fuel (cetane number and flash point) and reduce pollutant emissions, some authors have studied the behavior of mixtures with diesel [11–15]. The gaseous fraction is mainly composed of H₂, CO, and CO₂ and low-molecular-weight organic compounds such as ethylene, acetylene, or propylene and has a high heating value, 42–49 MJ/kg [16,17]. This fraction can be used as an energy source in the pyrolysis process or as a raw material in Fischer–Tropsch synthesis [18,19].

The resulting solid fraction is composed of the starting carbon black and the inorganic matter present in the composition of the tires [20]. Among the potential applications of recovered carbon black, its use as a substitute for commercial carbon black stands out [21,22], although some authors study its use as a precursor to obtain activated carbon [23].

The distribution of the products and their composition depends on the type of tires, as well as the reactor configuration and the operating conditions used [24,25]. Different reactor configurations for ELT pyrolysis, such as fixed bed [26,27], fluidized bed [28], auger [29], rotary kiln [30,31], and microwave [32] reactors, have been studied. The use of microwave technology in pyrolysis processes provides benefits with respect to conventional heating, such as the homogeneity of temperature in the irradiated sample, the high degree of temperature control, and the possibility of applying high amounts of energy over very short times and ease of implementation on an industrial scale [33–35]. Furthermore, the use of microwave technology in the ELT treatment is reported to improve the quality of the products and increase limonene concentration in oil [36,37]. Although polymeric materials do not have the ability to absorb microwaves and convert them into heat due to their poor dielectric properties, tires contain carbon black, which acts as an excellent microwave absorber [38].

The present work studies the microwave-assisted pyrolysis of two types of ELT rubber, truck tires, and mix tires (a 50:50 mixture of passenger car and truck tires). The influence of the specific power (SP) and the type of raw material used in the distribution of the products is analyzed. In addition, the characterization of the liquid and solid fractions obtained is performed to determine their potential applications as sources of resources for obtaining high-added value products. Numerous studies have reported the properties and composition of these fractions, but information about the weight percentage of the main compounds present in pyrolytic oil is still scarce. Accordingly, in this study, the concentration (wt. %) of the main components is analyzed to evaluate the potential of oil from ELT pyrolysis as a source of chemicals such as limonene and aromatic compounds in line with circular economy guidelines.

2. Materials and Method

2.1. Feedstock Materials

Tires are complex products made from many components: rubbers, carbon black, silica particles, additives, as well as steel and textile fibers. To produce ground rubber (granulates and powders) for recycling in several applications, ELT go through two steps: size reduction and separation of rubber and non-rubber parts (steel is separated by magnetic process

and textile fibers are separated by vacuum systems). Then, cuts, shreds, chips, granulates (1–10 mm), powders (<0.8 mm), steel, and textile fibers can be obtained.

Two different types of ELT rubber granulated with sizes between 2 and 4 mm have been used for this work, i.e., truck ELT rubber and Mix ELT. Mix ELT sample consists of a 50:50 mixture of passenger car and truck ELT rubber. Both granulate materials were supplied by Valoriza Servicios Medioambientales S.A. (Guadalajara, Spain).

The feedstock characterization is shown in Table 1. The elemental analysis results showed some differences between the two samples.

Table 1. Characterization of the feedstock material.

Sample	Truck ELT	Mix ELT
Elemental Analysis (wt. %)		
C	81.86	78.94
H	7.45	7.17
N	0.46	0.38
S	1.80	2.07
Cl	0.022	0.025
O + Others ^a	8.41	11.42
Proximate Analysis ^b (wt. %)		
Volatiles	65.70	64.50
Ash	5.40	10.02
Fixed Carbon	28.10	24.89
Moisture (wt. %)	0.80	0.59
LHV (MJ kg ⁻¹)	35.73	34.10

^a by difference. ^b on dry basis. LHV: Low Heating Value. Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

The sample from mix ELT contains a greater amount of ash due to the greater number of fillers, such as carbon black and silicam that are added in its formulation.

Thermogravimetric analysis (TGA) was carried out using a TGA 2 Excellence System equipment (Mettler Toledo, Columbus, Ohio, OH, USA) with a temperature rate of 5 °C/min from 20 °C to 1000 °C in N₂ atmosphere.

2.2. Experimental Set-Up

Pyrolysis system (Figure 1) consists of a Microsynth Microwave oven (Milestone Srl, Sorisole, Bergamo, Italy), a quartz flask (500 mL), and a glass condensation system connected to an MZ 2C vacuum pump (Vacuubrand, Wertheim, Baden-Wurtemberg, Germany). To ensure an inert atmosphere, the vacuum system was connected for 15 min before starting the heating process. Experiments were developed using three different specific power (10, 20, and 30 W/g). For each trial, ground rubber was placed in the quartz flask and heated under vacuum until it was fully pyrolyzed. Microwave power was kept constant at 1000 W and three different amounts of raw material were used: 100 g (10 W/g), 50 g (20 W/g), and 33 g (30 W/g). Volatile compounds were passed through the ethanol-cooled system (at 5 °C) to produce a liquid fraction (oil) and a non-condensable gas fraction. Gas fraction was collected in 500 mL metal bags (after 10 min since the reaction starts). Pyrolysis reaction is completed when no gas is appreciated within the cooling system (approximately 20 min). After that, the vacuum system continued working for 15 min to prevent condensation of pyrolysis oil on the solid residue surface. Temperature was measured with an infrared thermometer Gesa IT-900 (Gesa Termómetros S. L., Urduliz, Vizcaya, Spain) just when the pyrolysis reaction is finished. Each experiment was repeated three times. Temperature measured was 550 °C (10 W/g), 520 °C (20 W/g), and 520 °C (30 W/g) in Mix ELT samples pyrolysis experiments and 500 °C (10 W/g), 500 °C (20 W/g), and 500 °C (30 W/g) in Truck ELT samples.

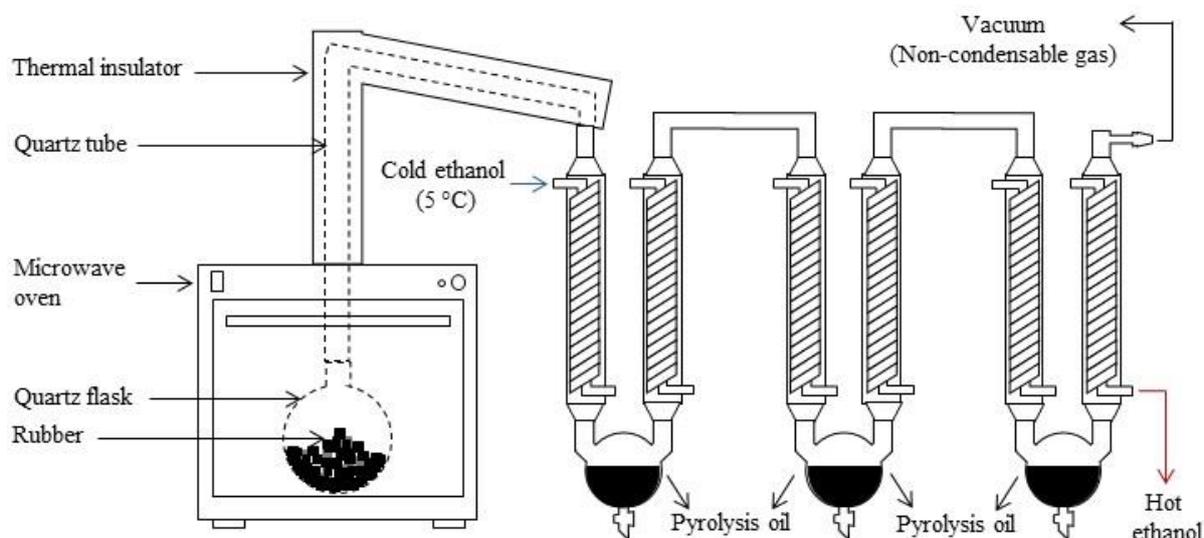


Figure 1. Schematic diagram of the microwave pyrolysis system.

The resulting pyrolysis oil and carbon residue, recovered from the quartz flask, were weighed. Mass balances were developed to assess the products distribution. Gas fraction was calculated by difference.

2.3. Product Analysis

2.3.1. CG-MS Analysis

The chemical composition of the liquid fractions was determined by gas chromatography using a method previously developed by our research group [39–41]. The analysis was carried out by means of an Agilent 7890 A gas chromatograph coupled with a 5977 A single quadrupole mass spectrometer (GC/qMS) (Agilent Technologies, Santa Clara, California, CA, USA) provided with a column Phenomenex ZB-624 (30 m; 0.25 mm i.d.; 0.25 μ m film thickness, 6% cyanopropylphenyl/94% dimethylpolysiloxane; Torrance, California, CA, USA). Peak identification was performed by comparison of the mass spectra available in the NIST I and NIST II libraries.

The quantification was developed using the internal standard method, by constructing a calibration curve for each of the following compounds: limonene, benzene, toluene, ethylbenzene, xylene, styrene, methylstyrene, and naphthalene. Quantification was performed from the areas obtained by the extraction of the quantifying ion of each compound, in both standards and samples.

2.3.2. Moisture Content

Water content of the oil samples was analyzed by Karl–Fischer (KF) analysis using a 701 KF Tritinio (Metrohm AG, Herisau, Switzerland) equipped with a 703 TI stand (Metrohm AG).

2.3.3. Elemental Analysis, Chlorine, Sulfur, Oxygen, and Calorific Value Determination

Liquid samples composition was determined using different techniques. Elemental composition (C, H, N) was analyzed by a LECO CHN600 elemental analyzer (LECO Corporation, St. Joseph, Michigan, MI, USA) according to ASTM 5291. Chlorine content was determined in a Metrohm 809 titrator (Metrohm AG) with a 0.80 Ag-Titrode electrode according to ASTM 2361 method and sulfur content on a LECO SC 132, according to ASTM 1552. The oxygen content was calculated by difference. Heating value measurements were determined on a LECO AC 600 calorimeter (LECO Corporation), according to ASTM 240.

2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the functional groups of oil samples. Spectra were recorded in an Agilent Cary 630 spectrophotometer (Agilent Technologies) equipped with ATR diamond crystal. The spectra were obtained with a resolution of 4 cm^{-1} by accumulation of 32 scans in the range of 3500 to 500 cm^{-1} .

2.3.5. Surface Area Determination

Recovered carbon black specific surface area was measured with an ASAP 2020 equipment (Micromeritics Instrument Corp. Norcross, GA, USA) using the BET (Brunauer–Emmett–Teller) method (UNE-ISO 9277). Samples were outgassed at 150 °C for 5 h under vacuum (9 mbar). This first external outgassing stage was developed as the presence of volatiles could alter the measurement and also damage the equipment. Once the sample was placed in the port, the degassing conditions were 120 °C for 90 min under vacuum (2 mbar).

3. Results and Discussion

3.1. Feedstock Characterization

Results obtained in the thermogravimetric analysis (TGA and DTGA) of Truck and Mix ELT samples are shown in Figure 2. These analyses conclude that volatile matter is higher in truck tires than that present in mix tires.

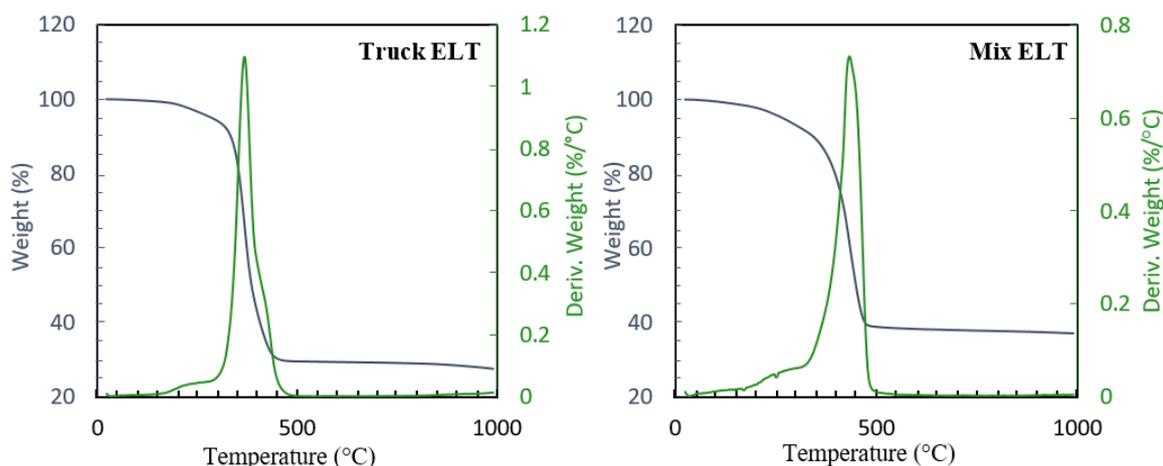


Figure 2. Thermo (TGA) and Derivate (DTGA) Gravimetric results. Results are obtained at a heating rate of 5 °C/min in N_2 atmosphere from 20 °C to 1000 °C for a sample mass of 10.0 mg. Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

During the first warm-up stage (20 °C to 300 °C), a slight loss of weight was observed for truck tire sample (5.86%) as well as for mix sample (6.93%). This mass loss is related to the volatilization of moisture as well as the more volatile organic compounds, such as plasticizers, oils, and other additives [42,43].

In the range from 300 to 500 °C , the highest weight loss occurred for both samples, being higher in truck tires (64.64%) than in mix tires (54.24%). In this interval, at 370 °C , truck ELT occurred the greatest weight loss, while mix ELT suffered the highest weight loss at 437 °C . These results can be attributed to the higher natural rubber (NR) content in truck tire, whose decomposition temperature is between 300 and 490 °C , while the degradation temperature for synthetic rubbers, styrene-butadiene rubber (SBR) and butadiene rubber (BR), is between 400 and 500 °C [42,44,45].

Finally, from 500 °C to 1000 °C , in both samples, the percentage of mass loss is quite small (1.75% for mix ELT and 1.99% for truck ELT). The resulting residue consists mainly of inorganic matter and carbon black present in tire formulation [46].

3.2. Distribution of Pyrolysis Products

The influence of the three specific powers used in this work (10 W/g, 20 W/g, and 30 W/g) on the products' distribution is presented in Figure 3.

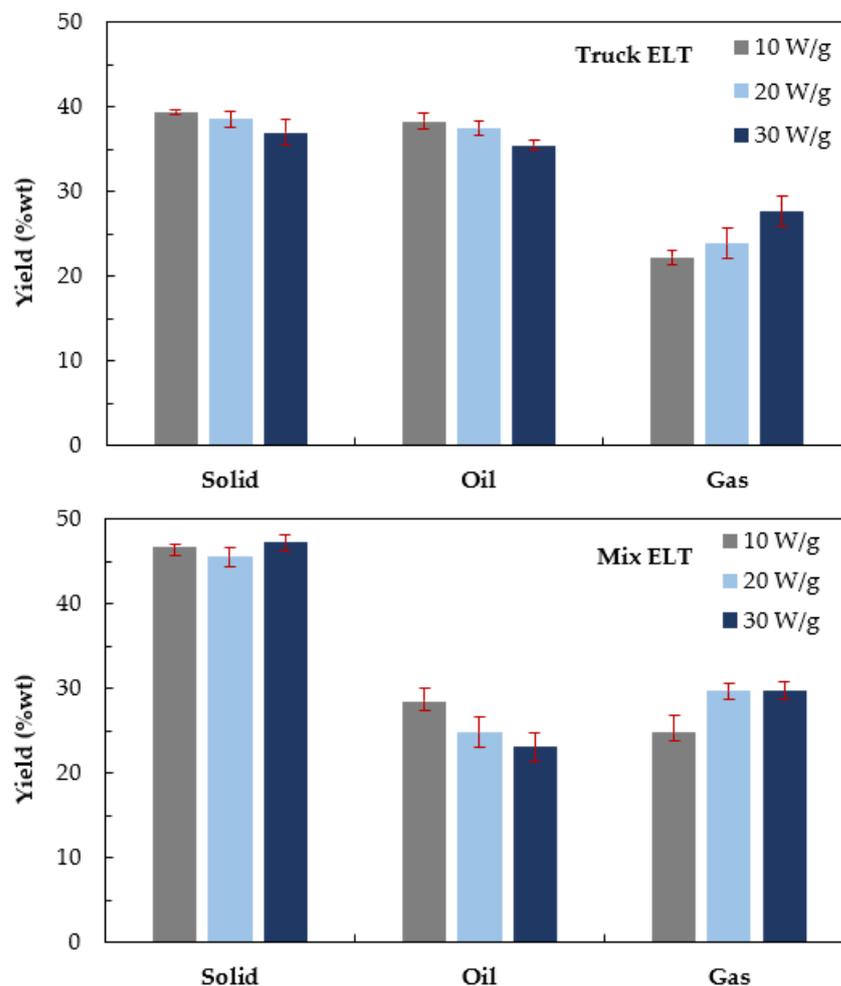


Figure 3. Mass balance ($n = 3$). Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

If the mass balances yielded by truck ELT pyrolysis are compared with those of the mix ELT under the same conditions, a significant difference in yield of the solid is observed. This fact is due to the higher proportion of filler compounds, such as silica, contained in the mix tires, which translates into a higher ash content [47]. As observed in ELT sample analysis (Table 1), the percentage of ash in truck tires is 5.40%, while in the mix tires sample, it is 10.02%. The higher solid yield in the tests performed from mix ELT translates into lower proportions of liquid and gaseous fractions. Ucar et al. also reported differences in the products distribution when truck and car tires were pyrolyzed. For all the temperatures studied, a higher oil yield and lower char yield were obtained in the treatment of truck tires [48]. On the other hand, Singh, R. K et al. studied the pyrolysis of three types of tires (motorcycle, bicycle tires, car tires, and bus and lorry tires), concluding that the low ash content of truck tires results in a higher oil yield and in the minimum proportion of char, while in car tires, a higher solid yield is obtained [47].

The most evident effects of the increase in the specific power in the tests performed from mix ELT were observed on the oil and the gas fractions. Increasing the specific power reduced the oil yield while increasing the gas. Thus, the yield in oil decreased from $28.47 \pm 1.62\%$ (10 W/g) to $24.83 \pm 1.83\%$ (20 W/g) and at $23.06 \pm 1.75\%$ (30 W/g), while the gas yield increased from $24.83 \pm 1.97\%$ (10 W/g) to $29.64 \pm 0.93\%$ (20 W/g). The increase in SP from 20 to 30 W/g did not affect the yield of the gas fraction, which

remained at $29.74 \pm 1.07\%$. The total amount of oil and gas was lower than the amount of volatiles determined in the proximate analysis ($64.50 \text{ wt.}\%$) due to the conversion of part of the primary pyrolysis products into solid at high temperatures by repolymerization processes [49]. This phenomenon resulted in solid fraction yields of 46.70 ± 0.36 (10 W/g), 45.53 ± 1.09 (20 W/g), and $47.20 \pm 0.96\%$ (30 W/g), values higher than the sum of fixed carbon and ash (34.91%) determined in the proximate analysis.

On the other hand, in the tests carried out with truck tires, when increasing the SP, the solid yield decreased slightly from $39.45 \pm 0.31\%$ (10 W/g) to $37.01 \pm 1.46\%$ (30 W/g). The liquid fraction, as in the case of the mix samples, decreases with the specific power, going from $38.28 \pm 0.96\%$ (10 W/g) to $35.32 \pm 0.53\%$ (30 W/g), while the gaseous fraction increases from $22.27 \pm 0.84\%$ (10 W/g) to $27.66 \pm 1.84\%$ (30 W/g). Idris et al. studied the microwave pyrolysis of truck tires and reported the maximum oil yield, 38.12% , at $500 \text{ }^\circ\text{C}$ [33].

In both truck and mix ELT tests, the highest liquid yield was obtained at a specific power of 10 W/g, while the highest gas yield was obtained at 30 W/g. Since microwave power is kept constant at 1000 W and the amount of the feedstock is modified, it should be pointed out that the number of vapors generated and the residence time play an important role. At 10 W/g, a higher number of vapors are generated; additionally, the volume occupied by tires in the reactor is greater. Therefore, the residence time of vapors in the reactor is shorter, so the incidence of secondary reactions is reduced, avoiding the cracking of the condensable fraction.

3.3. Liquid Products

The pyrolysis oils obtained are dark brown and have a low moisture content (0.32 ± 0.07 – $2.26 \pm 0.64\%$). The samples were characterized by elemental analysis and heating value, in addition to the study of their chemical composition by FTIR and CG-MS.

Table 2 shows the elemental analysis of the liquid fractions obtained from truck ELT and mix ELT at different specific powers.

Table 2. Elemental analysis and LHV of liquid samples.

Tire Type	Truck ELT			Mix ELT			
	Specific Power (W/g)	10	20	30	10	20	30
Elemental Analysis (wt. %)							
C		86.47 ± 1.21	81.90 ± 1.54	79.60 ± 4.11	85.43 ± 1.69	81.53 ± 1.29	80.90 ± 2.95
H		10.20 ± 0.10	10.20 ± 0.10	10.10 ± 0.17	9.63 ± 0.06	9.80 ± 0.10	9.80 ± 0.10
N		0.33 ± 0.03	0.35 ± 0.05	0.31 ± 0.03	0.36 ± 0.01	0.41 ± 0.09	0.37 ± 0.03
S		0.79 ± 0.02	0.86 ± 0.03	0.86 ± 0.03	0.97 ± 0.01	0.96 ± 0.04	0.89 ± 0.04
Cl		0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
O ^a		2.19 ± 1.10	6.67 ± 1.52	9.11 ± 3.96	3.59 ± 1.65	7.28 ± 1.34	8.02 ± 2.86
Moisture (wt.%)		0.32 ± 0.07	2.26 ± 0.64	0.99 ± 1.12	0.54 ± 0.07	0.73 ± 0.19	1.11 ± 0.19
LHV (MJ kg ⁻¹)		40.03 ± 0.51	38.14 ± 0.74	37.37 ± 1.62	39.79 ± 0.5	37.85 ± 0.57	37.71 ± 1.29

^a by difference. LHV: Low Heating Value. Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

The elemental analysis of the liquid fractions from the pyrolysis of truck and mix tires shows similar results. The carbon content varies between 85.43 ± 1.69 and 80.90 ± 2.95 in the case of oil from the mix tires and 86.47 ± 1.21 and 79.60 ± 4.11 in the case of truck tires. In both cases, the highest carbon content was reached in the tests carried out at a lower specific power, 10 W/g. The hydrogen content was maintained at approximately 9.63 ± 0.06 and 9.80 ± 0.10 in the case of mix samples and 10.10 ± 0.17 – 10.20 ± 0.10 in the truck samples. The amount of sulfur is between 0.79 and 0.97%. The heating values ranged between 37.37–40.03 MJ/kg. The results obtained in the analyses coincide with those reported by other authors [50,51].

In addition to its application as a fuel, another form of recovering the liquid fraction from the pyrolysis of tires is obtaining compounds with high added value. The pyrolysis oils obtained are composed of numerous organic compounds, especially paraffins, olefins, and aromatics [33,52,53]. Table 3 shows the compounds identified by GC-MS classified by chemical family.

Table 3. Chromatographic area of compounds identified in oil samples with an area percentage higher than 0.5%.

Specific Power (W/g)	Truck ELT			Mix ELT		
	10	20	30	10	20	30
Compounds	Area%	Area%	Area%	Area%	Area%	Area%
Monoaromatics	42.10 ± 9.94	38.99 ± 5.63	41.23 ± 5.08	54.25 ± 7.13	49.51 ± 7.00	51.89 ± 5.87
Benzene	1.32 ± 0.37	0.88 ± 0.23	0.97 ± 0.18	2.57 ± 0.73	1.52 ± 0.47	2.07 ± 0.51
Toluene	6.52 ± 1.10	4.98 ± 0.70	5.13 ± 0.91	10.33 ± 0.81	7.44 ± 1.66	9.69 ± 0.48
Ethylbenzene	1.05 ± 0.18	1.00 ± 0.16	0.97 ± 0.26	3.09 ± 0.38	2.75 ± 0.55	3.40 ± 0.42
o-Xylene	7.87 ± 0.87	7.25 ± 0.89	7.60 ± 0.69	8.68 ± 0.18	7.37 ± 0.31	8.35 ± 0.47
Styrene	1.69 ± 0.22	1.85 ± 0.11	1.97 ± 0.23	5.75 ± 0.30	5.16 ± 0.33	5.58 ± 0.38
Benzene, 1-ethyl-3-methyl-	2.18 ± 0.55	2.28 ± 0.12	2.50 ± 0.13	2.30 ± 0.31	2.29 ± 0.09	2.39 ± 0.24
Benzene, 1,2,3-trimethyl-	1.88 ± 0.49	1.90 ± 0.28	1.87 ± 0.13	1.78 ± 0.47	1.48 ± 0.33	1.74 ± 0.30
Benzene, 1-ethyl-2methyl-	0.80 ± 0.69	0.92 ± 0.19	0.93 ± 0.13	0.87 ± 0.21	0.78 ± 0.06	0.76 ± 0.06
α-Methylstyrene	1.45 ± 0.51	1.37 ± 0.42	1.38 ± 0.37	1.89 ± 0.32	1.79 ± 0.17	1.84 ± 0.12
Mesitylene	1.97 ± 0.50	1.77 ± 0.41	1.94 ± 0.14	1.97 ± 0.31	1.84 ± 0.04	1.76 ± 0.12
Benzene, 2-propenyl	1.03 ± 0.62	1.09 ± 0.38	1.40 ± 0.10	1.45 ± 0.12	1.51 ± 0.21	1.23 ± 0.27
Benzene, 1,2,4-trimethyl	0.96 ± 0.48	1.11 ± 0.13	1.13 ± 0.17	0.74 ± 0.18	0.95 ± 0.13	0.85 ± 0.18
Benzene, 1-ethynyl-4-methyl	0.76 ± 0.28	0.79 ± 0.02	0.79 ± 0.02	1.52 ± 0.46	1.68 ± 0.22	1.32 ± 0.13
Benzene, 1-methyl-2-(1- methylethyl)-	0.69 ± 0.26	0.74 ± 0.09	0.78 ± 0.07	0.39 ± 0.12	0.48 ± 0.15	0.44 ± 0.07
Benzene, 1-methyl-4-(1- methylethenyl)	2.42 ± 0.36	2.46 ± 0.09	2.42 ± 0.09	1.52 ± 0.16	1.58 ± 0.09	1.40 ± 0.08
Benzene, 1-methyl-4-(2-propenyl)-	0.57 ± 0.26	0.50 ± 0.17	0.61 ± 0.10	0.48 ± 0.08	0.50 ± 0.11	0.50 ± 0.08
Benzene, 2,4-diethyl-1methyl-	0.83 ± 0.11	1.08 ± 0.07	1.05 ± 0.17	0.33 ± 0.09	0.40 ± 0.03	0.32 ± 0.03
Benzene, 1-ethyl-2,3-dimethyl-	0.65 ± 0.06	0.58 ± 0.10	0.57 ± 0.13	0.44 ± 0.13	0.49 ± 0.06	0.38 ± 0.08
Isopropenyltoluene	0.59 ± 0.17	0.49 ± 0.05	0.49 ± 0.10	0.38 ± 0.12	0.49 ± 0.03	0.37 ± 0.11
Benzene, 2-methyl-4-(1- methylethenyl)	0.77 ± 0.08	0.74 ± 0.05	0.78 ± 0.05	0.74 ± 0.04	0.84 ± 0.03	0.86 ± 0.06
Benzene, 2-ethenyl-1,3,5-trimethyl-	0.49 ± 0.16	0.48 ± 0.07	0.55 ± 0.11	0.36 ± 0.04	0.59 ± 0.16	0.56 ± 0.21
1H-Indene, 3-methyl	1.60 ± 0.30	1.37 ± 0.11	1.54 ± 0.05	1.74 ± 0.35	1.94 ± 0.16	1.65 ± 0.20
1H-Indene, 1-methyl	1.26 ± 0.21	1.02 ± 0.09	1.15 ± 0.02	1.43 ± 0.27	1.58 ± 0.28	1.33 ± 0.20
1H-Indene, 1-ethylidene	0.85 ± 0.11	0.74 ± 0.08	0.84 ± 0.08	1.59 ± 0.26	1.67 ± 0.62	1.29 ± 0.17
1H-Indene, 4,7-dimethyl-	0.74 ± 0.12	0.57 ± 0.12	0.64 ± 0.07	0.75 ± 0.08	0.90 ± 0.11	0.60 ± 0.31
Polyaromatics	7.08 ± 1.13	5.77 ± 1.23	6.72 ± 1.50	7.96 ± 1.38	8.98 ± 2.75	7.76 ± 1.57
Naphthalene	0.75 ± 0.07	0.78 ± 0.13	0.87 ± 0.06	2.88 ± 0.78	2.59 ± 1.43	1.72 ± 0.18
Naphthalene, 2-methyl	1.70 ± 0.17	1.31 ± 0.22	1.57 ± 0.32	2.46 ± 0.43	2.48 ± 0.79	1.93 ± 0.16
Naphthalene, 1,7-dimethyl-	0.94 ± 0.21	0.60 ± 0.03	0.80 ± 0.14	0.63 ± 0.09	0.90 ± 0.15	0.71 ± 0.29
Naphthalene, 1,3-dimethyl-	1.21 ± 0.24	1.37 ± 0.21	1.16 ± 0.24	0.97 ± 0.09	1.18 ± 0.32	1.01 ± 0.13
Naphthalene, 2,3,6-trimethyl-	1.10 ± 0.13	n.d	1.10 ± 0.09	0.63 ± 0.08	0.65 ± 0.13	0.64 ± 0.05
Naphthalene, 1,2-dihydro-4-methyl-	0.97 ± 0.05	0.93 ± 0.11	0.92 ± 0.03	0.60 ± 0.07	0.69 ± 0.10	0.60 ± 0.13
Biphenyl	n.d	0.08 ± 0.14	0.08 ± 0.14	0.92 ± 0.15	0.95 ± 0.35	0.67 ± 0.14

Table 3. Cont.

Specific Power (W/g)	Truck ELT			Mix ELT		
	10	20	30	10	20	30
Compounds	Area%	Area%	Area%	Area%	Area%	Area%
Alkanes	0.54 ± 0.17	0.46 ± 0.17	0.45 ± 0.15	0.40 ± 0.08	0.16 ± 0.14	0.40 ± 0.10
Bicyclo[0,1,3]hexane, 1,5-dimethyl-	0.40 ± 0.05	0.39 ± 0.05	0.38 ± 0.02	0.24 ± 0.06	0.16 ± 0.14	0.30 ± 0.02
Alkenes	11.35 ± 4.12	11.14 ± 2.58	10.48 ± 1.90	7.38 ± 2.59	7.32 ± 2.41	8.86 ± 2.06
3,5-Dimethylcyclopentene	0.50 ± 0.10	0.38 ± 0.06	n.d	0.29 ± 0.08	0.18 ± 0.18	0.52 ± 0.03
1,3-Pentadiene, 2,3-dimethyl-	0.71 ± 0.11	0.58 ± 0.06	0.54 ± 0.05	0.21 ± 0.06	0.15 ± 0.14	0.27 ± 0.01
1-Methylene-2- vinylcyclopentane	0.56 ± 0.02	0.56 ± 0.10	0.52 ± 0.04	0.35 ± 0.15	0.36 ± 0.12	0.51 ± 0.12
1-Methylcyclohexa-1,3- diene	0.71 ± 0.10	0.67 ± 0.03	0.63 ± 0.03	0.31 ± 0.04	0.30 ± 0.06	0.40 ± 0.07
Cyclohexene, 1-methyl-4- (1-methylethyl)-, (R)	1.51 ± 0.69	1.75 ± 0.40	1.67 ± 0.22	0.64 ± 0.18	0.68 ± 0.05	0.59 ± 0.22
Cyclohexene, 5-methyl-6-(1- methylethenyl)-(3R-trans)-	0.58 ± 0.51	0.62 ± 0.24	0.62 ± 0.18	0.47 ± 0.10	0.48 ± 0.09	0.35 ± 0.29
1,5-Cyclooctadiene	0.73 ± 0.11	0.85 ± 0.12	0.83 ± 0.07	0.97 ± 0.22	0.95 ± 0.06	1.06 ± 0.23
2,4,6-Octatriene, 2,6-dimethyl-	0.71 ± 0.43	0.81 ± 0.33	0.85 ± 0.25	0.41 ± 0.25	0.41 ± 0.20	0.51 ± 0.16
2,6-Dimethyl-1,3,5,7- octatetraene, E,E-	1.14 ± 0.56	1.28 ± 0.21	1.17 ± 0.30	1.15 ± 0.18	1.43 ± 0.04	1.22 ± 0.07
Bicyclo[4.1.0]heptane, 7-(1-methylethylidene)	0.62 ± 0.29	0.72 ± 0.08	0.62 ± 0.11	0.37 ± 0.20	0.42 ± 0.08	0.35 ± 0.04
Limonene	21.62 ± 2.52	25.34 ± 2.94	23.48 ± 2.66	14.67 ± 0.81	16.67 ± 1.26	15.24 ± 2.01
L-Limonene	1.72 ± 0.66	2.08 ± 0.07	2.28 ± 0.26	1.47 ± 0.13	1.62 ± 0.14	1.53 ± 0.39
D-Limonene	19.90 ± 1.86	23.26 ± 2.87	21.20 ± 2.4	13.20 ± 0.68	15.05 ± 1.12	13.71 ± 1.62
Oxygenated	3.28 ± 0.60	3.08 ± 0.45	3.06 ± 0.41	2.65 ± 0.64	2.87 ± 0.98	3.29 ± 0.56
Propanoic acid, ethyl ester	1.42 ± 0.06	1.69 ± 0.20	1.66 ± 0.06	1.39 ± 0.31	1.73 ± 0.40	1.59 ± 0.36
3-Cyclohexene-1- methanol	0.87 ± 0.13	0.80 ± 0.05	0.77 ± 0.02	0.54 ± 0.14	0.47 ± 0.16	0.77 ± 0.03
Others	2.34 ± 0.12	2.51 ± 0.29	2.51 ± 0.02	1.62 ± 0.17	1.93 ± 0.30	1.65 ± 0.23
Benzothiazole	2.34 ± 0.12	2.51 ± 0.29	2.51 ± 0.02	1.62 ± 0.17	1.93 ± 0.30	1.65 ± 0.23

Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

The major compound identified in oil samples from tires pyrolysis is limonene, which is of great interest in the chemical industry because of its wide field of application as a solvent, manufacture of adhesives, fragrances, etc., [54]. Regarding the formation mechanism, some authors argue that the pyrolysis process gives rise to a homolytic breaking of one of the C-C single bonds between two double bonds (β -cleavage) present in the natural rubber monomer, producing a radical that, by intramolecular cyclization, yields limonene [32,55–57]. Another possible mechanism is the one that would take place through the dimerization of the isoprene molecules that are formed in the pyrolytic process at high temperatures through a Diels–Alder reaction [32,53,58,59]. Both mechanisms occur simultaneously during pyrolysis, although the contribution of each of them to the formation of total limonene depends on the reaction conditions and the type of tire used [8,32,60].

As observed in Table 3, the presence of limonene is higher in samples from truck tires, since it has a higher natural rubber content [8,61].

Aromatic compounds are the predominant group in all oil samples. The formation of this type of compound occurs through three distinct pathways: thermal degradation of the SBR, which contains aromatic rings in their structure. On the other hand, at high temperatures, some of the olefins formed in the first stage of pyrolysis can react with each other to give rise to cyclohexenes and their derivatives through the Diels–Alder reaction, which, after a dehydrogenation process, yield aromatic compounds [6,62–64]. The dehydrogenation of the limonene formed in the first stage of pyrolysis is another pathway for the formation of aromatic compounds [59].

Among the most abundant aromatic compounds are benzene, toluene, ethylbenzene, xylene, and styrene, all of which are of great economic interest for the petrochemical industry.

A higher presence of aromatic compounds results in a lower amount of limonene. At a specific power of 20 W/g, the highest area percentage of limonene is obtained, $25.34 \pm 2.94\%$ in the case of oil from the truck and $16.67 \pm 1.26\%$ in the mix samples. Bett et al. reported an area percentage of 20.23% in oil samples obtained in the microwave pyrolysis of truck tires [65]. Samples with the highest area percentage present the lowest area percentage of aromatic compounds, with values of 38.99 ± 5.63 and $49.51 \pm 7.00\%$, respectively. On the other hand, the lowest content of limonene and, therefore, the highest concentration of aromatic compounds was found in the samples obtained at 10 W/g.

Song et al. studied the influence of the specific power (9, 15, and 24 W/g) on the pyrolysis of tires using microwave technology and reported a similar trend in the concentration of limonene in the analyzed samples. First, there is an increase in the concentration of limonene from 9.30% to 9.83% when increasing the specific power from 9 to 15 W/g, followed by a slight decrease (9.16%) to 24 W/g [66]. In the same line, Wang et al. studied the microwave fast pyrolysis of truck tires and reported an increase of limonene area percentage up to 12% at 560 W [67].

On the other hand, the highest content of aromatic compounds is reached at 10 W/g, with values of 54.25 ± 7.13 and $42.10 \pm 9.94\%$ for the tests performed from the mix tires and truck tires, respectively. Undri et al. studied the influence of the P/M^2 ratio (power/tire mass squared) and reported that normally higher values of P/M^2 led to higher concentrations of aromatic compounds. However, the influence of other variables such as the temperature reached in the tests (in tests performed at 10 W/g, the maximum temperature measured at the end of the reaction is reached), as well as the amount of gas generated, the residence time of the vapors, and the temperature reached by the absorber, also influences the yield and composition of the products obtained [17].

As well as aromatic compounds and limonene, other components, such as alkanes, alkenes, polyaromatics, oxygen, and sulfur-containing compounds, are identified but with low area percentages. A higher area percentage of alkenes is identified in samples from truck tires, being cyclohexene, 1-methyl-4-(1-methylethyl)-, (R) the compound with the highest area percentage, 1.75 ± 0.40 and 1.67 ± 0.22 at 20 W/g and 30 W/g, respectively. Among the oxygenated compounds identified, ethyl propanoate is the component that present the highest area percentage in mix and truck ELT. The maximum area percentage is identified at 20 W/g with values of 1.73 ± 0.40 in mix samples and 1.69 ± 0.20 in truck samples. As far as sulfur-containing compounds is concerned, benzothiazole is identified in all samples. At 20 W/g the area percentage is 1.93 ± 0.30 and 2.51 ± 0.29 in mix tires and truck tires, respectively.

Table 4 shows the compositions by weight of the major compounds identified in oil samples. As was already observed, the composition of the starting tires influences the composition of the oil obtained. Pyrolytic oils obtained from truck tires contain the highest proportion of limonene, with values between 5.86 ± 0.87 (30 W/g) and 6.80 ± 2.37 wt. % (10 W/g). In samples from mix ELT, the concentration of limonene is between 3.76 ± 0.31 (10 W/g) and 4.04 ± 0.71 wt. % (30 W/g). The concentration of the quantified aromatic compounds varies between 13.64 ± 3.97 (20 W/g) and 17.61 ± 4.36 (10 W/g) in the case of mix ELT and 10.52 ± 0.98 (20 W/g) and 13.18 ± 3.51 (10 W/g) for the samples obtained

from truck ELT. In all cases, the major aromatic compounds are toluene and xylene and maximum concentrations are obtained at 10 W/g. In mix samples, toluene and xylene concentrations are 4.63 ± 1.29 and 4.01 ± 0.87 wt. %, respectively. In truck samples, weight percentage of toluene is 2.07 ± 0.42 wt. % and that of xylene is 3.12 ± 0.44 wt. %. The presence of styrene is significantly higher in samples obtained from mix tires due to the higher concentration of SBR in the feedstock. Concentration of styrene varies between 1.43 ± 0.65 wt. % at 10 W/g and 1.06 ± 0.07 wt. % at 30 W/g.

Table 4. Major compounds identified in oil samples (wt. %).

Specific Power (W/g)	Truck ELT			Mix ELT		
	10	20	30	10	20	30
Compounds	wt. %					
Benzene	0.51 ± 0.16	0.23 ± 0.04	0.28 ± 0.09	1.44 ± 0.34	0.88 ± 0.38	0.88 ± 0.20
Toluene	2.07 ± 0.42	1.22 ± 0.05	1.43 ± 0.24	4.63 ± 1.29	3.09 ± 0.91	3.42 ± 0.63
Ethylbenzene	0.26 ± 0.05	0.17 ± 0.02	0.20 ± 0.03	1.11 ± 0.30	0.79 ± 0.18	1.00 ± 0.29
Xylene	3.12 ± 0.44	2.21 ± 0.09	2.52 ± 0.27	4.01 ± 0.87	2.87 ± 0.52	3.38 ± 0.76
Styrene	0.19 ± 0.03	0.16 ± 0.02	0.19 ± 0.03	1.43 ± 0.65	1.16 ± 0.40	1.06 ± 0.07
α -Methylstyrene	0.08 ± 0.01	0.06 ± 0.01	0.07 ± 0.01	0.38 ± 0.17	0.30 ± 0.08	0.28 ± 0.05
Naphtalene	0.15 ± 0.03	0.11 ± 0.02	0.13 ± 0.02	0.85 ± 0.43	0.59 ± 0.35	0.42 ± 0.16
Limonene	6.80 ± 2.37	6.36 ± 0.73	5.86 ± 0.87	3.76 ± 0.31	3.96 ± 1.15	4.04 ± 0.71

Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

Since at 10 W/g, the highest concentration of the quantified compounds is obtained, and taking into account that at this specific power the highest yield of liquid fraction is produced, 10 W/g would be the optimal power to maximize the content of compounds of interest in the liquid fraction.

Most of the studies that analyze the pyrolysis of tires report the oil composition in area percentage. Studies where weight concentration is analyzed are very scarce. Previous studies have reported limonene concentrations of 1.88–9.42 wt. %, benzene 0.31–1.34 wt. %, toluene 1.55–2.79 wt. %, xylene 0.69–1.86 wt. %, styrene 1.3–5.66 wt. %, and ethylbenzene 0.69–0.97 wt. % in oil samples obtained from the pyrolysis of tires at 500 °C using different technologies [68–70].

The FTIR spectra of the pyrolysis oils analyzed in this work are shown in Figure 4. The six samples presented similar spectra to those found in the literature for other pyrolysis oils from tires [33,71,72]. The presence of aromatic compounds is confirmed by the presence of medium intensity bands at 690 and 730 cm^{-1} due to bending outside of the $\text{C}(\text{sp}^2)\text{-H}$ plane and at 1640 and 1450 cm^{-1} due to -C=C tension (also for alkenes) and at 3000 cm^{-1} due to the $\text{C}(\text{sp}^2)\text{-H}$ tension [30,73]. On the other hand, the bands located between 2900 and 2850 cm^{-1} , attributable to the tension of $\text{C}(\text{sp}^3)\text{-H}$, are caused by the presence of single bonds typical of alkanes. The presence of this type of compound is also evidenced by the existence of medium-low intensity bands located at 1370 cm^{-1} due to the symmetrical bending of -CH_3 . It is worth noting the presence of very weak bands at approximately 1700 cm^{-1} due to C=O tension, evidencing the presence of carbonyl compounds in low proportions, such as ethyl propionate [30]. The FTIR spectra of the six samples show the presence of aromatic compounds, alkenes and alkanes, confirming the results obtained by GC-MS.

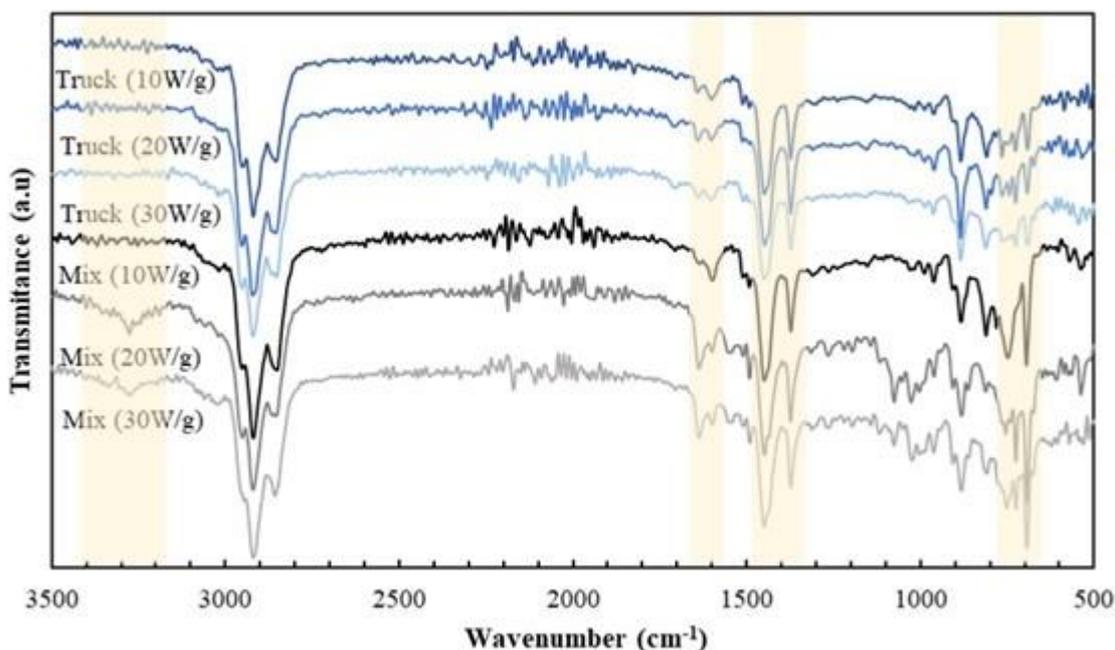


Figure 4. FTIR spectra (3500–500 cm^{-1}) of the tire pyrolysis oils.

3.4. Solid Products

The solid fraction from the ELT pyrolysis process consists of a carbonaceous material composed of the initial carbon black and the inorganic components added during the tire manufacturing processes (mainly Zn and Si) [21,74]. In addition, it may contain other carbonaceous materials since the vapors are transformed into coke through dealkylation or dehydrogenation reactions or are directly adsorbed on the char surface [49]. The structural characteristics, as well as the composition of the char, depend on the operating conditions as well as the composition of the tires used as raw material [46]. Table 5 shows the characterization of the char obtained in the pyrolysis tests.

Table 5. Elemental and proximate analysis, LHV, BET surface area, and pore volume of solid samples.

Tire Type	Truck ELT			Mix ELT			
	Specific Power (W/g)	10	20	30	10	20	30
Elemental Analysis (wt. %)							
C		80.37 ± 0.48	79.66 ± 0.20	79.80 ± 0.70	75.95 ± 0.47	74.86 ± 0.74	75.15 ± 0.48
H		0.58 ± 0.02	0.51 ± 0.08	0.41 ± 0.04	1.10 ± 0.45	0.86 ± 0.17	1.21 ± 0.12
N		0.30 ± 0.06	0.38 ± 0.04	0.38 ± 0.04	0.32 ± 0.05	0.30 ± 0.05	0.33 ± 0.03
S		3.13 ± 0.04	3.12 ± 0.04	3.11 ± 0.03	2.44 ± 0.04	2.48 ± 0.02	2.51 ± 0.01
Cl		0.08 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	0.05 ± 0.01	0.04 ± 0.00	0.05 ± 0.01
O + Others ^a		15.54 ± 0.60	16.24 ± 0.25	16.23 ± 0.80	20.15 ± 0.11	21.47 ± 0.66	20.75 ± 0.54
Proximate Analysis ^b (wt. %)							
Moisture (wt. %)		0.45 ± 0.12	0.52 ± 0.07	0.58 ± 0.29	1.69 ± 1.23	1.16 ± 0.02	1.85 ± 0.69
Volatiles		3.05 ± 0.24	3.18 ± 0.06	2.95 ± 0.53	4.50 ± 3.78	3.25 ± 0.30	5.11 ± 0.65
Ash		15.47 ± 0.68	16.25 ± 0.24	16.12 ± 0.60	20.16 ± 0.09	21.45 ± 0.66	20.60 ± 0.48
LHV (MJ kg^{-1})		28.51 ± 0.13	28.12 ± 0.08	27.91 ± 0.25	27.41 ± 0.47	26.74 ± 0.27	27.22 ± 0.17
Surface Properties							
BET (m^2/g)		67.81 ± 2.86	74.68 ± 0.57	75.42 ± 2.91	53.56 ± 10.49	59.29 ± 1.57	54.88 ± 2.66
V_{poro} (cm^3/g)		0.574 ± 0.014	0.575 ± 0.012	0.535 ± 0.094	0.423 ± 0.069	0.461 ± 0.019	0.430 ± 0.036

^a by difference. ^b on dry basis. LHV: Low Heating Value. Mix ELT: 50:50 mixture of passenger car and truck ELT rubber.

The char obtained has a carbon content between $74.86 \pm 0.74\%$ and $75.95 \pm 0.47\%$ in the case of the samples from the mix ELT and $79.66 \pm 0.20\%$ and $80.37 \pm 0.48\%$ in the case of truck tire samples. The sulfur content remains at approximately 2.5% and 3.1% in the case of mix and truck ELT, respectively. The great thermal stability of sulfur compounds, both organic and inorganic, means that most of the sulfur contained in the tires, approximately 67% in the case of truck tires and 56% in the case of mix tires, remains in the solid fraction [75,76].

The ash content of the char from mix tires (27.41–26.74%) is higher than that obtained from truck ELT (16.25–15.47%). This indicates a higher content of inorganic compounds in the solid fraction obtained from mix samples, which translates into a lower content of fixed carbon. In addition, it should be noted that the amount of volatile matter present in char is low (2.95–5.11%), so the presence of tar adsorbed on the surface of the char is scarce. Therefore, it can be concluded that the specific power used in each of the tests is sufficient to achieve a complete degradation of tires.

The surface area of the recovered carbon black was also evaluated. The results obtained for the recovered carbon black from mix ELT are in the range of 53.56 ± 10.49 and $59.29 \pm 1.57 \text{ m}^2/\text{g}$. The surface area of char obtained from truck tires is between 67.81 ± 2.86 and $75.42 \pm 2.91 \text{ m}^2/\text{g}$. These values coincide with those obtained by Undri et al., who studied microwave-assisted tire pyrolysis. The BET surface area of the degassed samples (350 °C, 80 Pa for 5 h) varies between 32.6 and 65.5 m^2/g [77]. On the other hand, Ucar et al. reported BET surface area results of 55.5–63.5 and 56.5–66.0 m^2/g for samples from pyrolysis in a fixed bed reactor of car and truck tires, respectively [48].

The most significant difference between the recovered carbon black from tires pyrolysis and the commercial carbon black is the high content of inorganic matter. Carbon black utilized in the manufacture of tires has an ash percentage of less than 0.5% [78]. Therefore, in recent years, several studies related to demineralization processes have been carried out to dissolve this large number of impurities. Demineralization processes can use acidic or basic solutions, although previous results have shown that acidic compounds to be more efficient for this purpose [79,80]. In addition to its use as an additive in rubber compounding [4,21,22,52,74], another main application of pyrolytic carbon black is its use as a precursor in the production of activated carbon [81,82]. The study of these applications for recovered carbon black is of vital importance so that the chemical recycling process of end-of-life tires is economically viable.

4. Conclusions

In this study, two different types of end-of-life tires were pyrolyzed in a batch microwave reactor. The feedstock and specific power (10, 20, 30 W/g) influence on mass distribution and products composition was analyzed. The maximum liquid yield is reached at 10 W/g with values of $28.47 \pm 1.62\%$ and $38.28 \pm 0.96\%$ for mix and truck ELT, respectively. At 30 W/g, the gas yield increased up to $29.74 \pm 1.07\%$ in test developed from mix ELT and $27.66 \pm 1.84\%$ in those carried out from truck ELT. Samples obtained from truck tires have a major concentration on limonene, while aromatic compounds yield are higher in oil obtained from mix tires. BTEX maximum weight percentage, $11.19 \pm 2.80 \text{ wt. } \%$, is obtained in oil from mix ELT at 10 W/g, while the maximum limonene yield, $6.80 \pm 2.37 \text{ wt. } \%$, is obtained from truck ELT at 10 W/g. Toluene is the main aromatic compound with a concentration of 2.07 ± 0.42 and 4.63 ± 1.29 for truck and mix ELT, respectively. Oil fractions are valuable sources of chemicals to obtain high value-added products. Recovered carbon black presented a surface area of 53.56 ± 10.49 and $59.29 \pm 1.57 \text{ m}^2/\text{g}$ in the case of mix ELT and 67.81 ± 2.86 and $75.42 \pm 2.91 \text{ m}^2/\text{g}$ in truck ELT. Samples from truck tires present a lower ash content, and therefore, higher surface area. Recovered carbon black could be used as activated carbon precursor. To ensure the economic feasibility of the chemical recycling process of end-of-life tires, it is crucial to look for potential applications for each of the products obtained in the pyrolysis process. Further studies will be focused

on gas fraction characterization to assess its application as feedstock in the Fischer–Tropsch synthesis to produce chemicals such as methanol.

Author Contributions: Conceptualization, J.L.A., S.G., M.T.M. and J.B.-G.; methodology, J.L.A., S.G., M.T.M. and J.B.-G.; software, J.L.A., M.T.M. and J.B.-G.; validation, J.L.A., S.G., M.T.M. and J.B.-G.; formal analysis, J.L.A., M.T.M. and J.B.-G.; investigation, J.L.A., M.T.M. and J.B.-G.; resources, J.L.A., S.G., L.S.-R. and R.P.-A.; data curation, J.L.A., M.T.M. and J.B.-G.; writing—original draft preparation, M.T.M.; writing—review and editing, M.T.M., J.L.A., J.B.-G., L.S.-R. and R.P.-A.; visualization, J.L.A., S.G., M.T.M. and J.B.-G.; supervision, J.L.A., S.G., L.S.-R. and R.P.-A.; project administration, J.L.A., L.S.-R. and R.P.-A.; funding acquisition, L.S.-R. and R.P.-A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by SIGNUS.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank the Centro de Química Aplicada y Biotecnología of Universidad de Alcalá (CQAB) and the Laboratorio Regional de Combustibles of Junta de Castilla y León (Larecom) for the technical support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Grammelis, P.; Margaritis, N.; Dallas, P.; Rakopoulos, D.; Mavrias, G. A review on management of end of life tires (Elts) and alternative uses of textile fibers. *Energies* **2021**, *14*, 571. [\[CrossRef\]](#)
2. Cardona-Urbe, N.; Betancur, M.; Martínez, J.D. Towards the chemical upgrading of the recovered carbon black derived from pyrolysis of end-of-life tires. *Sustain. Mater. Technol.* **2021**, *28*, e00287. [\[CrossRef\]](#)
3. Shulman, V.L. Management of end-of-life tires. In *Tire Waste and Recycling*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 43–67.
4. Dwivedi, C.; Manjare, S.; Rajan, S.K. Recycling of waste tire by pyrolysis to recover carbon black: Alternative & environment-friendly reinforcing filler for natural rubber compounds. *Compos. Part B Eng.* **2020**, *200*, 108346. [\[CrossRef\]](#)
5. Hita, I.; Arabiourrutia, M.; Olazar, M.; Bilbao, J.; Arandes, J.M.; Castaño Sánchez, P. Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tires. *Renew. Sustain. Energy Rev.* **2016**, *56*, 745–759. [\[CrossRef\]](#)
6. Quek, A.; Balasubramanian, R. Liquefaction of waste tires by pyrolysis for oil and chemicals—A review. *J. Anal. Appl. Pyrolysis* **2013**, *101*, 1–16. [\[CrossRef\]](#)
7. Laresgoiti, M.F.; Caballero, B.M.; De Marco, I.; Torres, A.; Cabrero, M.A.; Chomón, M.J. Characterization of the liquid products obtained in tyre pyrolysis. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 917–934. [\[CrossRef\]](#)
8. Januszewicz, K.; Kazimierski, P.; Kosakowski, W.; Lewandowski, W.M. Waste tyres pyrolysis for obtaining limonene. *Materials* **2020**, *13*, 1359. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Williams, P.T.; Brindle, A.J. Temperature selective condensation of tyre pyrolysis oils to maximise the recovery of single ring aromatic compounds. *Fuel* **2003**, *82*, 1023–1031. [\[CrossRef\]](#)
10. Campuzano, F.; Gani, A.; Jameel, A.; Zhang, W.; Emwas, A.; Agudelo, F.; Daniel, J.; Sarathy, S.M. On the distillation of waste tire pyrolysis oil: A structural characterization of the derived fractions. *Fuel* **2021**, *290*, 120041. [\[CrossRef\]](#)
11. Karagöz, M. Investigation of performance and emission characteristics of an CI engine fuelled with diesel—Waste tire oil—Butanol blends. *Fuel* **2020**, *282*, 118872. [\[CrossRef\]](#)
12. Umeki, E.R.; de Oliveira, C.F.; Torres, R.B.; Santos, R.G. dos Physico-chemistry properties of fuel blends composed of diesel and tire pyrolysis oil. *Fuel* **2016**, *185*, 236–242. [\[CrossRef\]](#)
13. Suchocki, T.; Witanowski, Ł.; Lampart, P.; Kazimierski, P.; Januszewicz, K.; Gawron, B. Experimental investigation of performance and emission characteristics of a miniature gas turbine supplied by blends of kerosene and waste tyre pyrolysis oil. *Energy* **2021**, *215*, 119125. [\[CrossRef\]](#)
14. Yaqoob, H.; Heng, Y.; Ahmad, M.; Gulzar, M. Potential of tire pyrolysis oil as an alternate fuel for diesel engines: A review. *J. Energy Inst.* **2021**, *96*, 205–221. [\[CrossRef\]](#)
15. Arya, S.; Sharma, A.; Rawat, M.; Agrawal, A. Materials Today: Proceedings Tyre pyrolysis oil as an alternative fuel: A review. *Mater. Today Proc.* **2020**, *28*, 2481–2484. [\[CrossRef\]](#)
16. Czajczyńska, D.; Krzyżyńska, R.; Jouhara, H.; Spencer, N. Use of pyrolytic gas from waste tire as a fuel: A review. *Energy* **2017**, *134*, 1121–1131. [\[CrossRef\]](#)
17. Undri, A.; Meini, S.; Rosi, L.; Frediani, M.; Frediani, P. Microwave pyrolysis of polymeric materials: Waste tires treatment and characterization of the value-added products. *J. Anal. Appl. Pyrolysis* **2013**, *103*, 149–158. [\[CrossRef\]](#)
18. Falkenhagen, J.P.; Maisonneuve, L.; Paalanen, P.P.; Coste, N.; Malicki, N.; Weckhuysen, B.M. Cobalt-Iron-Manganese Catalysts for the Conversion of End-of-Life-Tire-Derived Syngas into Light Terminal Olefins. *Chem. A Eur. J.* **2018**, *24*, 4597–4606. [\[CrossRef\]](#)
19. Matamela, K. *Synthesis and Performance Evaluation of Co/H-ZSM-5 bi-Functional Catalyst for Fischer-Tropsch Synthesis*; University of the Witwatersrand: Johannesburg, South Africa, 2016.

20. Hoang, A.T.; Nguyen, T.H.; Nguyen, H.P. Scrap tire pyrolysis as a potential strategy for waste management pathway: A review. *Energy Sources Part A Recovery Util. Environ. Eff.* **2020**, *1*, 1–18. [[CrossRef](#)]
21. Cardona, N.; Campuzano, F.; Betancur, M.; Jaramillo, L.; Martínez, J.D. Possibilities of carbon black recovery from waste tyre pyrolysis to be used as additive in rubber goods—A review. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *437*, 012012. [[CrossRef](#)]
22. Anjum, A.; Ramani, B.; Bramer, E.; Brem, G.; Dierkes, W.; Blume, A. Role of recovered carbon black ash content composition on in-rubber performance. In Proceedings of the International Rubber Conference, IRC, London, UK, 3–5 September 2019.
23. Saleh, T.A.; Danmaliki, G.I. Influence of acidic and basic treatments of activated carbon derived from waste rubber tires on adsorptive desulfurization of thiophenes. *J. Taiwan Inst. Chem. Eng.* **2016**, *60*, 460–468. [[CrossRef](#)]
24. Mkhize, N.M.; Danon, B.; Alvarez, J.; Lopez, G.; Amutio, M.; Bilbao, J.; Olazar, M.; van der Gryp, P.; Görgens, J.F. Influence of reactor and condensation system design on tyre pyrolysis products yields. *J. Anal. Appl. Pyrolysis* **2019**, *143*, 104683. [[CrossRef](#)]
25. Parthasarathy, P.; Choi, H.S.; Park, H.C.; Hwang, J.G.; Yoo, H.S.; Lee, B.K.; Upadhyay, M. Influence of process conditions on product yield of waste tyre pyrolysis—A review. *Korean J. Chem. Eng.* **2016**, *33*, 2268–2286. [[CrossRef](#)]
26. Aziz, M.A.; Rahman, M.A.; Molla, H. Design, fabrication and performance test of a fixed bed batch type pyrolysis plant with scrap tire in Bangladesh. *J. Radiat. Res. Appl. Sci.* **2018**, *11*, 311–316. [[CrossRef](#)]
27. Akkouche, N.; Balistrout, M.; Loubar, K.; Awad, S.; Tazerout, M. Heating rate effects on pyrolytic vapors from scrap truck tires. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 419–429. [[CrossRef](#)]
28. Raj, R.E.; Kennedy, Z.R.; Pillai, B.C. Optimization of process parameters in flash pyrolysis of waste tyres to liquid and gaseous fuel in a fluidized bed reactor. *Energy Convers. Manag.* **2013**, *67*, 145–151.
29. Martínez, J.D.; Campuzano, F.; Agudelo, A.F.; Cardona-Urbe, N.; Arenas, C.N. Chemical recycling of end-of-life tires by intermediate pyrolysis using a twin-auger reactor: Validation in a laboratory environment. *J. Anal. Appl. Pyrolysis* **2021**, *159*, 105298. [[CrossRef](#)]
30. Yazdani, E.; Hashemabadi, S.H.; Taghizadeh, A. Study of waste tire pyrolysis in a rotary kiln reactor in a wide range of pyrolysis temperature. *Waste Manag.* **2019**, *85*, 195–201. [[CrossRef](#)] [[PubMed](#)]
31. Xu, J.; Yu, J.; He, W.; Huang, J.; Xu, J.; Li, G. Recovery of carbon black from waste tire in continuous commercial rotary kiln pyrolysis reactor. *Sci. Total Environ.* **2021**, *772*, 145507. [[CrossRef](#)] [[PubMed](#)]
32. Song, Z.; Liu, L.; Yang, Y.; Sun, J.; Zhao, X.; Wang, W.; Mao, Y.; Yuan, X.; Wang, Q. Characteristics of limonene formation during microwave pyrolysis of scrap tires and quantitative analysis. *Energy* **2018**, *142*, 953–961. [[CrossRef](#)]
33. Idris, R.; Chong, C.T.; Ani, F.N. Microwave-induced pyrolysis of waste truck tyres with carbonaceous susceptor for the production of diesel-like fuel. *J. Energy Inst.* **2019**, *92*, 1831–1841. [[CrossRef](#)]
34. Motasemi, F.; Afzal, M.T. A review on the microwave-assisted pyrolysis technique. *Renew. Sustain. Energy Rev.* **2013**, *28*, 317–330. [[CrossRef](#)]
35. Lam, S.S.; Chase, H.A. A review on waste to energy processes using microwave pyrolysis. *Energies* **2012**, *5*, 4209–4232. [[CrossRef](#)]
36. Lewandowski, W.M.; Januszewicz, K.; Kosakowski, W. Efficiency and proportions of waste tyre pyrolysis products depending on the reactor type—A review. *J. Anal. Appl. Pyrolysis* **2019**, *140*, 25–53. [[CrossRef](#)]
37. Formela, K.; Hejna, A.; Zedler, L.; Colom Fajula, X.; Cañavate Ávila, F.J. Microwave treatment in waste rubber recycling—Recent advances and limitations. *Express Polym. Lett.* **2019**, *13*, 565–588. [[CrossRef](#)]
38. Undri, A.; Rosi, L.; Frediani, M.; Frediani, P. Upgraded fuel from microwave assisted pyrolysis of waste tire. *Fuel* **2014**, *115*, 600–608. [[CrossRef](#)]
39. Martín, M.T.; Sanz, A.B.; Nozal, L.; Castro, F.; Alonso, R.; Aguirre, J.L.; González, S.D.; Matía, M.P.; Novella, J.L.; Peinado, M.; et al. Microwave-assisted pyrolysis of Mediterranean forest biomass waste: Bioproduct characterization. *J. Anal. Appl. Pyrolysis* **2017**, *127*, 278–285. [[CrossRef](#)]
40. Aguirre, J.L.; Baena, J.; Martín, M.T.; Nozal, L.; González, S.; Manjón, J.L.; Peinado, M. Composition, Ageing and Herbicidal Properties of Biomass Pyrolysis. *Energies* **2020**, *23*, 2418. [[CrossRef](#)]
41. Baena-González, J.; Santamaria-Echart, A.; Aguirre, J.L.; González, S. Chemical recycling of plastic waste: Bitumen, solvents, and polystyrene from pyrolysis oil. *Waste Manag.* **2020**, *118*, 139–149. [[CrossRef](#)]
42. Han, J.; Li, W.; Liu, D.; Qin, L.; Chen, W.; Xing, F. Pyrolysis characteristic and mechanism of waste tyre: A thermogravimetry-mass spectrometry analysis. *J. Anal. Appl. Pyrolysis* **2018**, *129*, 1–5. [[CrossRef](#)]
43. Gao, N.; Li, A.; Li, W. Research into fine powder and large particle tyre pyrolysis. *Waste Manag. Res.* **2009**, *27*, 242–250. [[CrossRef](#)]
44. Kan, T.; Strezov, V.; Evans, T. Fuel production from pyrolysis of natural and synthetic rubbers. *Fuel* **2017**, *191*, 403–410. [[CrossRef](#)]
45. Rofiqul Islam, M.; Haniu, H.; Rafiqul Alam Beg, M. Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: Product yields, compositions and related properties. *Fuel* **2008**, *87*, 3112–3122. [[CrossRef](#)]
46. Martínez, J.D.; Puy, N.; Murillo, R.; García, T.; Navarro, M.V.; Mastral, A.M. Waste tyre pyrolysis—A review. *Renew. Sustain. Energy Rev.* **2013**, *23*, 179–213. [[CrossRef](#)]
47. Kumar Singh, R.; Ruj, B.; Jana, A.; Mondal, S.; Jana, B.; Kumar Sadhukhan, A.; Gupta, P. Pyrolysis of three different categories of automotive tyre wastes: Product yield analysis and characterization. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 379–389. [[CrossRef](#)]
48. Ucar, S.; Karagoz, S.; Ozkan, A.R.; Yanik, J. Evaluation of two different scrap tires as hydrocarbon source by pyrolysis. *Fuel* **2005**, *84*, 1884–1892. [[CrossRef](#)]
49. Zhang, X.; Wang, T.; Ma, L.; Chang, J. Vacuum pyrolysis of waste tires with basic additives. *Waste Manag.* **2008**, *28*, 2301–2310. [[CrossRef](#)]

50. Roy, C.; Chaala, A. Vacuum pyrolysis of automobile shredder residues. *Resour. Conserv. Recycl.* **2001**, *32*, 1–27. [[CrossRef](#)]
51. Antoniou, N.; Zabaniotou, A. Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery. *Renew. Sustain. Energy Rev.* **2013**, *20*, 539–558. [[CrossRef](#)]
52. Tian, X.; Zhuang, Q.; Han, S.; Li, S.; Liu, H.; Li, L.; Zhang, J.; Wang, C.; Bian, H. A novel approach of reapplication of carbon black recovered from waste tyre pyrolysis to rubber composites. *J. Clean. Prod.* **2021**, *280*, 124460. [[CrossRef](#)]
53. Alvarez, J.; Lopez, G.; Amutio, M.; Mkhize, N.M.; Danon, B.; van der Gryp, P.; Görgens, J.F.; Bilbao, J.; Olazar, M. Evaluation of the properties of tyre pyrolysis oils obtained in a conical spouted bed reactor. *Energy* **2017**, *128*, 463–474. [[CrossRef](#)]
54. Zhang, G.; Chen, F.; Zhang, Y.; Zhao, L.; Chen, J.; Cao, L.; Gao, J.; Xu, C. Properties and utilization of waste tire pyrolysis oil: A mini review. *Fuel Process. Technol.* **2021**, *211*, 106582. [[CrossRef](#)]
55. Mkhize, N.M.; Danon, B.; van der Gryp, P.; Görgens, J.F. Kinetic study of the effect of the heating rate on the waste tyre pyrolysis to maximise limonene production. *Chem. Eng. Res. Des.* **2019**, *152*, 363–371. [[CrossRef](#)]
56. Gauthier-Maradei, P.; Tavera Ruiz, C.P.; Capron, M. Oil and Aromatic Yield Maximization during Pyrolysis of Scrap Tire Rubber. *Waste Biomass Valorization* **2019**, *10*, 3723–3733. [[CrossRef](#)]
57. Ahmad, N.; Abnisa, F.; Wan Daud, W.M.A. Synthesis of valuable intermediate products from natural rubber under supercritical alcohol conditions. *J. Anal. Appl. Pyrolysis* **2019**, *139*, 196–204. [[CrossRef](#)]
58. Ourak, M.; Marin Gallego, M.; Burnens, G.; Largeau, J.F.; Kordoghli, S.; Zagrouba, F.; Tazerout, M. Experimental Study of Pyrolytic Oils from Used Tires: Impact of Secondary Reactions on Liquid Composition. *Waste Biomass Valorization* **2021**, *12*, 4663–4678. [[CrossRef](#)]
59. Ma, S.; Leong, H.; He, L.; Xiong, Z.; Han, H.; Jiang, L.; Wang, Y.; Hu, S.; Su, S.; Xiang, J. Effects of pressure and residence time on limonene production in waste tires pyrolysis process. *J. Anal. Appl. Pyrolysis* **2020**, *151*, 104899. [[CrossRef](#)]
60. Pakdela, H.; Panteaa, D.; Roy, C. Production of d-limonene by vacuum pyrolysis of used tires. *J. Anal. Appl. Pyrolysis* **2001**, *57*, 91–107. [[CrossRef](#)]
61. Januszewicz, K.; Kazimierski, P.; Suchocki, T.; Kardaś, D.; Lewandowski, W.; Klugmann-Radziemska, E.; Łuczak, J. Waste rubber pyrolysis: Product yields and limonene concentration. *Materials* **2020**, *13*, 4435. [[CrossRef](#)] [[PubMed](#)]
62. Choi, G.G.; Jung, S.H.; Oh, S.J.; Kim, J.S. Total utilization of waste tire rubber through pyrolysis to obtain oils and CO₂ activation of pyrolysis char. *Fuel Process. Technol.* **2014**, *123*, 57–64. [[CrossRef](#)]
63. Li, W.; Huang, C.; Li, D.; Huo, P.; Wang, M.; Han, L.; Chen, G.; Li, H.; Li, X.; Wang, Y.; et al. Derived oil production by catalytic pyrolysis of scrap tires. *Cuihua Xuebao/Chin. J. Catal.* **2016**, *37*, 526–532. [[CrossRef](#)]
64. Cunliffe, A.M.; Williams, P.T. Composition of oils derived from the batch pyrolysis of tyres. *J. Anal. Appl. Pyrolysis* **1998**, *44*, 131–152. [[CrossRef](#)]
65. Bett, R.k.; Kumar, A.; Siagi, Z.O. Optimization of Liquid Fuel Production from Microwave Pyrolysis of Used Tyres. *J. Energy* **2021**, *2021*, 3109374. [[CrossRef](#)]
66. Song, Z.; Yang, Y.; Sun, J.; Zhao, X.; Wang, W.; Mao, Y.; Ma, C. Effect of power level on the microwave pyrolysis of tire powder. *Energy* **2017**, *127*, 571–580. [[CrossRef](#)]
67. Bing, W.; Hongbin, Z.; Zeng, D.; Yuefeng, F.; Yu, Q.; Rui, X. Microwave fast pyrolysis of waste tires: Effect of microwave power on product composition and quality. *J. Anal. Appl. Pyrolysis* **2021**, *155*, 104979. [[CrossRef](#)]
68. Li, S.Q.; Yao, Q.; Chi, Y.; Yan, J.H.; Cen, K.F. Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor. *Ind. Eng. Chem. Res.* **2004**, *43*, 5133–5145. [[CrossRef](#)]
69. Olazar, M.; Aguado, R.; Arabiourrutia, M.; Lopez, G.; Barona, A.; Bilbao, J. Catalyst effect on the composition of tire pyrolysis products. *Energy Fuels* **2008**, *22*, 2909–2916. [[CrossRef](#)]
70. Lopez, G.; Olazar, M.; Aguado, R.; Elordi, G.; Amutio, M.; Artetxe, M.; Bilbao, J. Vacuum pyrolysis of waste tires by continuously feeding into a conical spouted bed reactor. *Ind. Eng. Chem. Res.* **2010**, *49*, 8990–8997. [[CrossRef](#)]
71. Singh, R.K.; Mondal, S.; Ruj, B.; Sadhukhan, A.K.; Gupta, P. Interaction of three categories of tyre waste during co-pyrolysis: Effect on product yield and quality. *J. Anal. Appl. Pyrolysis* **2019**, *141*, 104618. [[CrossRef](#)]
72. Mohan, A.; Dutta, S.; Madav, V. Characterization and upgradation of crude tire pyrolysis oil (CTPO) obtained from a rotating autoclave reactor. *Fuel* **2019**, *250*, 339–351. [[CrossRef](#)]
73. Farooq, M.Z.; Zeeshan, M.; Iqbal, S.; Ahmed, N.; Shah, S.A.Y. Influence of waste tire addition on wheat straw pyrolysis yield and oil quality. *Energy* **2018**, *144*, 200–206. [[CrossRef](#)]
74. Martínez, J.D.; Cardona-Urbe, N.; Murillo, R.; García, T.; López, J.M. Carbon black recovery from waste tire pyrolysis by demineralization: Production and application in rubber compounding. *Waste Manag.* **2019**, *85*, 574–584. [[CrossRef](#)] [[PubMed](#)]
75. Lopez, G.; Alvarez, J.; Amutio, M.; Mkhize, N.M.; Danon, B.; van der Gryp, P.; Görgens, J.F.; Bilbao, J.; Olazar, M. Waste truck-tyre processing by flash pyrolysis in a conical spouted bed reactor. *Energy Convers. Manag.* **2017**, *142*, 523–532. [[CrossRef](#)]
76. Pan, Y.; Yang, D.; Sun, K.; Wang, X.; Zhou, Y.; Huang, Q. Pyrolytic transformation behavior of hydrocarbons and heteroatom compounds of scrap tire volatiles. *Fuel* **2020**, *276*, 118095. [[CrossRef](#)]
77. Undri, A.; Sacchi, B.; Cantisani, E.; Toccafondi, N.; Rosi, L.; Frediani, M.; Frediani, P. Carbon from microwave assisted pyrolysis of waste tires. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 396–404. [[CrossRef](#)]
78. Zhong, R.; Xu, J.; Hui, D.; Bhosale, S.S.; Hong, R. Pyrolytic preparation and modification of carbon black recovered from waste tyres. *Waste Manag. Res.* **2020**, *38*, 35–43. [[CrossRef](#)] [[PubMed](#)]

79. Dong, P.; Maneerung, T.; Ng, W.C.; Zhen, X.; Dai, Y.; Tong, Y.W.; Ting, Y.P.; Koh, S.N.; Wang, C.H.; Neoh, K.G. Chemically treated carbon black waste and its potential applications. *J. Hazard. Mater.* **2017**, *321*, 62–72. [[CrossRef](#)]
80. Sugatri, R.I.; Wirasadewa, Y.C.; Saputro, K.E.; Muslih, E.Y.; Ikono, R.; Nasir, M. Recycled carbon black from waste of tire industry: Thermal study. *Microsyst. Technol.* **2018**, *24*, 749–755. [[CrossRef](#)]
81. Al-Rahbi, A.S.; Williams, P.T. Production of activated carbons from waste tyres for low temperature NO_x control. *Waste Manag.* **2016**, *49*, 188–195. [[CrossRef](#)] [[PubMed](#)]
82. Hadi, P.; Yeung, K.Y.; Guo, J.; Wang, H.; McKay, G. Sustainable development of tyre char-based activated carbons with different textural properties for value-added applications. *J. Environ. Manag.* **2016**, *170*, 1–7. [[CrossRef](#)]