



“Gheorghe Asachi” Technical University of Iasi, Romania



EFFICIENT RECOVERY OF NON-SHREDDED TIRES VIA PYROLYSIS IN AN INNOVATIVE PILOT PLANT

Loris Giorgini^{1,2*}, Tiziana Benelli^{1,2}, Chiara Leonardi^{1,2}, Laura Mazzocchetti^{1,2},
Giorgio Zattini^{1,2}, Massimo Cavazzoni³, Ivan Montanari³, Cristian Tosi³

¹University of Bologna, Department of Industrial Chemistry “Toso Montanari”, 4 V.le del Risorgimento, 40136 Bologna, Italy

²University of Bologna, Interdepartmental Center for Industrial Research on Advanced Applications in Mechanical Engineering and Materials Technology, CIRI-MAM, 2 V.le del Risorgimento, 40136 Bologna, Italy

³CURTI S.p.A Divisione Energia, 181 Via Emilia Est, 41100 Modena, Italy

Abstract

New and end of life tires have been pyrolyzed in an innovative pilot plant that processes whole tires, thus saving the energy costs of shredding while allowing energy and materials recovery. Furthermore, the presence of a hydraulic guard guarantees high process safety. Several tests at different temperatures have been performed and the collected solid, liquid and gaseous products have been quantified and characterized. The influence of the maximum process temperature on yields and chemical-physical properties of pyrolysis products has also been evaluated. In view of a plant scale-up to continuous mode, we have studied the influence of variation of tires type and wear and the effects of the final products aging.

Key words: char, pyrolysis, pyrolysis gas, tires recovery, waste management.

Received: December, 2014; *Revised final:* June, 2015; *Accepted:* June, 2015

1. Introduction

The management of end-of-life tires (ELTs) is becoming increasingly worrying owing to a number of concurrent factors such as the massive, and still growing, amount of exhausted tires involved (estimated annual world production of tires at 23.3 million tonnes (ETRma, 2014)), the almost complete lack of biodegradability of such a kind of waste and the tendency to get rid of them wildly, with no concern at all of their destiny.

Presently, several disposal techniques are available though they all present some drawbacks: for example re-treading can only be performed on undamaged carcasses while material recovery involves necessarily some preliminary shredding with a significant energy consumption. On the other hand, energy recovery, which mainly consists of incineration treatments of mixed waste streams, leads

to the loss of valuable materials and the production of polluting emissions, thus imposing expensive gas cleaning devices (Kandasamy et al., 2015).

Pyrolysis is a process in which organic materials are thermally decomposed into simpler components when subjected to high heat, under an oxygen free atmosphere (Fig. 1). The pyrolysis of ELTs involves the thermal cracking of the rubber and other ingredients generating a volatile fraction composed of condensable (pyrolysis oil) and non-condensable (pyrolysis gas) fractions (Quek and Balasubramanian, 2013). The solid residue consists of steel wires and char. Steel, char, oil and gas are all highly valuable products. Char is a carbonaceous residue with a Gross Calorific Value (GCV) of about 28.8 MJ/kg (de Marco Rodriguez et al., 2001) which makes it suitable as fuel. Moreover, some activation studies were conducted to increase its surface area and improve its attractiveness as carbon black or

* Author to whom all correspondence should be addressed: e-mail: loris.giorgini@unibo.it; Phone: +390512093688; Fax: +390512093675

active carbon (Zabaniotou and Stavropoulos, 2003). Pyrolysis oil is a complex mixture of organic compounds with a high fraction of aromatics (Laresgoiti et al., 2000) which can be used either as a fuel or as chemical feedstock. Finally, pyrolysis gas is a combustible gas (GCV of about 68-84 MJ/m³) composed of CH₄, aliphatic C₂-C₆ compounds, H₂, CO, CO₂ and H₂S which can fuel internal combustion engines to generate electricity and heat, thus reducing greenhouse gas emissions (de Marco Rodriguez et al., 2001).

Different technologies have been applied to tires pyrolysis: the process can be performed with or without a catalyst in order to maximize the yields of valuable volatile products (Williams and Brindle, 2003). A number of different reactors can be used, such as conical spouted bed reactor (Lopez et al., 2009), autoclave (de Marco Rodriguez et al., 2001; Laresgoiti et al., 2000), circulating fluid bed reactor (Dai et al., 2001), rotatory oven reactor (Acevedo et al., 2014a 2014b), fixed bed reactor (Aydin and Ilklic, 2012; Rofiqul Islam et al., 2008) and high vacuum process (Roy et al., 1999).

In this context, Curti S.p.A. has recently built an innovative static bed batch pilot reactor (Bortolani et al., 2014; Giorgini et al., 2015) that combines in one single process, the main advantages of different disposal techniques: in particular pyrolysis can be performed on whole tires to save the shredding costs while recovering energy and materials as previously discussed, and thanks to an innovative hydraulic guard, the plant guarantees a high process safety. The pilot plant has been used to pyrolyze new tires (NTs) and end-of-life tires (ELTs) at different temperatures, namely 400, 450, 500, 550 and 600°C in presence of steam due to water evaporation from the hydraulic guard.

The main objective of this research is to evaluate the influence of the maximum process temperature on yields and on chemical-physical properties of pyrolysis products. In addition, in view of a scale-up of the plant to continuous mode, we have studied the influence of the variation of the feedstock on the pyrolysis output and the effects of the final products aging.

2. Experimental

2.1. Pilot plant

A scheme of the pilot plant is shown in Fig. 2. The system is easily controllable and safe owing to a hydraulic seal that prevents air infiltration into the treatment chamber. The batch reactor has an internal volume of 5.5 m³ and can treat up to 70 kilograms of tires. It is composed of two parts, the lower being a tank containing water, which acts as hydraulic guard, the upper a mobile bell whose lifting allows the sample insertion and the removal of the solid residue at the end of the process. The latter element is double walled hosting electric resistances with a total power of 21000 W.

The pyrolysis batches have been performed isothermally at different temperatures, namely 400, 450, 500, 550 and 600°C, as defined upon preliminary TGA investigation. All the gases generated in the process are conveyed outside the reactor and partially condensed in a water cooled coil (2). The obtained oil (and water) is collected through a demister, picked up at point B and subsequently characterized.

The uncondensed gas proceeds encountering a H₂S scrubber (3) and a fan (4), required to adjust the pressure of the gaseous stream. Along the line connecting the fan to the burners there is a bleed point for the gas analysis (C). Different indicators and monitoring points for the operating variables are distributed along the system and everything is supervised through a centralized electronic control panel.

In a typical run, tires are placed into the reactor. After closing the lid, the reaction chamber is initially flushed with nitrogen in order to remove air, then the system is heated at 8°C/min up to the set point, and kept at the desired temperature up to 150 min total residence time. During heating the water from the hydraulic guard facing the inner chamber evaporates, forming steam that adds up to the pyrolysis products flow, hence requiring a separation step of the vaporized water from the oily products in the demister.

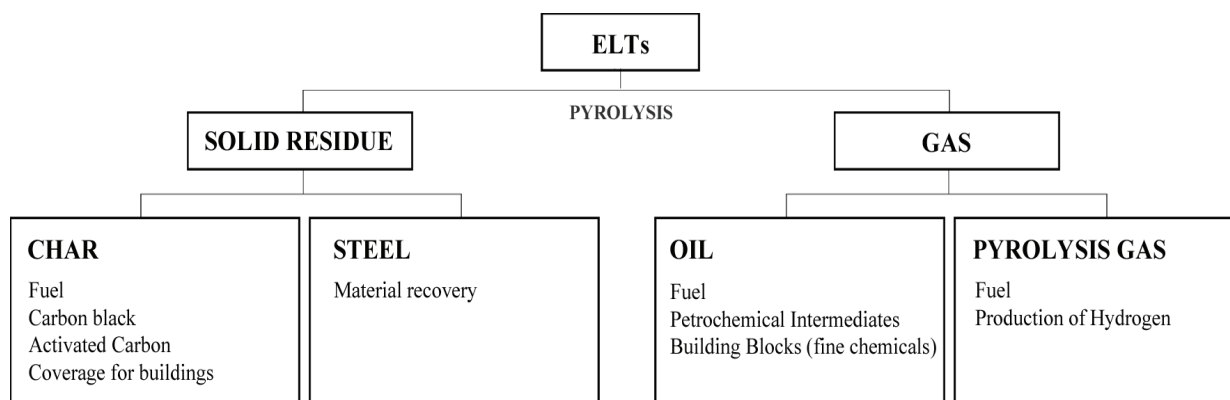


Fig. 1. Schematic plot of ELTs pyrolysis products evolution

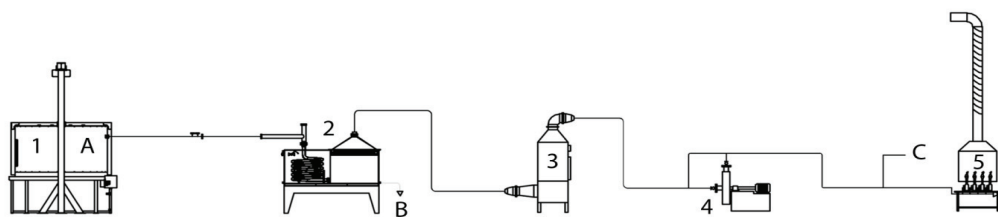


Fig. 2. Schematic layout of the experimental pyrolysis pilot plant: 1, pyrolysis chamber; 2, demister; 3, H₂S scrubber; 4, fan; 5, burners; A, collection point of solid residue; B, collection point of pyrolysis oil; C, bleed point of gas

After 150 min the resistances are switched off and the reactor begins to cool down; this is considered the end-point of the test. When the temperature goes down below 100°C, the upper bell of the reactor is opened for removal of the solid residue (char and steel) and the liquid (oil and water) is removed through the demister sampling point.

2.2. Feed materials

The tests with ELTs have been performed on tire sets in different state of wear and with a random mix of brands and models (the details are reported in Table 1 with respect to each run) while, for all the NT experiments, Lassa model Atracta has been used. For each set of tires, at least two tests have been carried out at each selected temperature with a 150 min overall residence time, while at 400°C tentative longer runs were also carried out. Several further tests have been carried out at 500°C that appears the optimal process temperature, sufficient to guarantee complete thermal degradation of whole tires, while leading to a considerable energy saving in terms of heating. The yields data of the pyrolysis products and composition of the gas have been averaged for analogous runs.

The different tires wear status implies the variation, from set to set, of the degradable/non-degradable components weight ratio. In particular, NTs are characterized by steel fraction in the 9–10wt% range while the ELTs are richer in steel ranging from 11 to 13wt%.

2.3. Analysis of the final products

At the end of each test, the pyrolysis solid and liquid products have been recovered, the char has been manually separated from the steel wires, then steel, oil, and char weighed. The gas fraction has been obtained by difference. The char produced through similar tests has been collected and then sampled and characterized to evaluate its possible use as fuel or as raw material. Ashes, water and volatile materials contents have been determined by TA instruments SDT Q600 according to the ASTM D 7582. The elemental composition CHN-O/S has been used to calculate the higher heating value (Gross Heating Value, GHV) and lower heating value (Net Heating Value, NHV). X-Ray Fluorescence spectra have been recorded on a PANalytical AxiosMAX Advanced XRF Spectrometer, equipped with a

rhodium X-ray tube target, set to a power of 2.4 kW in order to quantify the sulfur and zinc contents and detect the presence of heavy metals. Finally, the determination of the total surface area has been carried out by nitrogen adsorption at –196°C using Carlo Erba SORPTY 1750 equipment which uses the simplified BET model.

The particular characteristic engineering plant involves co-condensation of oil and process water. For this reason, after draining the demister, the two fractions have been separated with a centrifuge operating at 4200 rpm for 6 minutes. The oil fraction has been characterized by GC-MS analysis using a Thermo FOCUS GC, coupled to a DSQ mass spectrometer as detector and equipped with a Supelco SPB™ fused silica capillary column. This analysis allows the identification of compounds in the lighter oil fraction. The dynamic viscosity has been determined at 25°C using a digital Brookfield viscometer – Model DV-II +, spindle “I” with a rotational speed of 100 rpm. The values have been compared with those obtained for a common commercial diesel fuel. To assess the effect of shelf life on the physical properties of the oil, the density and dynamic viscosity of some significant samples has been re-measured after 6 and 12 months. Simulated distillation using the thermogravimetric method (SimDis TGA) has been performed on oil samples of about 15 mg in platinum pans suitable for liquids (heating rate of 5°C/min from room temperature (RT) to 500°C in a 100 mL/min nitrogen flow).

The gaseous phase has been analyzed *in situ* with a Micro-Gas Chromatograph Agilent 490 Micro-GC placed on-line in the pilot plant so no active sampling is required. Two columns have been used for analysis: a Molsieve 5 Å (MS, 20 m) with molecular sieves made with zeolites as stationary phase and argon as carrier gas. The MS column has been held at 80°C throughout the experiment. This apparatus has been designed for separating H₂, O₂, N₂, CO and CH₄. The second column is a PoraPLOT U (PPU, 10 m) with divinylbenzene-ethylene glycol/dimethylacrylate as stationary phase and helium as carrier gas. The PPU column has been maintained at 90°C throughout the experiment. This apparatus has been designed to separate H₂S, CO₂, C₂H₄, C₂H₆ and hydrocarbons up to C₃, with the possibility of detecting even the C₄. The detector used by the device is a Thermal Conductivity Detector (TCD).

Table 1. List of experimental runs

Test Code	T (°C)	Brand and model of tires	Number of tires	Weight (kg)
NT400.01	400	Atracta 155/70R13 79T	2	12.92
NT400.02	400	Atracta 155/70R13 84T	3	18.75
ELT400.01	400	Driver couvier 185/65 R15 88H, Firestone Firehawk 185/65 R15 88H, Driver Couvier 185/65 R15 88H	1+1+1	19.69
ELT400.02	400	Dunlop Sport 205/55 R16 91V, Firestone Firehawk 185/65 R15 88H	1+2	19.12
NT450.01	450	Atracta 155/70R13 79T	2	12.96
NT450.02	450	Atracta 165/70R13 84T	3	20.91
ELT450.01	450	Dunlop Sport 205/55 R16 91V, Bridgestone turaz 195/55 R15 87 H, Firestone fire hawk Tz 88H	1+1+1	22.84
ELT450.02	450	Bridgestone turaz 195/55 R15 87 H, Michelin energy 175/65 R13 82T, Dunlop SP sport 205/60 R13 91H	1+1+1	18.94
NT500.01	500	Atracta 155/70R13 79T	2	12.24
NT500.02	500	Atracta 165/70R13 79T	2	12.32
NT500.03	500	Atracta 155/70R13 79T	2	12.65
NT500.04	500	Atracta 155/70R13 79T	2	12.71
NT500.05	500	Atracta 155/70R13 79T	2	12.82
NT500.06	500	Atracta 165/70R13 79T	2	12.82
NT500.07	500	Atracta 165/70R13 79T	2	12.89
NT500.08	500	Atracta 165/70R13 79T	2	12.95
NT500.09	500	Atracta 155/70R13 79T	2	12.96
NT500.10	500	Atracta 155/70R13 79T	2	13.02
NT500.11	500	Atracta 155/70R13 79T	2	13.16
NT500.12	500	Atracta 155/70R13 79T	2	13.77
ELT500.01	500	Matador Stella 195/65 R14 79T, Continental ContiWinterContact 205/55 R16 91H, Pirelli P3000 175/65 R15 84T	1+1+1	19.66
ELT500.02	500	Michelin Energy 165/70 R14 81T, Pirelli P7 205/55 R16 91V	1+2	20.53
ELT500.03	500	Michelin Energy 175/65 R13 82T, Pirelli P7 215/55R16 93V, Firestone CV 2000 195 R14C 102/110 N6 P.R.	1+1+1	22.4
ELT500.04	500	Miratta Lassa 175/70 R14 88H, Pirelli P6000 195/60 R15 88H, Toyo Proxer R32, 205/50 R17 89W	1+1+1	24.24
ELT500.05	500	Bridgestone Turanza ER 300 205/55 R16 91H, Dunlop SP sport 205/60 R13 91H	2+1	25.65
ELT500.06	500	Pirelli P7 205/55 R16 91V, Lassa Impetus revo 205/65 R16 99H, Michelin Primacy HP 225/55 R1797W	1+1+1	26.96
NT550.01	550	Atracta 165/70R13 79T	2	12.93
NT550.02	550	Atracta 175/70R13 84T	2	13.97
ELT550.01	550	Atracta 165/65R13 77T, Atracta 155/70R13 75T, Atracta 165/70R13 79T	1+1+1	19.37
ELT550.02	550	Pirelli P3000 175/65 R15 84T; Pirelli Pzero 205/50 ZR17 93W, Pirelli P3000 165/65 R13 77T	1+1+1	19.63
NT600.01	600	Atracta 155/65R13 73T	3	17.59
NT600.02	600	Atracta 175/70R13 84T	2	13.94
ELT600.01	600	Pirelli Pzero 205/50 ZR17 93W, Michelin Classic 185/75 R14 PR8	2+1	18.65
ELT600.02	600	Michelin Energy 185/60 R15 84H, Michelin Classic 185/75 R14 PR8	1+2	20.54

Quantification has been performed by comparison with a blend of gases of known composition. The calorific value of the gas (GCV) has been calculated, according to the UNI 7839, based on the obtained composition.

3. Results and discussion

3.1. Pyrolysis yields

The aim of this research is to study the influence of the maximum reached temperature and of the state of wear on tires pyrolysis products in

presence of steam. Since the steel content in each set of tires is variable, as discussed in the Experimental, the products yields (Fig. 3) are net of steel. The obtained trends reported in Fig. 3 are similar for both tire series in the studied temperature range. It is worth noting that the highest carbonaceous residue (char) has been achieved in tests carried out at 400°C for both NT (49.6 wt%) and ELT (49.5 wt%). Such a behaviour suggests that at this temperature, even for protracted times, it is not possible to achieve a complete thermal degradation of the polymeric fraction. Furthermore, the composition of the pyrolyzed gaseous fraction is rich in light compounds

(pyrolysis gas) due to the cracking of the long molecular chains (oil) which is favoured at long residence time. In other words, at 400°C, the low amount of degraded rubber forms heavy products and longer residence time involves additional molecular cracking (Leung et al., 2002). Between 450 and 600°C, the thermal degradation of tires increases, as demonstrated by the decrease of the char fraction that reaches a constant value around 40 wt%.

At these temperatures, the produced volatile fraction tends to spontaneously flow out the reaction dome, favoured also by the increase of the thermal expansion of the gases, thus cooling down and interrupting the subsequent cracking reactions that might occur at higher temperatures. This effect results in an important increase of the oil fraction between 400 and 450°C for both series (from 14.0 to 29.9 wt% for NT and from 12.1 to 26.0 wt% for ELT) and a slight decrease of the incondensable fraction. Between 450 and 600°C, a further slight enhancement of the oil fraction with a corresponding decrease of gas takes place. It is important to note that for both sets of experiments, between 500 and 550°C, the oil/gas weight ratio reaches the value of 1.

Many scientific investigations on pyrolysis of shredded tires are reported in the literature. In Table 2 we have collected the results of some of them, thus showing how different technologies (i.e. type of reactor) and process parameters (i.e. temperature, pressure, heating rate, residence time) can lead to very different products yields. The oil fraction, for example, covers an extremely wide range of percentage and its trend with the increase in temperature is not constant. In the tests carried out with experimental conditions similar to those presently reported, the oil yield has a stable/slow increasing trend with the increase in temperature (Aydin and Ilklic, 2012; Berruoco et al., 2005; Dai et al., 2001; de Marco Rodriguez et al., 2001; Fernandez et al., 2012; Laresgoiti et al., 2000). In these tests, the yield in gas, also at low temperatures, is noticeably higher than what reported by other

authors (Table 2). In particular, pyrolysing non-shredded tires at 500°C, Roy et al. (1999) obtained a smaller amount of incondensable gas and a bigger oil fraction. Furthermore, according to Kaminsky and Mennerich (2001) that evaluated the effects of the presence of steam on the pyrolysis process of tires at 500°C in a fluidized bed reactor, the yield of pyrolysis products results not significantly influenced by this process parameter.

3.2. Char characterization

The solid residue is the product most influenced by the compositional variability of the processed tires, because in the char are concentrated, among others, sulfur and metals introduced as fillers and adjuvants in the process of vulcanization. The proximate and elemental analysis, conducted on char samples produced by pyrolysis at 500°C compared to previously reported data of char obtained in similar conditions, are reported in Table 3. Proximate analysis shows no significant differences between the char obtained by ELT and NT at the same temperature. The values obtained for moisture and ashes are in line with the values reported by other authors. The content of volatile compounds, which in literature covers a wider range, is similar to that reported by Diez et al. (2004).

Zinc is originally present in the rubber as vulcanization activator, as inorganic filler in replacing the silica and/or as resulting from the galvanizing of steel reinforcing mesh which produces the iron. This element has been found in the range 3.73–4.06 wt% similarly to the values reported by Helleur (4.2±0.3 wt%) and below those reported by Conesa (6.68 wt%). Silicon is more than five times lower than what reported in the literature (Conesa et al., 2004; Helleur et al., 2001). Heavy metals, such as nickel, vanadium, chromium, lead, detected in low concentrations in some reported testing (Galvagno et al., 2002), are not detectable in the obtained chars (<5 ppm).

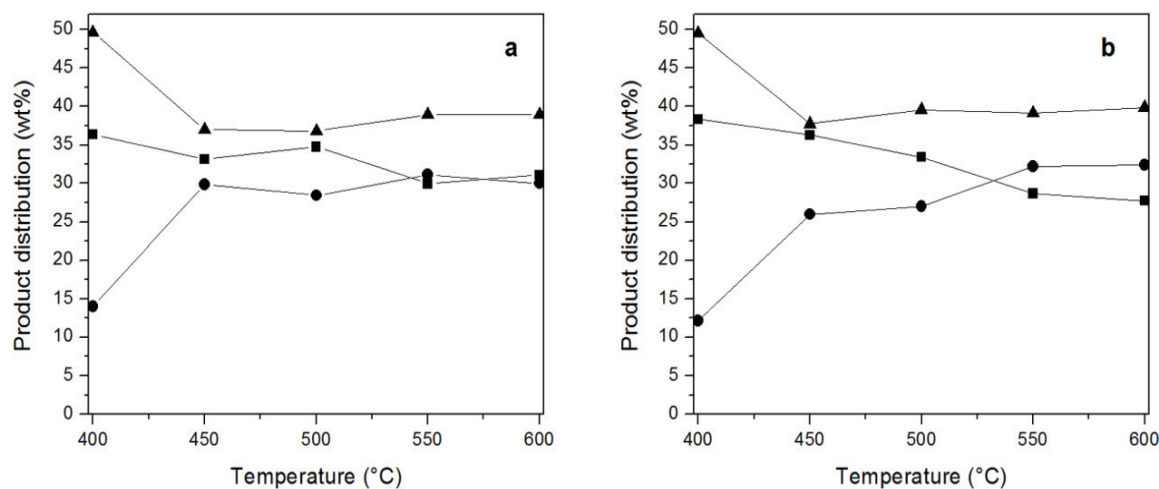


Fig. 3. Effect of temperature on the yield of the different pyrolysis products: a) NT and b) ELT: (▲) Solid residue; (■) Gas; (●) Oil

Table 2. Literature survey of results of the waste tires pyrolysis

Experimental system	Reference	Process (°C)	Note	Yields (wt%)		
				Char	Oil	Gas
Conical spouted bed reactor	Lopez et al. (2009)	425-600	feedstock size <1mm	34-36	64-56	2-8
Fluidized bed reactor	Dai et al. (2001)	360-810	feedstock size 0.32mm	40-30	50-30	10-40
	Kaminsky and Mennerich (2001)	500-600	feedstock size 1-2mm	30-40	65-51	5-9
500		feedstock size 1-2mm presence of steam	31	65	3.5	
Pyrocycling process	Roy et al. (1999)	500	under vacuum (7 kPa), whole tires, 10% steel	37	47	5
Fixed bed reactor	Aydin and Ilklic (2012)	400-700	shredder sample	62-41	31-40	7-19
	Choi et al. (2014)	500-800	feedstock size 1-2mm heating rate 10°C/min	37-37	38-30	23-30
Static-bed batch reactor	Cunliffe and Williams (1998)	450-600	feedstock size 4.5cm ³ , including metallic and textile part	37-38	58-53	4-9
	Berruoco et al. (2005)	400-700	feedstock size 2cm, including metallic and textile part	64-51	30-43	2-4
Rotary kiln	Galvagno et al. (2002)	550-680	feedstock size <2cm	49-49	38-32	2-11
Horizontal oven	Fernandez et al. (2012)	400-900	feedstock size <2cm	68-38	31-57	1-5
Autoclave	de Marco Rodriguez et al. (2001)	300-700	feedstock size ≈3cm ² ; heating rate 15°C/min	88-44	5-38	7-18
	Laresgoiti et al. (2000)	400-700	Radial portion (175g) heating rate 15°C/min	53-43	28-40	7-9

Table 3. Proximate average and elemental analysis of char produced at 500°C for NT and ELT compared with literature data

	NT	ELT	Conesa et al. (2004)	Helleur et al. (2001)	Galvagno et al. (2002)	Diez et al. (2005)	Diez et al. (2004)	
Process (°C)	500	500	450	550	550	550	450	550
Proximate analysis (wt%)								
Moisture	2.1	1.0	0.37		3.57	0.9-1.14	1.5	1
Volatile Matter	0.0	1.5	7.78		12.78	2.9-3.5	3.1	1.2
Ash	9.9	9.5	8.27	15.2±0.2	15.33	14.3-13.6	16.0	16.5
Char Composition (wt%)								
Zn	4.06	3.73	6.68	4.2±0.3				
S	2.51	2.67	1.9	2.0±0.1				
Mg	0.06	0.07	0.147	0.1±0.02				
Al	0.04	0.05	-	1.0±0.3				
Si	0.29	0.31	1.69	1.6±0.2				
K	0.12	0.08	0.0969	-				
Ca	0.18	0.16	0.127	-				
Ti	0.00	0.02	0.0171	1.3±0.2				
Fe	0.03	0.03	0.0393	0.3±0.1				

The specific surface area, the elemental analysis and the calorific values (Gil-Lalaguna et al., 2014), essential parameters for assessing the quality of the char, are reported in Table 4. In the solid samples produced by pyrolysis at 500°C 0.84 wt% (NTs) and 0.87 wt% (ELTs) sulfur content with respect to the total weight of the pyrolyzed tires is found. The sulfur content, reported as weight fraction of the char (2.51 wt% for NTs and 2.50 wt% for ELTs), is similar to the average values reported by analogous processes (Table 4).

The Gross Calorific Value (GHV) is over 32000 kJ/kg, higher than other char residues and this is mainly due to its higher hydrogen content. The specific surface area (SSA), about 63 m²/g, is in line with literature data and could be increased considerably through specific activation processes to

obtain active carbon (Zabaniotou and Stavropoulos, 2003).

3.3. Oil characterization

To evaluate the influence of the process parameters, the oils obtained from different pyrolysis tests have been analyzed in terms of both fuel characteristics and chemical composition. The influence of the pyrolysis temperature on the oil density and dynamic viscosity is reported in Fig. 4. The density values tend to slightly increase with increasing pyrolysis temperature and are quite narrowly distributed (0.93-0.97 kg/m³), in line with the value (0.95 kg/m³) reported in the literature (Lopez et al., 2009; Roy et al., 1999) and higher than those measured on a commercial diesel (Eni-Blue

diesel+, 0.84 kg/m³). The dynamic viscosity of the oils tends to decrease rapidly between 400 and 550°C (from 36.73 to 18.20 cPs) where it reaches its minimum. The viscosity of oils produced between 500 and 600°C is similar to the one of commercial diesel fuel. In order to evaluate the possible effects of the oils aging, the samples have been analyzed immediately after the process and after further 6 and 12 months (Fig. 4). The density and the viscosity of the oils do not show substantial variations with aging and with the wear status of the tires. These results are in good agreement with previous reports (Rofiqul Islam et al., 2008).

Elemental composition of the presently investigated samples is similar to that of previously reported pyrolytic oils (Table 5).

However, the determined sulfur content (about 1.0-1.1 wt%) is lower than that reported in the literature and it is interestingly close to the threshold for the potential marketing of this product as a low sulfur containing fuel.

From these data it is possible to calculate (Koo et al., 2014) the relative calorific values (around 10300 kcal/kg) which, as expected, are similar or slightly higher than what reported in the literature for similar processes.

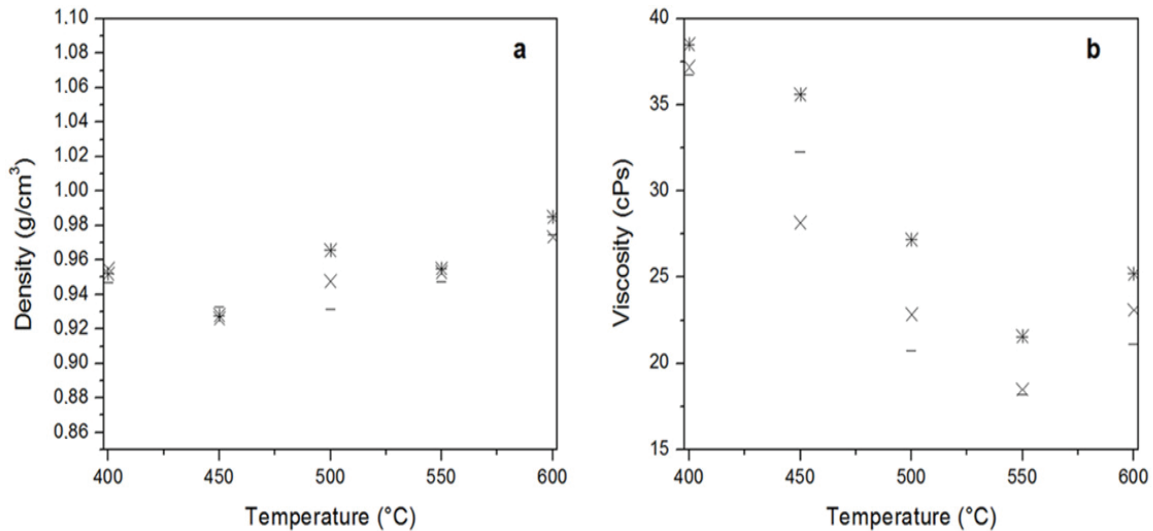


Fig. 4. Density (a) and dynamic viscosity (b) at 25°C of investigated pyrolysis oils at three different aging times: immediately after the process (-), at 6 (x) and 12 (*) months

Table 4. Specific surface area (SSA), CHN-O/S analysis and calorific values of the chars produced at 500°C compared with literature data

Sample	Process (°C)	Elemental composition (wt%)					SSA (m ² /g)	GHV (kcal/kg)	NHV (kcal/kg)
		C	H	N	O	S			
NT	500	86.40	3.10	0.30	4.43	2.51	63.1	7900	7800
ELT	500	85.50	3.30	0.40	4.90	2.50	63.7	7900	7700
Conesa et al. (2004)	450	88.19	0.60	0.10	-	1.90	93	-	7367
Lopez et al. (2009)	500	86.62	1.39	0.75	-	2.24	65.2	-	-
Diez et al. (2005)	550	95.9	0.5	0.2	<0.1	3.3	-	6831	-
de Marco Rodriguez et al. (2001)	500	83.5	0.6	0.3	1.1	2.4	-	6979	-
Galvagno et al. (2002)	550	85.31	1.77	0.34	-	2.13	-	7336	-
Ucar et al. (2005)	550	-	-	-	-	-	55.5	-	-

Table 5. CHN-O/S analysis and calorific values for the investigated oils compared with literature data

Sample	Process (°C)	Elemental composition (wt%)					GHV (kcal/kg)	NHV (kcal/kg)
		C	H	N	O	S		
NT	400	86.0	11.1	0.6	1.2	1.1	10300	9700
	450	85.9	11.2	0.5	1.4	1.0	10300	9700
	500	85.8	11.3	0.6	1.3	1.0	10300	9700
	550	85.7	11.3	0.6	1.4	1.0	10300	9700
	600	85.7	11.5	0.5	1.3	1.0	10400	9800
ELT	500	85.9	11.2	0.5	1.3	1.1	10300	9700
Diez et al. (2004)	450	78.2	10.0	0.4	-	1.4	9268	8696
Cunliffe and Williams (1998)	500	84.9	10.2	0.5	3.1	1.3	10071	-
de Marco Rodriguez et al. (2001)	500	85.6	10.1	0.4	-	1.4	10055	-
Ucar et al. (2005)	650	87.57	10.35	<1	-	1.35	9952	-

GC-MS allows identifying and quantifying the chemical composition of the lighter fractions of the oil. Significant amount of benzene, toluene, ethylbenzene, xylene and styrene derived by Styrene-Butadiene rubber component are produced (Table 6). These species, due to thermal decomposition of styrenic rubbers and to cyclization of olefin structures followed by dehydrogenation and Diels Alder reactions, tend to increase with the temperature process, as reported by other authors (Cunliffe and Williams, 1998; Lopez et al., 2009).

High concentration of these compounds suggests a potential recovery of high value products as chemicals: xylenes can be employed in the plastics industries; toluene in the production of pesticides, dyestuffs, surfactants and solvents; styrene is one of the most utilized building blocks in the production of polymeric materials. The increase in temperature causes the formation of lower molecular weight species. The sum of the identified $C_{\leq 12}$ fractions shows a considerable increase with temperature: at 400°C, only 3% of the oil is composed of light fraction while at 600°C this value rises up to 25%. Moreover, the analysis of the C_{5-12} components

shows that this is mainly made up of lighter compounds ($C_{<9}$). This trend can be attributed to the increase of thermal cracking due to the increasing temperature (Cunliffe and Williams, 1998; Lopez et al., 2009). For comparison, the same analysis has been carried out on the oil produced at 500°C by ELTs pyrolysis. The obtained data highlight that there are no significant differences with the NT 500 sample. Furthermore, the oil composition confirms the similarity found between the oil fractions for both density and viscosity and the limited aging changes, as confirmed by GC-MS analysis repeated on the same samples after 12 months.

In order to evaluate possible destinations for the pyrolysis oils, a simulated distillation using thermogravimetric method (SimDis TGA) in inert atmosphere has been performed. The obtained results are shown in Table 7 and Fig. 5. As reported in Fig. 5, the trend of the obtained curves is almost linear until the distilled masses reach 85–90 wt%. It is worth noting that oils produced at lower pyrolysis temperatures (400 and 450°C) show higher distillation temperature and dynamic viscosity, due to the greater content of heavier molecules.

Table 6. Yields (wt% on total oil) of the identified major compounds in C_5 - C_{12} fraction oil

Process temperature (°C)	NT					ELT
	400	450	500	550	600	500
TOT C_5	0.05	0.05	0.02	0.03	0.02	0.04
Aliphatic acyclic hydrocarbons	0.05	0.04	0.02	0.02	0.02	0.03
3-methylthiophene	0.00	0.01	0.00	0.01	0.00	0.01
TOT C_6	0.04	0.24	2.16	1.98	2.16	1.00
Benzene	0.02	0.23	2.15	1.97	2.15	0.99
Phenol	0.02	0.01	0.01	0.01	0.01	0.01
TOT C_7	0.37	2.69	9.30	9.79	9.98	7.23
Substituted cyclopentenes	0.00	0.02	0.01	0.01	0.01	0.02
Benzothiazole	0.02	0.02	0.01	0.01	0.01	0.02
Methyl phenols	0.03	0.02	0.01	0.01	0.01	0.01
Toluene	0.32	2.63	9.27	9.76	9.95	7.18
TOT C_8	1.49	5.28	11.15	11.93	12.19	10.26
Ethylbenzene	0.56	2.06	2.70	3.67	3.00	2.70
p-xylene	0.72	2.56	6.67	6.50	7.20	6.33
Styrene	0.21	0.66	1.78	1.76	1.99	1.23
TOT C_9	0.22	0.21	0.21	0.22	0.21	0.21
Indene	0.01	0.00	0.03	0.02	0.03	0.01
Methylstyrenes	0.04	0.04	0.02	0.03	0.02	0.03
Substituted benzenes	0.17	0.17	0.16	0.17	0.16	0.17
TOT C_{10}	0.35	0.32	0.26	0.22	0.24	0.33
1,4-Dihydronaphthalene	0.02	0.01	0.04	0.03	0.03	0.02
D,L- Limonene	0.03	0.06	0.02	0.02	0.02	0.04
Naphtalene	0.03	0.01	0.05	0.03	0.06	0.01
Substituted benzenes	0.27	0.24	0.15	0.14	0.13	0.26
TOT C_{11}	0.11	0.05	0.08	0.09	0.09	0.08
Methyl dihydronaphthalenes	0.02	0.01	0.02	0.02	0.02	0.02
Methyl naphtalenes	0.05	0.02	0.04	0.04	0.05	0.03
Substituted indenenes	0.04	0.02	0.02	0.03	0.02	0.03
TOT C_{12}	0.05	0.01	0.05	0.04	0.05	0.03
Substituted benzenes	0.05	0.01	0.05	0.04	0.05	0.03
$C_{>12}$ Others	0.03	0.09	0.01	0.01	0.01	0.01
$C_{\leq 12}$ NOT ATTRIBUTED	0.36	0.37	0.14	0.17	0.19	0.24
TOTAL DETECTED	2.68	8.85	23.23	24.30	24.94	19.18

The increase of the pyrolysis temperature, instead, leads to a progressive lowering of distillation temperatures and viscosities, due to the presence of lighter compounds.

This fact is also detectable observing the distillate masses in typical temperature ranges for commercial petrol and diesel (de Marco Rodriguez et al., 2001), as reported in Table 8. The amount of distillate in the lowest temperature range (petrol, 70–210°C) increases with pyrolysis temperature process whereas for the highest temperature range (diesel, 150–370°C) the trend is opposite. These data demonstrate that the composition of the pyrolysis oils, in terms of distillable fractions, is intermediate

between the composition of petrol and diesel, as also reported by Ucar et al. (2005). The pyrolysis oil produced at 500°C from ELTs is richer in light compounds and more similar to petrol than other reported oils obtained in similar conditions (Table 7).

3.4. Pyrolysis gas characterization

The gas mixture produced by pyrolysis of both NTs and ELTs samples has been analyzed online on the plant, in order to correlate the volatile composition with the applied pyrolysis conditions. A typical trend recorded during a run is shown in Fig. 6.

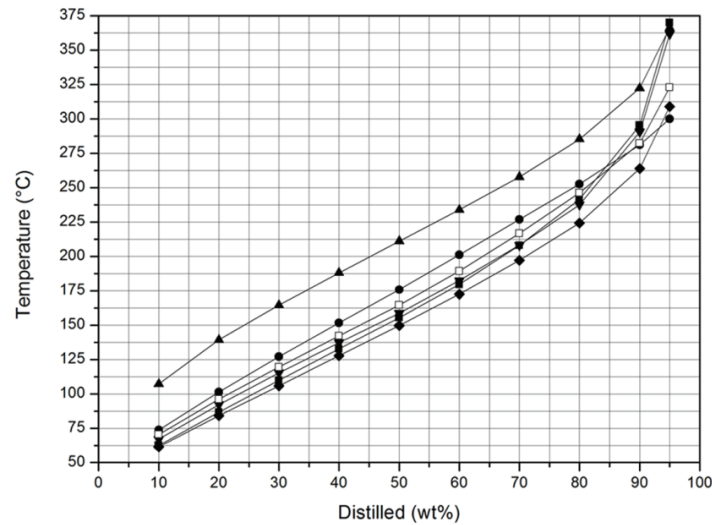


Fig. 5. Simulated distillation curves of pyrolytic oils obtained by means of SimDis TGA: (▲) NT, 400°C; (●) NT, 450°C; (■) NT, 500°C; (◆) NT, 550°C; (▼) NT, 600°C; (□) ELT, 500°C

Table 7. Distillation temperatures of investigated oils and other reported pyrolysis oils

Process (°C)	NT					ELT	Aydin and Ilklic (2012)	Ucar et al. (2005)	de Marco Rodriguez et al. (2001)
	400	450	500	550	600	500	Diesel Fuel	500	500
Distilled (wt%)	Distillation temperature (°C)								
10	109.1	81.0	62.5	60.5	67.22	65.6	175	150	114.5
20	141.3	110.2	87.5	83.3	93.3	91.4	185	177	168.8
30	166.0	135.7	110.8	104.9	116.7	114.8	195	185	198.2
40	189.1	159.4	133.9	126.9	138.9	137.8	-	-	249.3
50	211.8	182.6	156.6	148.9	160.8	160.3	214	234	296.1
60	234.0	206.4	181.1	171.5	184.9	184.7	-	-	333.8
70	257.1	230.7	210.0	196.3	212.3	211.8	250	293	359.8
80	283.2	257.0	244.9	224.1	245.6	240.8	-	-	373.9
90	319.0	288.4	303.9	265.4	306.7	276.4	310	359	386.4
95	371.4	310.6	392.2	312.6	405.9	309.6	334	402	388.7

Table 8. Distillate mass of investigated pyrolytic oils in the typical temperature ranges for diesel and petrol

Pyrolysis temperature (°C)	NT					ELT
	400	450	500	550	600	500
Temperature range (°C)	Distillate (wt%)					
70-210 (petrol)	46.6	54.1	57.2	61.1	58.3	57.8
150-370 (diesel)	71.7	62.8	47.2	46.6	49.0	52.0

The average compositions of the gas produced during the different pyrolytic experiments are reported in Table 9 and Fig. 7. The measured gases are H₂, CH₄, CO, CO₂, ethylene, ethane and H₂S. C₃ is the sum of propane and propylene while C₄ is the sum of 1-butene, n-butane, 1,3-butadiene and isobutylene. The sum of other indeterminate incondensable species is labelled as "Others".

It is worth noting that gas produced by pyrolysis of NTs or ELTs at the same temperature are composed of comparable amounts of different species. By increasing the batch temperature, a decrease in concentration of heavier molecular weight compounds (C₃ and C₄) and a simultaneous increase of lighter species, in particular methane and hydrogen, are observed. The main compound, at process temperature ≤450°C, for both series, is the sum of the C₄ (between 27.2 and 39.2 mol%). Starting from 500°C the formation of hydrogen and methane increases, and at 600°C, the latter reaches almost 40 mol%. This trend, observed for both NTs and ELTs and reported also by other authors

(Berrueco et al., 2005; de Marco Rodriguez et al., 2001), can be related to further cracking of evolved volatile matter at elevated temperatures. At the same time a reduction in CO₂ and CO content is registered (Fig. 7).

Kaminsky and Mennerich (2001) reported that the use of steam as fluidizing medium at 500°C did not significantly affect neither yield, nor the compositions of the reaction products. However, they reported that when the experiment is carried out in the presence of steam, there are high yields of CO₂ and CO which increase with the process temperatures, and lower yields of C₃ and C₄ compounds. Such a behavior has been attributed to the reaction with water.

In our case, the amount of carbon oxides decreases with the temperature, showing that in this experimental pilot batch pyrolyzer, the presence of steam at low temperature ≤ 600°C did not affect the composition of the pyrolysis gas. Thus the trend of production of H₂, CH₄ and hydrocarbons C₃-C₄ can be justified by the thermal cracking reactions only.

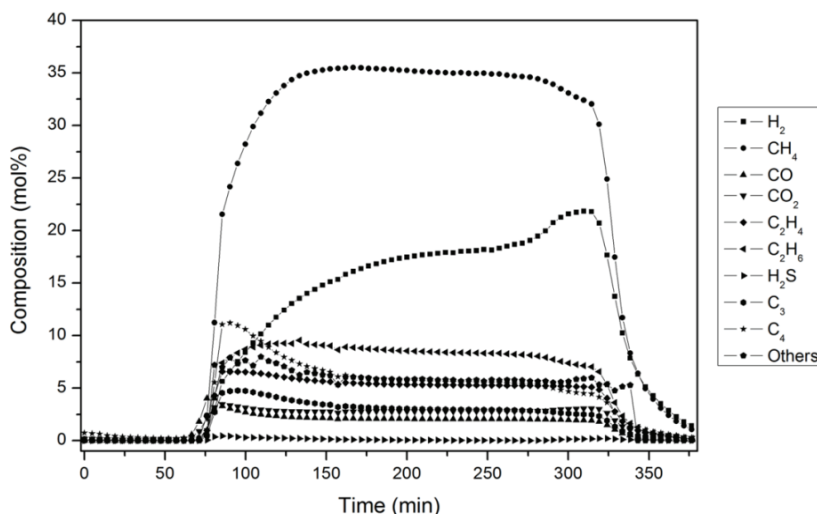


Fig. 6. Composition of the gas during a run, at 600°C with NT

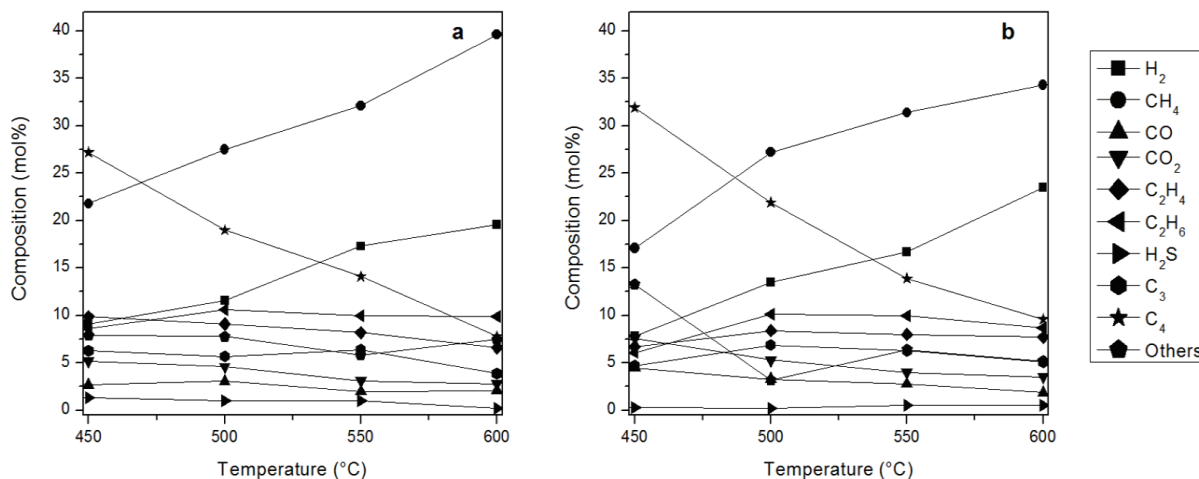


Fig. 7. Trend of the chemical species of the pyrolysis gas as a function of temperature: (a) NTs and (b) ELTs

Table 9. Chemical composition (mol %) and GCV (MJ/Nm³) of the pyrolysis gas produced at different process temperatures

	NT					ELT				
	Process Temperature (°C)					Process Temperature (°C)				
	400	450	500	550	600	400	450	500	550	600
H ₂	8.0	9.1	11.6	17.3	19.6	5.3	7.8	13.5	16.7	23.5
CH ₄	20.3	21.8	27.5	32.1	39.6	17.0	17.1	27.2	31.4	34.3
CO	4.5	2.7	3.1	2.0	2.1	3.4	4.5	3.3	2.8	1.9
CO ₂	5.8	5.2	4.6	3.1	2.8	6.0	7.6	5.3	4.0	3.5
C ₂ H ₄	9.2	9.9	9.1	8.2	6.6	11.6	6.7	8.4	8.0	7.7
C ₂ H ₆	6.6	8.6	10.6	10.0	9.9	5.9	6.1	10.1	10.0	8.7
H ₂ S	0.9	1.3	1.0	1.0	0.2	0.3	0.3	0.2	0.5	0.5
C ₃	6.5	6.3	5.7	6.4	3.9	7.3	4.7	6.9	6.3	5.1
C ₄	31.8	27.2	19.0	14.1	7.8	39.2	31.9	21.9	13.9	9.6
Others	6.4	7.9	7.8	5.8	7.5	4.0	13.3	3.2	6.4	5.2
GCV (MJ/Nm ³)	62.5	61.9	57.0	52.6	47.9	67.0	63.9	55.7	52.4	46.9

Finally, as reported in Table 9, the GCV values calculated according to UNI 7839, in the range 47-67 MJ/m³, decrease with process temperature for both series. This trend is mainly due to the reduction of C₃ and C₄ molar fractions in the pyrolysis gas mixture caused by the increase of the process temperature. In agreement with the very similar compositions of gas obtained at the same temperature, the calorific values of the two series are also almost coincident. These values are intermediate between those previously reported: 75.3-84 MJ/m³ (de Marco Rodriguez et al., 2001) and 47.7-39.6 MJ/m³ (Diez et al., 2004).

4. Conclusions

New and end of life tires have been pyrolyzed in an innovative pilot plant able to process whole tires, saving the energy costs of shredding, and allowing energy and materials recovery. By performing pyrolysis above 450°C, the process leads to:

- a char fraction (40wt%) with high GHV and promising specific surface area;
- an oil fraction rich in high commercial value compounds, with high GHV and low sulphur content (1wt%);
- a gas fraction enriched with hydrogen and methane.

The characterization of the oil fraction, repeated after one year, shows negligible changes during this period.

Acknowledgments

Authors wish to acknowledge Curti S.p.A. and POR FESR 2007-2013 Regione Emilia Romagna - Attività I.1.1 funded by Regione Emilia Romagna for financial support.

References

- Acevedo B., Barriocanal C., (2014a), Fuel-oils from co-pyrolysis of scrap tyres with coal and a bituminous waste. Influence of the oven configuration, *Fuel*, **125**, 155-163
- Acevedo B., Barriocanal C., (2014b), The influence of the pyrolysis conditions in a rotary oven on the

characteristics of the products, *Fuel Processing Technology*, **131**, 109-116.

- Aydin H., Ilklic C., (2012), Optimization of fuel production from waste vehicle tires by pyrolysis and resembling to diesel fuel by various desulfurization methods, *Fuel*, **102**, 605-612.
- Berruoco C., Esperanza E., Mastral F.J., Ceamanos J., Garcia-Bacaicoa P., (2005), Pyrolysis of waste tyres in an atmospheric static-bed reactor: Analysis of the gases obtained, *Journal of Analytical and Applied Pyrolysis*, **74**, 245-253.
- Bortolani G.N., Giorgini L., Tosi C., Bianchi M., (2014), Plant for transforming into secondary raw material, or disposing used tires, made of rubber or other carbon matrices comprising pyrolysis chamber, comprises first hydraulic sealing means, first evacuating means, and second evacuating means, Patent *WO2014057430-A1*.
- Choi G., Jung S., Oh S., Kim J., (2014), Total utilization of waste tire rubber through pyrolysis to obtain oils and CO₂ activation of pyrolysis char, *Fuel Processing Technology*, **123**, 57-64.
- Conesa J.A., Martin-Gullon I., Font R., Jauhiainen J., (2004), Complete study of the pyrolysis and gasification of scrap tires in a pilot plant reactor, *Environmental Science & Technology*, **38**, 3189-3194.
- Cunliffe A.M., Williams P.T., (1998), Composition of oils derived from the batch pyrolysis of tyres, *Journal of Analytical and Applied Pyrolysis*, **44**, 131-152.
- Dai X., Yin X., Wu C., Zhang W., Chen Y., (2001), Pyrolysis of waste tires in a circulating fluidized-bed reactor, *Energy*, **26**, 385-399.
- de Marco Rodriguez I., Laresgoiti M.F., Cabrero M.A., Torres A., Chomon M.J., Caballero B., (2001), Pyrolysis of scrap tyres, *Fuel Processing Technology*; **72**, 9-22.
- Diez C., Martinez O., Calvo L.F., Cara J., Moran A., (2004), Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered, *Waste Management*, **24**, 463-469.
- Diez C., Sanchez M.E., Haxaire P., Martinez O., Moran A., (2005), Pyrolysis of tyres: A comparison of the results from a fixed-bed laboratory reactor and a pilot plant (rotary reactor), *Journal of Analytical and Applied Pyrolysis*, **74**, 254-258.
- ETRma, (2014), Statistics, European Tyre and Rubber manufacturers' association, European Tyre and Rubber Industry, Edition 2014, On line at: <http://www.etrma.org/uploads/Modules/Documentsma nager/20141013-statistics-booklet-2014-final.pdf>.

- Fernandez A.M., Barriocanal C., Alvarez R., (2012), Pyrolysis of a waste from the grinding of scrap tyres, *Journal of Hazardous Materials*, **203-204**, 236-243.
- Galvagno S., Casu S., Casabianca T., Calabrese A., Cornacchia G., (2002), Pyrolysis process for the treatment of scrap tyres: preliminary experimental results, *Waste Management*, **22**, 917-923.
- Gil-Lalaguna N., Sanchez J.L., Murillo M.B., Atienza-Martinez M., Gea G., (2014), Energetic assessment of air-steam gasification of sewage sludge and of the integration of sewage sludge pyrolysis and air-steam gasification of char, *Energy*, **76**, 652-662.
- Giorgini L., Benelli T., Mazzocchetti L., Leonardi C., Zattini G., Minak G., Dolcini E., Cavazzoni M., Montanari I., Tosi C., (2015), Recovery of carbon fibers from cured and uncured carbon fiber reinforced composites wastes and their use as feedstock for a new composite production, *Polymer Composite*, DOI: 10.1002/pc.23440.
- Helleur R., Popovic N., Ikura M., Stanculescu M., Liu D., (2001), Characterization and potential applications of pyrolytic char from ablative pyrolysis of used tires, *Journal of Analytical and Applied Pyrolysis*, **58-59**, 813-824.
- Kaminsky W., Mennerich C., (2001), Pyrolysis of synthetic tire rubber in a fluidised-bed reactor to yield 1,3-butadiene, styrene and carbon black, *Journal of Analytical and Applied Pyrolysis*, **58-59**, 803-811.
- Kandasamy J., Gokalp I., (2015), Pyrolysis, combustion, and steam gasification of various types of scrap tires for energy recovery, *Energy & Fuels*, **29**, 346-354.
- Koo W., Jung S., Kim J., (2014), Production of bio-oil with low contents of copper and chlorine by fast pyrolysis of alkaline copper quaternary-treated wood in a fluidized bed reactor, *Energy*, **68**, 555-561.
- Laresgoiti M.F., de Marco I., Torres A., Caballero B., Cabrero M.A., Chomon M.J., (2000), Chromatographic analysis of the gases obtained in tyre pyrolysis, *Journal of Analytical and Applied Pyrolysis*, **55**, 43-54.
- Leung D.Y.C., Yin X.L., Zhao Z.L., Xu B.Y., Chen Y., (2002), Pyrolysis of tire powder: influence of operation variables on the composition and yields of gaseous product, *Fuel Processing Technology*, **79**, 141-155.
- Lopez G., Olzar M., Amutio M., Aguado R., Bilbao J., (2009), Influence of tire formulation on the products of continuous pyrolysis in a conical spouted bed reactor, *Energy Fuels*, **23**, 5423-5431.
- Quek A., Balasubramanian R., (2013), Liquefaction of waste tires by pyrolysis for oil and chemicals, *Journal of Analytical and Applied Pyrolysis*, **101**, 1-16.
- Rofiqul Islam M., Tushar M.S.H.K., Haniu H., (2008), Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes, *Journal of Analytical and Applied Pyrolysis*, **82**, 96-109.
- Roy C., Chaala A., Darmstadt H., (1999), The vacuum pyrolysis of used tires End-uses for oil and carbon black products, *Journal of Analytical and Applied Pyrolysis*, **51**, 201-221.
- Ucar S., Karagoz S., Ozkan A.R., Yanik J., (2005), Evaluation of two different scrap tires as hydrocarbon source by pyrolysis, *Fuel*, **84**, 1884-1892.
- Williams P.T., Brindle A.J., (2003), Aromatic chemicals from the catalytic pyrolysis of scrap tyres, *Journal of Analytical and Applied Pyrolysis*, **67**, 143-164.
- Zabaniotou A.A., Stavropoulos G., (2003), Pyrolysis of used automobile tires and residual char utilization, *Journal of Analytical and Applied Pyrolysis*, **70**, 711-722.