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Scrap tyre pyrolysis: Are the effluents valuable products?

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Abstract

Scrap tyre pyrolysis under nitrogen is studied at atmospheric pressure with the aim of producing a solid residue to be burned simultaneously with coal dust in a coal burning power plant. The experimental device maintains isothermal conditions. The temperatures of treatment are: 380, 450 and 550°C. Three phases are obtained after pyrolysis: solid, liquid and gas and their composition is studied in relation to the temperature of the thermal treatment. The solid phase (char)—approximately 40% weight of the initial sample (steel free) mostly constituted of carbon, also contains the main mineral matter initially present in the used tyre. The char produced is brittle and has a high burning power which makes it suitable for burning when mixed with coal dust in coal burning power plants. The steel weave is easily separated from the solid carbon residue after the thermal treatment and recovered without physical or chemical change and can be recycled. The gas phase contains a mixture of light hydrocarbons, dihydrogen and carbon dioxide. The IRTF spectra of evolved gases shows a change in the ratio of every gas while the pyrolysis takes place. The liquid phase is a complex hydrocarbon mixture in which some components have been identified. The chemical valorization of the liquid phase is an alternative to a thermal valorization. The pyrolysis appears to be a technique which is able to reduce a bulky, high polluting industrial waste, while producing energy and/or valuable chemical compounds. © 1997 Elsevier Science B.V.

Keywords: Scrapped tyre pyrolysis; Influence of temperature

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1. Introduction

In the developed countries, a large part of the non-metallic waste generated by industrial and domestic activity is represented by used car and truck tyres. This waste material constitutes a potential source of energy and valuable products [1]. Only 20% of this waste is actually recycled by various processes; its energetic valorization includes use as supplementary fuel in cement kilns, incinerators [2] or in co-combustion with coal [3–7]; shredded or powdered tyres can be used as additives to asphalt in road pavement [8], or in rubber compounding [9]. Among the thermal treatment processes, pyrolysis has received increasing interest as an alternative process to obtain storable liquid fuels and basic raw materials. A large pyrolysis temperature range and heating rate as well as various pressure pyrolysis conditions have been studied at laboratory or pilot scale [10–17]. The solid phase has been mostly investigated for its ability to be converted into activated carbon [18–21] or carbon black for industrial purposes [22,23].

An estimated 500 000 tons of scrap tyres are generated each year in France; 15 000 tons are produced in our region. Because of the future legislation concerning waste disposal and transport, particularly for used tyres, it seems to be relevant to solve this waste problem at a regional scale. One way is to produce a solid combustible for burning mixed with powdered coal in a coal dust burning power plant.

In this paper, the influence of the temperature pyrolysis on the solid, liquid and gas yield and composition has been investigated at a laboratory scale. The thermal treatment temperature was fixed at 380, 450 and 550°C.

2. Experimental

The experimental device is presented in Fig. 1. The reactor glass tube (diameter 30 mm, length 500 mm) was heated by an electric vertical, tubular furnace with nitrogen as the carrier gas. A sliding tube in the inferior part of the reactor immediately allowed the introduction of the sample into the hot area for a 15 min thermal treatment.

The steel free sample (1 cm diameter, 3 mm thickness, about 1 g weight) was taken from the sidewall rubber of a used tyre. While the pyrolysis takes place, nitrogen sweeps across the reactor tube from the inferior part (flow rate: 0.2 l min⁻¹) and transports the evolved gases to refrigerated traps, where the heaviest fractions condense. In a prior series of experiments, the pyrolysis reactor was coupled to an FTIR spectrometer (Perkin Elmer 1760X) equipped with a gas cell (15 cm³ volume, KBR sides, frequency range: 4000–500 cm⁻¹, MCT detector).

Allowing to the evolution of the nature of the gases versus time of treatment, another series of experiments were conducted: the light gases were collected in four tubular tanks filled up with a confining liquid for gas analysis [24]. Each tank was filled successively with the evolved gas collected for 3 min of treatment. The pyrolysis gas splitting enables us to analyse separately the different fractions by

chromatography with a Delsi GC 122 device, fitted out with a thermal-conductivity detector (injector and detector at 200°C) with two filled columns: a 5 Å, 60–80 mesh, molecular sieve column (3 m, 1/8) for dihydrogen analysis and a Hayesep D 100/200 (6 m, 1/8) column for the carbon monoxide and light hydrocarbons analysis. The carrier gases are Ar and He, respectively (20 ml min⁻¹ flow for the 2 columns). The furnace temperature is maintained at 50°C.

The collected oil fractions in the traps were weighed and analysed by gas chromatography (Chromatograph Perichrom; FID detector fitted with a Petrocol column (100 m × 0.25 mm × 0.50 μm). The temperatures of the injector and detector are maintained at 250°C; the flow of the carrier gas (He) was 0.9 ml min⁻¹ (split 1/100). The oil obtained was fluid enough to be injected without solvent. The furnace temperature was set at 35°C for 15 min then raised to 100°C (2°C min⁻¹) and maintained at this temperature for 2 h. A standard mixture of ethylbenzene, *o*- and *p*-xylene, 1,5 cyclooctadiene and limonene (5 μl of each diluted in 1 ml chloroform) was analysed under the same conditions.

After the pyrolysis, the solid residue was weighed. As the char is to be used in co-combustion with coal in a pulverized coal thermal power plant, comparative analysis of granulometry, calorific power, volatile matter, sulphur and ash content of char and coal were conducted. The granulometry test were made after a previous grinding in the same conditions for char and coal. The calorific powers were measured with a calorimetrical bomb.

Some pyrolysis experiments were conducted on samples taken from the tread rubber including the steel weave. This one was easily separated from the char and

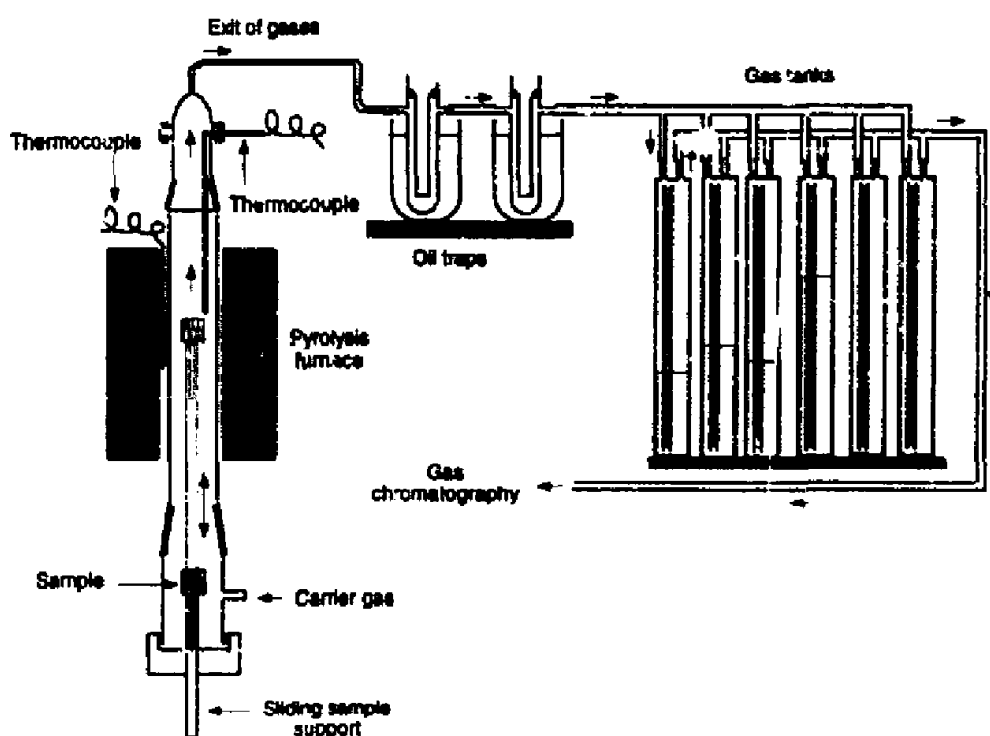


Fig. 1. Schematic drawing of the experimental device.

Table 1

Total mass yield results (wt %) for the tyres samples (steel free) after 15 min of pyrolysis

Thermal treatment temperature	380°C	450°C	550°C
Char	81 ^b	40	35
Liquid	15	19	12
Gas ^a	4	41	53

^a Obtained by difference.^b After 15 min at 380°C the pyrolysis was unfinished; this temperature was maintained for 1 h to get 52%wt of char.

observed by Scanning Electronic Microscopy to be compared to a reference unpyrolysed sample.

3. Results

The total mass yield for the tyres samples pyrolysed at 380, 450 and 550°C is reported in Table 1.

3.1. Gas phase

The IRTi² spectrometer coupling with the outlet of reactor allows to exhibit qualitative evolution of gas composition during the thermal treatment. In Fig. 2 is presented a series of spectra obtained during tyre pyrolysis at 450°C. The first spectral bands that appeared are those of carbon dioxide (2400 cm⁻¹) followed by characteristic bands of aliphatic (2900 cm⁻¹) and olefinic compounds (3100 cm⁻¹). On Fig. 3 are reported the major constituents of the gas against the treatment temperature. The gas was collected during time periods: 0–3, 3–6, 6–9 and 9–12 min. At 380°C, the gas was constituted of small quantities of carbon dioxide and methane and the total gas volume did not exceed 0.5 N·m³ kg⁻¹. At 450°C, the total gas volume reached 3 N·m³ kg⁻¹. Carbon dioxide appeared at the beginning of pyrolysis, and remained the major constituent in the following fractions; the light hydrocarbons (CH₄, C₂H₄, C₂H₆) appeared after a few minutes treatment. Their total volume reached about 1 N·m³ kg⁻¹. The dihydrogen was produced last, its volume was 0.7 N·m³ kg⁻¹. At 550°C, the total gas volume evolved was about 4.5 N·m³ kg⁻¹, for the half part constituted by hydrocarbons (mostly methane) and dihydrogen. The gas production is over during the initial stage of the reaction. Dihydrogen and methane increasing against temperature was reported in the literature [13,25] and attributed to dehydrogenation reactions and structural arrangements of gaseous hydrocarbons and oil.

3.2. Oil phase

Elemental analysis of the oils fractions obtained are reported in Table 2. The carbon content of the oil increases while the dihydrogen content decreases with temperature, corresponding to olefins and/or aromatics hydrocarbon production as

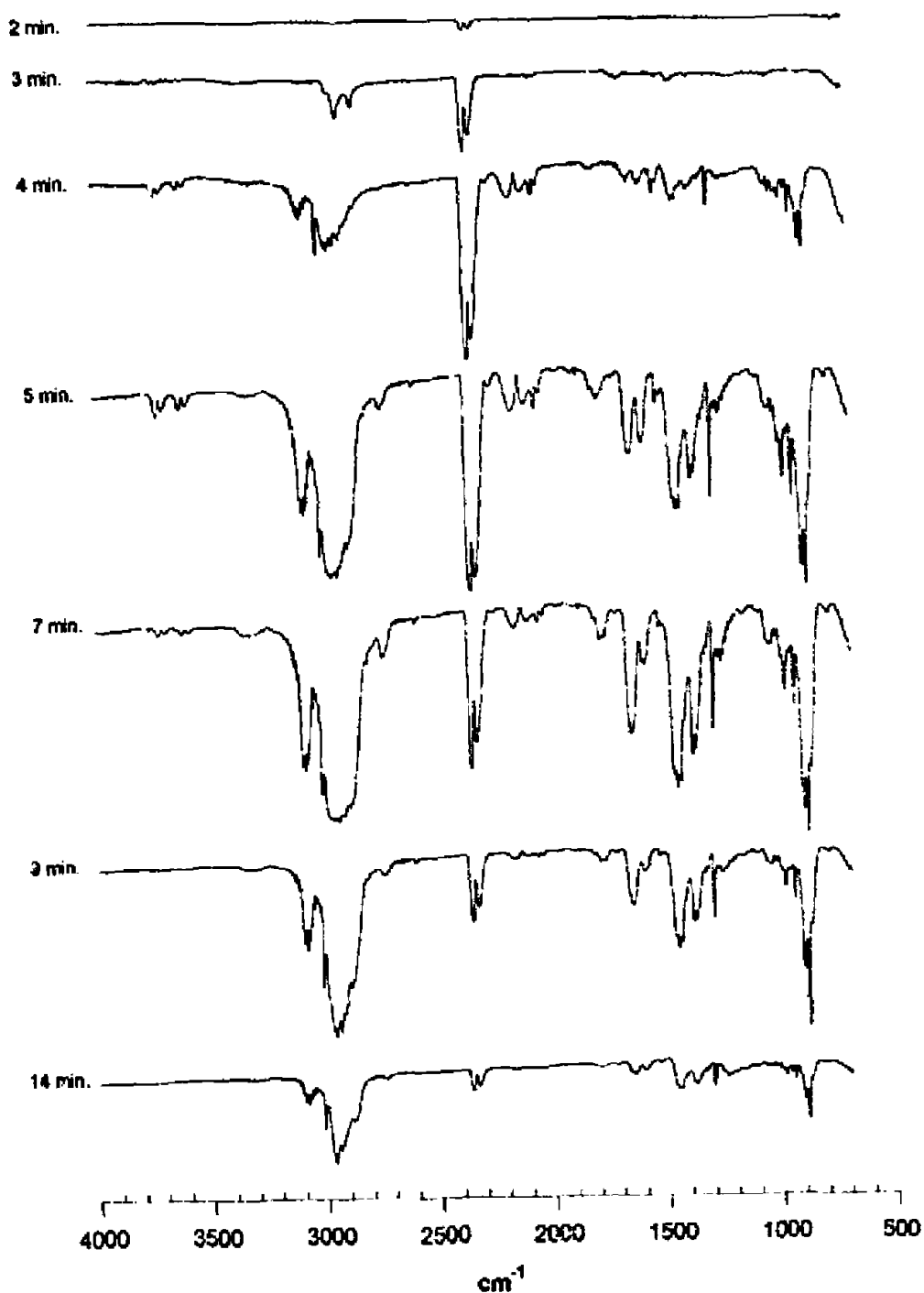


Fig. 2. IRTF spectra of the evolved gas as a function of time pyrolysis.

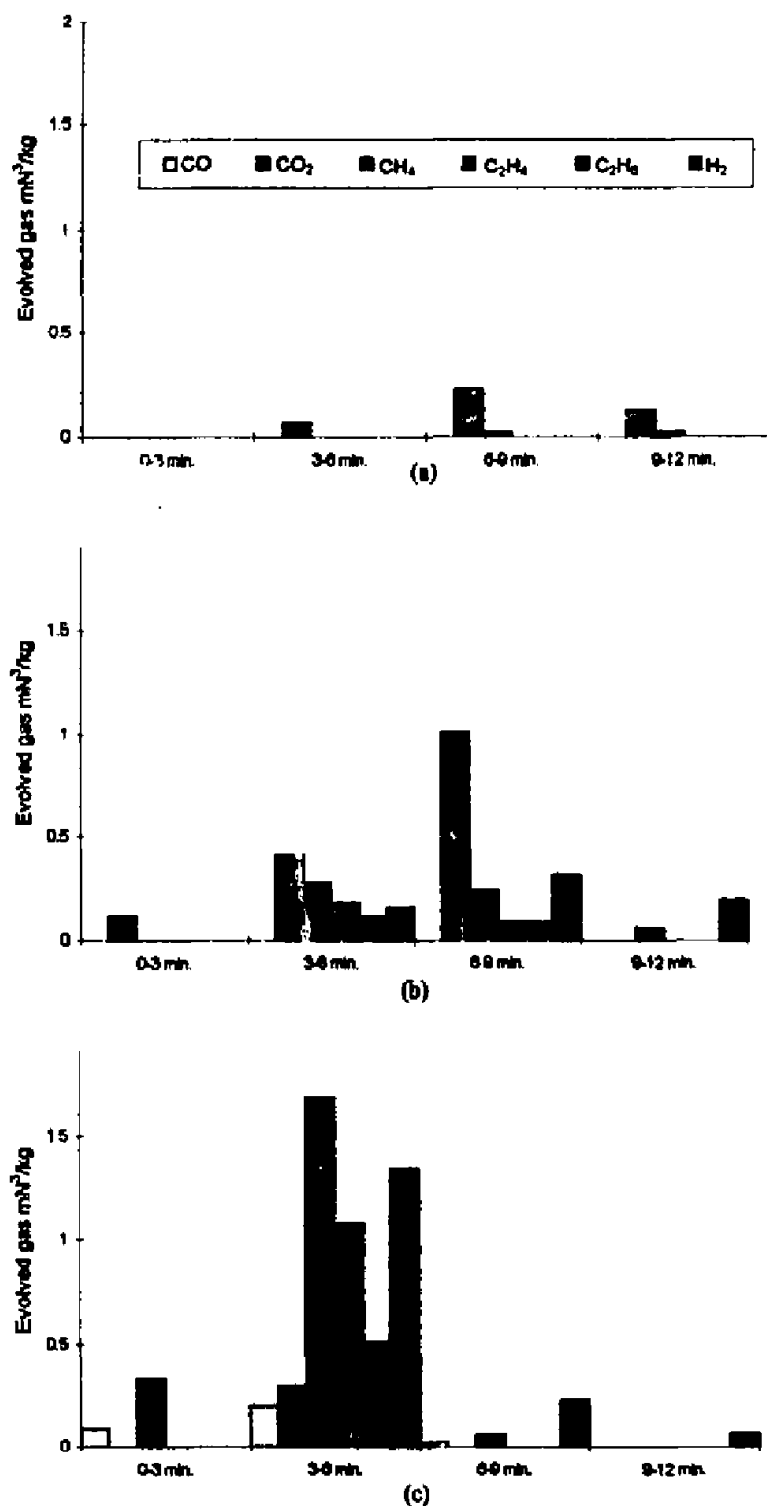


Fig. 3. Gas chromatogram of the pyrolysis gas collected during the thermal treatment, as a function of pyrolysis temperature (a) 380°C; (b) 450°C; (c) 550°C.

reported before [13,14]. The calorific value of the oil at 450°C was 36.5 MJ kg⁻¹, approximately of the same order than previously reported [10,11]. The chromatogram of a reference mixture and of the oil obtained at 450 and 550°C are given

Table 2
Ultimate analysis of the oils fractions vs. temperature

Ultimate analysis (wt%)	380°C ^a	450°C	550°C
C	81.1	83.5	84.9
H	11.4	11.0	10.3
N	0.5	0.5	0.8
S	1.6	2.2	1.8
Total ^b	93.6	97.2	97.8

^a Oil obtained after 1 h of treatment.

^b Oxygen balance to 100%.

Fig. 4. In both case, oil chromatograms can be related to a very complex mixture in which only a few compounds have been identified: ethylbenzene, *o*- and *p*-xylene and limonene.

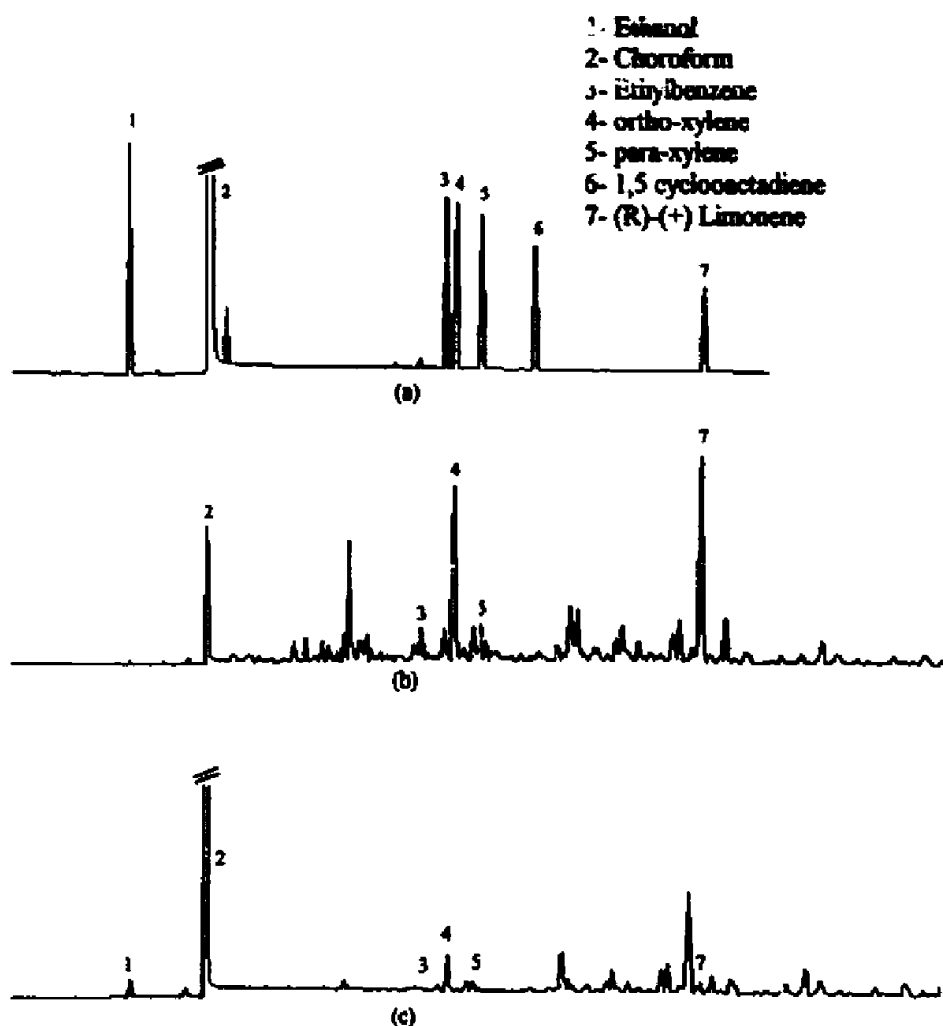


Fig. 4. Oil chromatogram: (a) Reference mixture; (b) oil obtained at 450°C; (c) oil obtained at 550°C.

Table 3
Ultimate analysis of tyre, char and coal

Ultimate analysis (wt%)	Tyre ^a	Char			Coal
		380°C	450°C	550°C	
C	87.2	88.8	88.0	89.4	71.6
H	7.3	3.8	1.7	0.3	4.9
N	—	0.2	0.3	0.1	1.8
S	1.7	1.0	1.1	0.8	0.9

^a Wt% (steel free).

3.3. Solid residue

The solid residue obtained after 15 min treatment both at 450 and 550°C has a brittle aspect; its weight is about 40% of the initial sample (steel free). At 380°C, the weight loss is less than 20% and the residue has a viscous and plastic aspect. A thermal treatment of 1 h is necessary to get a 50% weight loss residue having a similar aspect to those obtained for higher temperatures. Owing to the aim of producing a solid combustible that can be used in co-combustion with coal, standard coal measurements have been realised on the char: elemental analysis, granulometry, calorific power, volatile matter and ash contents. In Table 3 are reported elemental analysis of the initial tyre, of the char and of the coal actually used in the power plant mentioned above. The combustion properties are given on Table 4. The granulometry was measured on coal and char samples, both ground in similar conditions. The size distribution and the summarised percent of char and coal particles are represented Fig. 5. The distribution of particle size is in the range 0.4–1000 µm for coal and in a narrower range for char (0.4–300 µm); 60 and 80% for the coal and char particles, respectively, are smaller than 100 µm. Owing to the high carbon content of the char, its calorific value is greater than those of coal. Percentage sulphur mass values are similar for char and coal and ash content is lower for the char. The pyrolysis treatment has concentrated in the solid residue, zinc initially present in tyre which can appear to be a disadvantage for the

Table 4
Combustion properties

	Char		Coal
	450°C	550°C	
Lower calorific value (kJ kg ⁻¹)	31 400	30 900	29 000
Volatile Mater (wt.%)	7.1	3.5	19.9
Ash (wt.%)	8.4	7.7	23.8
Zn (wt.%) ^a	3.9	3.1	< 0.1

^a In the whole tyre, Zn is about 1.3 (wt.%, steel free).

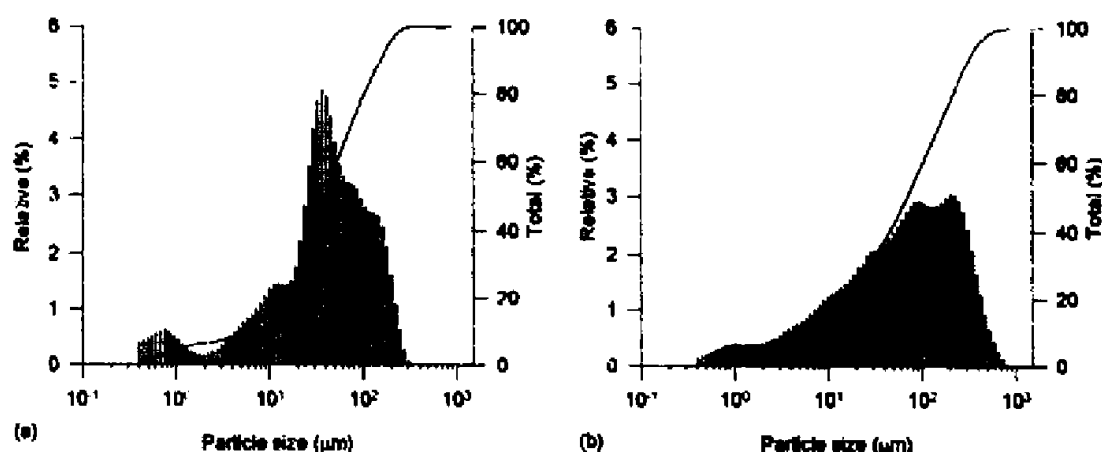


Fig. 5. Char and coal size distribution: (a) char; (b) coal.

combustion. Nevertheless, assuming that the whole used tyre feedstock produced in the area ($15000 \text{ tons year}^{-1}$) will be treated by pyrolysis, the resulting char does not reach more than 1% of the coal burned in a coal dust power plant. So, the zinc content stays at a very low level.

After pyrolysis, the steel weave from the tread rubber is recovered unchanged as can be seen by SEM comparison to a reference unpyrolysed sample.

4. Conclusion

Pyrolysis experiments on small used tyre samples are achieved in isothermal conditions. A 450°C thermal treatment temperature for 15 min is sufficient to obtain a good yield of solid product, which can be easily separated from the steel weave and converted into a fine powder. Thermophysical and combustion properties of the char are in good agreement with those of coal dust; so, the co-combustion of coal and char is possible in a coal dust power plant, without any burner modification.

The oil phase contains some valuable compounds but their separation from the complex liquid mixture obtained is difficult. Yet, regarding to its calorific value, the oil valorization as a fuel is always possible.

The gas evolved during thermal treatment are mostly composed of light combustible hydrocarbons and can be used as a supplementary heating resource in the pyrolysis process.

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