ENERGY RECOVERY FROM TYRES WASTE THROUGH THERMAL OPTION

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Procesele de piroliză şi combustie a anvelopelor uzate sunt opțiuni utilizate pentru valorificarea lor energetică. În acestă lucrare analiza elementară şi puterea lor calorică sunt prezentate. Aceste procese au fost analizate cu ajutorul unui spectometru termogravimetric şi cromatograf de masă TG-MS/TG-GC-MS. De la descompunerea termică a anvelopei rezultă: un gaz (20%), un ulei de piroliză (TPO,40%) şi un char solid (40%). Puterea calorică superioară şi inferioara determinate pentru TPO şi pentru char-ul solid au fost 49,5 şi 46,7 MJ şi 34.7 şi 33.7 MJ / kg, respective. Un exemplu de aplicare a procesului este prezentat în acest articol.

Pyrolysis and combustion of worn out tyres are increasing options for their energetic valorization. In the present paper the elemental analysis and calorific values of a tyre are presented. Results from TG-MS/TG-GC-MS analyzer and lab-scale reactor tests are also reported. From the thermal decomposition of the tyre, a gas (20%), a tyre pyrolysis oil (TPO, 40%) and a solid char (40%) resulted. The TPO calorific values, HHV and LHV, resulted 49.5 and 46.7 MJ/kg, while for solid char were 34.7 and 33.7 MJ/kg, respectively. An example of process application is also presented in this paper.

Keywords: calorific value, pyrolysis, SRF, tyre.

1. Introduction

The disposal of worn-out tyres represents a topical and an important problem in the waste sector. The forecasts of the European Association for Tyre Recycling [1] indicate a steady increase of the worn-out tyres production, which nowadays is estimated around 35 million tons by year. Approximately 1 billion of waste tyres are generated worldwide each year, USA producing 4.6 million tons and in the Europe 3.4 million tons respectively, yearly [2]. In Italy every year

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500,000 tons of tyres are discarded, for a volume of more than 3 million cubic meters [3].

The disposal of waste tyres is a major problem in environmental management and it has been estimated that about 3.4 and 4.6 million tons of waste tyres are produced respectively in Europe and in the USA annually [2].

The European Directive 99/31/EC, transposed in Italy with the Legislative Decree 36/2003 prevents the landfill disposal of worn-out automobile tyres. At the same time, the End-of-Life Vehicle Directive 2000/53/EC, and the Waste Incineration Directive 2000/76/EC have been designed to ensure that 40% of waste tyres are recycled by alternative technologies. These Directives encourage the recovery of tyres through several available techniques for energy proposes.

Scrap tyres are extremely difficult to be recycled, indeed elastomers have high resistance to microorganisms activity. Scrap tyres are a waste of complex chemical structure thanks to the use of different materials that represent the best state of art of the metallurgical, textile, and chemical industries. Specific substances are incorporated by these materials to give performance, durability, and safety. These include mineral oils, reinforcing fillers (carbon black and silica), sulphur and vulcanizing promoters. These tyres do not degrade in landfills because they have highly resistant chemical, biological and physical properties. Moreover, the disposal of tyres in landfill implies the loss of large space beside a considerable energy resource, prevents waste compaction and causes potential health and environmental hazards. In fact, accidental fires with highly polluting emissions can take place. Finally, tyres can be a seat for colony of insects and vermin, such as tiger mosquito [4].

The lower calorific value (LHV) of a scrap tyre is typically 33-35 MJ/kg [5]. This high value suggests that thermal treatments (incineration, co-combustion with coal, co-combustion in cement kilns, in paper mill or in thermal power plants) are the most indicated solutions for the recovery of the energy content of the scrap tyres. Pyrolysis and gasification are pursued as emerging technologies to convert scrap tyres in valuable products and energy source.

From the pyrolysis process it is possible to recover [6]:

- tar pyrolysis oil (TPO), that has similar fuel properties to those of a diesel fuel oil, if desulphurised and distilled (< 1% sulphur) and has generally a calorific value of 42 MJ/kg. TPO is a mixture of organic compounds of 5-20 carbon, with a higher proportion of aromatics and can be easily blended with diesel [7,8];
- char, that is a solid product, containing 2-3% sulphur and approximately 4-5% zinc and has a calorific value of 28-33 MJ/kg;
- syngas, that is a hydrocarbon mixture with low sulphur content and a calorific value in the range 19 - 45 MJ/m^3.

In the present paper, some data regarding the energy valorization of scrap tyres from a region in the North of Italy are presented. The processes taken into account were co-combustion and pyrolysis applied to scrap tyres.

Preliminary data from pyrolysis tests carried out by thermogravimetric coupled mass spectrometric analysis (TG-MS) and thermogravimetric coupled gas cromatography and mass spectrometric analysis (TG-GC-MS), which allows the detection in real time of the gaseous species released during the thermal decomposition of the solid scrap tyres, are also presented in this paper. Also data regarding the characterization of liquid tar and solid char are presented from tests on lab-scale batch reactor.

2. Materials and methods

For the present research, an area characterized by a mountaineous zone (in the North of Italy) having 519,800 inhabitants was chosen. The vehicle fleet for the study area is composed by a total number of 301,757 Passenger Cars (PCs) [9]. Heavy vehicles are not taken into account in this paper. Gasoline fueled cars are the majority of the total PCs (53.1%), followed by diesel PCs (41.6%), LPG PCs (4.6%) and methane fueled PCs (0.7%) [9]. With respect to the emission standards, 6.5% of the total PCs are pre-EURO 1 cars, 4.4% comply with the EURO 1 standard, 19.7% with EURO 2, 23.7% with EURO 3, 42.5% with EURO 4 and 3.2% with the EURO 5 standard (Table 1). The total number of tyres in use in the region is 1,207,028 (considering 4 tyres per car). Only 80% wt (weight percentage) of the tyres quantity can be suitable for energy purposes, while 20%wt is made by steel and fillers [10].

Table 1

Characterization of the vehicle fleet for the study area, in terms emission standards and fuel type (only PCs)

Fuel Type	Emission Standards						Total
	pre-EURO 1	EURO 1	EURO 2	EURO 3	EURO 4	EURO 5	
Gasoline	16,046	10,879	40,839	27,999	60,655	3,848	160,266
LPG	1,093	641	1,842	1,173	8,888	275	13,912
Methane	68	73	204	220	1,336	183	2,084
Gas Oil	2,523	1,657	16,441	42,249	57,368	5,287	125,499
Total	19,730	13,250	59,296	71,641	128,247	9,593	301,757

For the presented work, a passenger car tyre, without steel in it, was shredded and crumbed in order to obtain a material with a size of 8-10 mm. The crumbed material and its pyrolysis products were characterized by elemental analysis and its calorific value.

The elemental analysis of the waste was carried out by the Analytical Chemistry Laboratory of University of Padua, Department of Chemistry, Italy.

For the calorific value of used materials determination, the Mahler calorimeter (Calorimat CBM Cecchinato) was used. The runs were developed in the saturated bomb with pure oxygen (21-25 bar).

Pyrolysis tests were carried out on lab-scale reactor and TG-MS and TG-GC-MS analyses. The lab-scale apparatus, used for the conduction of worn-out tyres pyrolysis tests, is a quartz tube immersed into a horizontal furnace heated up to 400°C [11]. The tyre sample, in scales, was wrapped by a metallic mesh, that kept the pyrolysis solid char. After the process, the pyrolysis oil was collected around the quartz tube and recovered for its characterization.

TG-MS and TG-GC-MS analyses were carried out by a home-assembled instrumental apparatus; a thermo-balance interfaced with a mass spectrometer and a gas-chromatograph [12]. This apparatus allows the real time monitoring of the process. The sample was treated in inert atmosphere up to 1000°C, with a heating rate of 10° C/min, under a 100 mL/min He flow.

Finally, the differential scanning calorimetry (DSC) on scrap tyres was made by using a DSC 92 SETARAM instrument. For experimental procedure, about 20 mg of sample were used. This instrument operates in a range that goes from environmental temperature (25˚C) until 600˚C. The chosen speed of heating was 10 ˚C/min, in a nitrogen atmosphere.

An energy balance analysis of the overall process was made, taking into account the obtained data. Starting from the generated data, a scheme with a hypothetical pyrolysis reactor was analyzed.

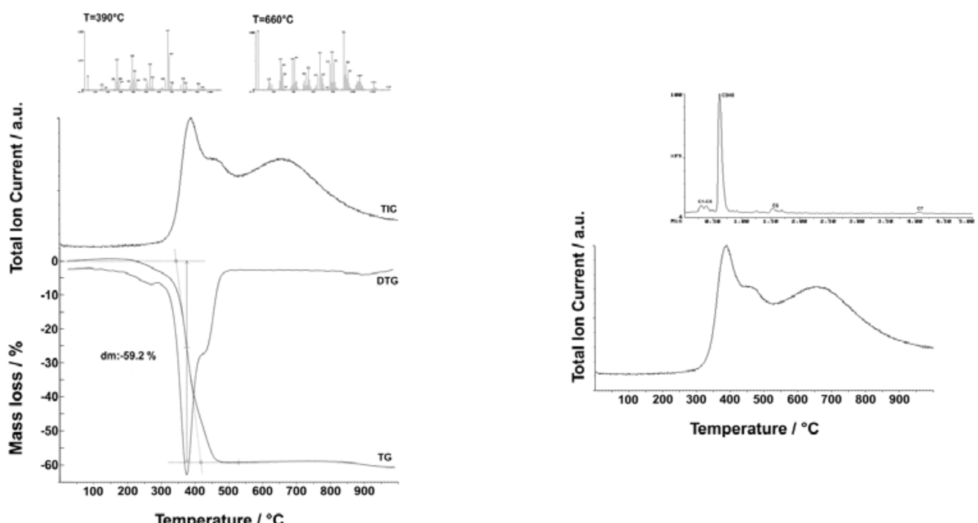
3. Results and discussion

In the analyzed case study, the total number of tyres in use in the region is 1.207.028 (considering 4 tyres per car). Assuming an annual mileage per car and a tyre life of about 50,000 km, the average substitution rate resulted about 200,000 tyres by year for the whole studied area. Generally, the weight of a typical scrapped automobile tire is 9 kg [10]; hence, the total annual quantity of scrapped tyres produced within the study area is 1.800 tyres.

The elemental analysis of the scrap tyre sample gave the following percentages of C: 85.9%, H: 7.8%, N: 0.4%, S: 0.5%, ashes 5.0% and O: 0.4% (determined by difference). These values are coherent with the literature ones [13]. Generally tyres have low nitrogen and chlorine content, about 0.5% [14]. The higher heating value (HHV) of the scrap tyre sample was determined using the Dulong’s formula [15].

Since December 2010, in Italy with the introduction of the Decree 205/2010 that refers to the technical documents (mainly in the range of norms UNI CEN/TS 15357 - 15747), tyres can be assimilated to Solid Recovery Fuel (SRF). Taking into account the LHV, chlorine and mercury content, in our case study, our scrap tyres can be assimilated to a very good SRF, class: 1, 2, 1.

In Fig. 1(part a), the thermogravimetric coupled mass spectrometric analysis of the scrap tyre sample is presented. The thermogravimetric curve (TG) shows an intense mass loss in the 300-500°C interval, with intensity of -59.2%, while DTG curve (derivative thermogravimetric curve) shows an intense peak centred at 380°C, with a pronounced shoulder at 430°C. A similar thermogravimetric behaviour was observed also by Berrueco et al. (2005).



part a) part b)

Fig. 1. Thermogravimetric coupled mass spectrometric analysis of the waste tyre sample. TG, DTG and Total ion current (TIC) curves recorded in the TG-MS measurement. In the insets mass spectra recorded corresponding to selected pyrolysis temperatures (part a)) and Gas chromatographic elution of the gas phase evolved and sampled at 390°C, during the pyrolysis of the analyzed worn-out tyres (part b))

The mass spectrometric analysis of the gas phase evolved during the overall thermal treatment of the sample, also reported in Fig. 1, shows a total ion current (TIC) curve which is characterized by a first intense peak, centred at 390°C, with a shoulder at 450°C. This peak is followed by a less intense broad band, due to the presence of a liquid oil (TPO) that condenses into the cold parts of the thermogravimetric balance, and distorts the real time monitoring of the evolved gas phase. In correspondence of the TIC peak at 390°C, mass spectra show the contemporaneous evolution of more species. The composition of the gas phase evolved at this temperature was studied by TG-GC-MS analysis, sampling the gas phase released from the solid sample with a gas phase sampling valve, and identifying the single chemical compounds by GC-MS analysis. The main evolution of isoprene is observed, beside small amounts of CO, CO2, and hydrocarbons up to C7, saturated and unsaturated.

Fig. 1b shows the gas-chromatogram of the gas phase evolved at 390°C, analyzed by TG-GC-MS analysis, while Table 2 summarizes its chemical composition. On the basis of these preliminary results, tyres pyrolysis reactions were carried out on a quartz tube batch reactor immersed into a lab-scale furnace, heated up to 400°C.

Tabelul 2

Chemical composition of the syngas evolved at 390°C in the pyrolysis of the waste tyre sample. Percent values are calculated from peak areas of gas chromatographic elutions (TG-GC-MS analyses)

Retention time [min]	Evolvel chemical species	Gas phase composition/mol [%]
0.30	Mixture : C2H4, C3H6, CO, CO2,	2.1
0.40	C4H8	2.5
0.50	C5H10	0.5
0.62	C5H8	82.1
1.27 – 1.55	C6H8 isomers	11.0
4.07	C7H10	1.8

The pyrolysis reaction led to the production of a gas phase (20% wt of the waste tyre mass), that was previously characterized. Other products were a tyre pyrolysis oil (40% wt of the waste tyre mass), and a solid char (another 40% wt). The amount of TPO and char was very similar to that observed by other authors [16,17].

Elemental analysis of TPO showed C and H percentages of 84.6% and 14.2% respectively, with very small amount of N about 0.2%, while S was not detected. The C/H molar ratio was very close to ½. Calorific values of TPO were measured with an adiabatic oxygen bomb calorimeter, and resulted 49.5 MJ/kg (HHV) and 46.7 MJ/kg (LHV), respectively, coherent with literature data.

The solid char, that resulted 40% wt of the scrap tyre mass, presented the following elemental analysis: C: 82.2%, H: 4.9%, N: 0.4%, S: 1.0%, O: 0.4%, and ashes: 11.1%. Adiabatic oxygen bomb calorimeter revealed for the combustion of the solid char the calorific values, HHV and LHV, of 34.7 and 33.7 MJ/kg respectively (close to the highest values reported in the literature [18]).

By considering the syngas composition (Table 2), a HHV of 46.5 MJ/kg and a LHV of 45.5 MJ/kg were estimated.

Yang et al. (1995) [19] studied the pyrolysis of a tyre rubber, and found the thermal properties and energy parameters, such as: specific heat of tyre (1,230 J/kgK), reaction heat for the thermal decomposition of a styrene butadiene rubber (5×105 J/kg), and the total heat for the evaporation of the volatile matter (181 kJ/kg). Thus, the energy required for promoting the pyrolysis of tyres at 500°C results about 850 kJ/kg.

Taking into account this data, an hypothetical real case is proposed. To this concern the lowest feasible capacity of the hypothetical plant has been found of 1 t/h. That capability means that, if referred to car tyres only, the area of interest must be significantly higher than the provincial case-study. Moreover, a grinded scrap tyre, with 20% of steel was considered.

In Figure 2 the process diagram, developed on the basis of the considered hypotheses is presented. The scrap tyre is heated in inert atmosphere up to 500°C. Taking into account that the scrap tyre presents a 20% wt of steel, the remaining 80% of rubber undergoes to pyrolysis reaction, and furnishes 16% of syngas (160 kg/h) and 32% (320 kg/h) of TPO and char (32%), respectively. The combustion of this syngas can furnish an amount of heat of 7.3 MJ/h, satisfying the energy demand of the endo-thermal process.

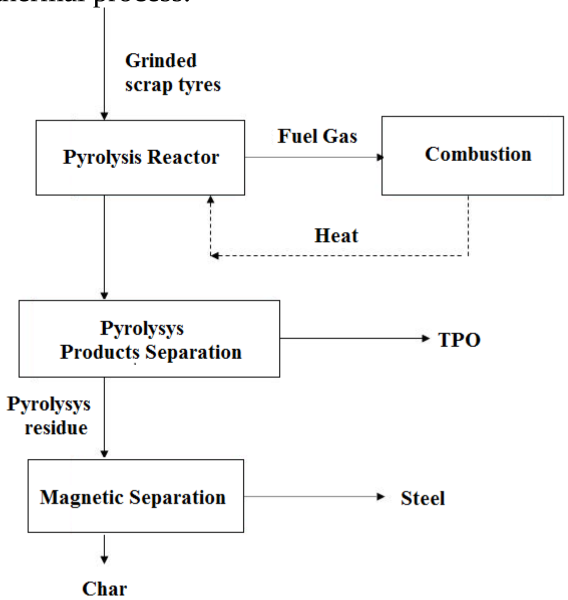


Figure 2. Process diagram of the waste tyres pyrolysis process.

The produced tyre pyrolysis oil can be recovered and successively treated for its blending with diesel, or can be available for other neighboring plant devices. [20]. It must be taken into consideration that the consumption of oil and its relative price keep increasing, while the amount of scrap tyres addressable to pyrolysis treatment is an inexhaustible resource. In case of use in an engine for electricity generation by an alternator, an electrical efficiency of 40% can be obtained.

Finally, also the solid char, expected to be classified as SRF 1,2,1, can be used for energy production in cement works or in thermal power plants. In this last case co-combustion with coal can take advantage of the high efficiency of electricity generation (thanks to the scale effect).

For the case study that means the weighted overall electrical efficiency could be around 23% (considering a 32% efficiency from char used in a thermal power plant) if no electricity is assumed to be generated from syngas in excess of the pyrolysis needs. Taking into account also this contribution, the presented approach shows interesting efficiencies in electricity conversion even in a relatively small scale.

4. Conclusions

The energy valorization of scrap tyres was studied in this paper and gave the following results:

- the pyrolysis reactions carried out on scrap tyres showed that the scrap tyres decompose by thermal treatment giving a gas phase, an oil and a solid char: 20%, 40% and 40% wt, respectively;
- tar and char can be available for other processes opening to alternative scenarios;
- steel clothes of the tyres can be recovered;
- the gas phase evolved from pyrolysis presented a HHV that can satisfy the overall energy demand of the endo-thermal process;
- the tyre pyrolysis oil has a C/H molar ratio of ½, but the most important aspects is the very low amount of S, which suggests the possible use of this oil as fuel, in TPO-diesel blends;
- the char was characterized by a low sulphur percentage of 1.0%, and can be classified as SRF 1,2,1. The use of this char as carbon black in chemical processes, or its combustion/co-combustion with other solid fuels can be hypnotized, after its separation from the tyres steel clothes.

For real scale application, a critical factor is the extension of the area of scrap tyres generation. The developed case study pointed out that an area like a small Italian province is not wide enough for an adequate feeding of the plant. Of course inter-provincial initiatives can be promoted and the sector of trucks can contribute to the necessary input.

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