



## Steam gasification of waste tyre: Influence of process temperature on yield and product composition

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### ABSTRACT

An experimental survey of waste tyre gasification with steam as oxidizing agent has been conducted in a continuous bench scale reactor, with the aim of studying the influence of the process temperature on the yield and the composition of the products; the tests have been performed at three different temperatures, in the range of 850–1000 °C, holding all the other operational parameters (pressure, carrier gas flow, solid residence time). The experimental results show that the process seems promising in view of obtaining a good quality syngas, indicating that a higher temperature results in a higher syngas production (86 wt%) and a lower char yield, due to an enhancement of the solid–gas phase reactions with the temperature. Higher temperatures clearly result in higher hydrogen concentrations: the hydrogen content rapidly increases, attaining values higher than 65% v/v, while methane and ethylene gradually decrease over the range of the temperatures; carbon monoxide and dioxide instead, after an initial increase, show a nearly constant concentration at 1000 °C. Furthermore, in regards to the elemental composition of the synthesis gas, as the temperature increases, the carbon content continuously decreases, while the oxygen content increases; the hydrogen, being the main component of the gas fraction and having a small atomic weight, is responsible for the progressive reduction of the gas density at higher temperature.

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### 1. Introduction

The disposal of waste tyres represents a relevant problem within the waste management strategy of the European Community: the world production amounts to 7 millions of tons (according to the [European Tyre Recycling Association, Report 2008](#)), 3 million of which are generated in Europe, that is 2% of total solid waste production, and even today the final destination of nearly 65–70% of such an amount is the landfill, with the consequent loss of high added value materials ([Mui et al., 2004](#)) and the relevant environmental impact.

Attempts on waste tyre reuse as solid fuel are largely documented: waste tyres have been used as principal or secondary fuel source in the production of steam, electricity, cement, lime, paper, steel and into the incineration of garbage; however these experiences have been severely limited by the scarce market demand and by the overall operational costs of the plants ([Sharma et al., 1998](#)). Anyway, it is well known that tyres possess high volatile and low ash contents with a heating value greater than that of coal and biomass. These properties make them an ideal material for

thermal processes like pyrolysis and gasification ([Kiran et al., 2000](#); [Morris and Waldheim, 1998](#); [Bridgwater, 2003](#)), that, unlike combustion, convert the intrinsic chemical energy of a carbon-rich material in valuable by-products ([Leung et al., 2002](#); [Zabanitoutou and Stavropoulos, 2003](#); [Malkow, 2004](#)). Among the thermal technologies, the gasification of waste tyres seems to be attractive since the gaseous fuel derived from the process can be stored, transported and easily fueled for existing boilers and combustors with little modifications ([Belgiorno et al., 2003](#); [Franco and Giannini, 2005](#)). Another alternative consists in conveying the syngas in a fuel cell, thus improving the overall efficiency of the process ([McKendry, 2002](#); [Chaudhari et al., 2003](#)); in a modern fuel cell, such as a molten carbonate type, a steady stream of hydrogen is required as fuel and for this reason the syngas must be adequately cleaned from trace contaminants and the composition must be properly upgraded ([Lobachyov and Richter, 1998](#); [Wu et al., 2006](#)). In any case at moment the experiences are limited to bench or pilot scale studies ([Galvagno et al., 2002](#); [Donatelli et al., 2010](#)).

Most part of the literature data on the waste tyre gasification are collected in fluidized bed reactors and using air as oxidizing agent, while data concerning other experimental designs are hardly found. Within this framework, the present study reports the results of an experimental survey of waste tyre gasification,

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conducted with steam on a bench-scale continuous rotating reactor, with the final goal of determining the influence of the process temperature on the yields and the composition of the products.

## 2. Materials and methods

### 2.1. Materials

The waste tyres used for the experimental work were supplied by an Italian producer (Elastrade). Granulated tyre samples of maximum 6 mm mean diameter were selected and kept at ambient conditions. About 250 g of material was used for each test.

### 2.2. Apparatus

The schematic diagram of the experimental device is reported in Fig. 1. The gasification tests were conducted on a bench scale apparatus designed and assembled at ENEA “Portici” Research Center.

Rotary kilns and similar equipments have not been widely used for gasification treatment, meanwhile, they offer such flexible adjustments configurations to be able to achieve an easy management of the process even with a highly heterogeneous material (Galvagno et al., 2006).

The materials was loaded in a feeder hopper of maximum capacity 5 dm<sup>3</sup>, with an airtight closure system and a mechanical stirrer, which was fitted with a screw device operating over the whole length of the equipment, heated zone included. The screw rotation speed was ruled by an inverter. The reactor was enclosed in a split furnace, Carbolite HST 12/600, and externally heated. Due to this configuration, the material enters the reactor from the hopper and rolls down the length of the kiln. The steam for the tests was produced by injecting water into the reactor at controlled rate (with a peristaltic pump) through a series of spatially distributed holes located on the central screw feeder. The solid residue was continuously discharged into a tank at the outlet of the reactor while the process gas was headed for the cleaning system.

The cleaning system firstly consists of an ice jacketed condenser trap that cooled the gas from the reactor further to room temperature and removed the most part of the oil particles from the gaseous products, together with the excess steam; subsequently first the gas was filtered by a ceramic wool filter, for the soot and the oil removal, then it bubbled into a 1 M NaOH solution, that fulfilled a basic scrubber for the acid removal; an additional filter prevented any further charcoal transport; the extent of the products condensation throughout the cleaning system was detected by weight difference.

In any test, nitrogen was used as carrier gas, to create safety working conditions. Before starting the gasification experiments, the initial nitrogen flow rate was maintained at 1.5 dm<sup>3</sup> min<sup>-1</sup> to completely purge the system till the prescribed process temperature was reached.

### 2.3. Characterization

A thermogravimetric system (TA Instruments TGA 2950), coupled with a Thermo Optek FTIR spectrometer, was used to set up the thermal process and characterize the waste tyre samples, with respect to proximate analysis (Mayoral et al., 2001) (that is, moisture, volatile matter, fixed carbon, and ash content of the material); thermogravimetric curves were recorded at different heating rates, using pure nitrogen as inert purge gas, at constant flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>.

Proximate analyses were verified according to the CTI (Italian Technical Committee) Standard 2/156.6 and CTI 2/156.7 (volatile content is calculated by burning the sample in a closed metallic pot at 850 °C for nearly 7 min; ash residue is further burned at 750 °C till a constant weight is obtained; the fixed carbon is obtained by the difference). The organic matter is the sum of the volatile fraction plus the fixed carbon, on dry basis.

Ultimate analysis was obtained with a Thermo Quest model EA 1110 analyzer. Such analysis gives the weight percent of carbon, hydrogen, nitrogen, and sulfur in the samples simultaneously; afterward, the determination of the oxygen content can be obtained by difference.

The heating value of the material was estimated using a bomb calorimeter (model IKA C5000) in adiabatic modality. Flue gas from the combustion chamber was allowed to pass through a sampling bottle filled with a NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer solution, to be further analyzed for chlorine determination.

On-line gas analysis was conducted with a gas chromatograph (Agilent model 3000A) that was able to provide precise analysis of the principal gas components (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) within no more than 2–3 min. The instrument was equipped with two different columns that were working in parallel (Molsieve 5A e Poraplot Q) and used a thermal conductivity detector (TCD); the carrier gas was argon in all analyses.

### 2.4. Gasification tests

The steam gasification of tyres were performed in a series of trials at different processing temperatures, in the range of 850–1000 °C, holding all the other operational parameters constant (screw rotational speed, water feeding rate, carrier gas flux), as

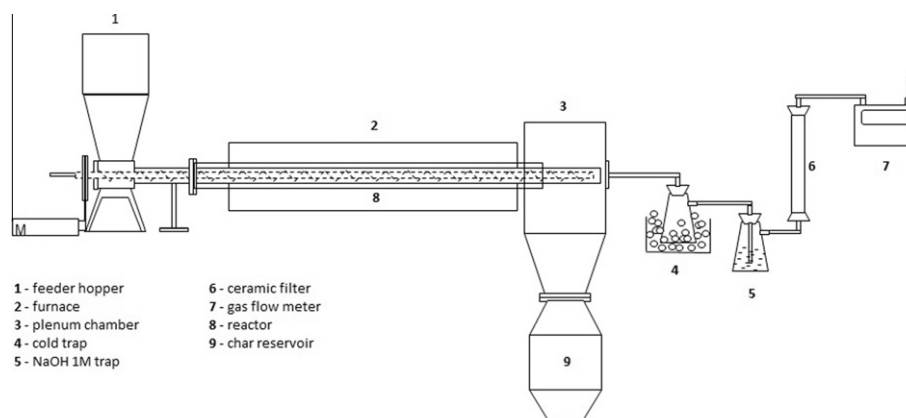


Fig. 1. Bench scale gasification system.

reported in Table 1; such parameters, in turn, fix the solid and the gas residence times. Experiments set-up and calculations methods have been already discussed in a previous work (Galvagno et al., 2009; Sullivan et al., 1927).

The gas residence time ( $t_g$ ) is calculated assuming an ideal behavior, according to the following equation:

$$T_g = V/F_T$$

where  $V$  is the heating zone volume and  $F_T$  is the flux at the processing temperature.

The influence of the temperature on the process has been studied through the comparison of the different trials, with respect to the yields, to the chemical composition and to the mass balances of the main components of the process. In this respect, it is important to remark that a large amount of soot was produced during the tests, which was appreciably reduced only at high temperature (1000 °C); consequently, to prevent the plugging of the pipes, a severe filtration with ceramic wool was necessary, which rendered extremely difficult the separation between tar and soot. For this reason, both fractions were collected together and coded as “oil”. The application of an in bed or ex bed catalytic upgrading could improve the process. This issue has been already discussed in a previous work (Portofino et al., 2011).

### 3. Results and discussion

#### 3.1. Characterization of waste tyres

According to the decomposition profile (Fig. 2), the thermal decomposition of the waste tyre starts at about 220 °C and is practically complete at ≈600 °C. The decomposition occurs through a series of peaks which account for the simultaneous degradation of the main components of the tyre, principally natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR) (Sułkowski et al., 2004). The maximum degradation rates are located in the temperature range of 375 °C for NR, 445 °C for SBR and 465 °C for BR.

Fig. 3 shows the FTIR analysis of the volatile products; relevant spectra have been selected from the series collected by combined TGA/FTIR experiment. The analysis revealed the presence of the compounds normally ascribed to the decomposition of the single elastomers present in the tyre (Sułkowski et al., 2004; Williams and Besler, 1995; Leung and Wang, 1998), that are mainly branched alkenes (methyl-butylene/pentene/hexane/heptene), toluene and benzene, and their corresponding degradation products (methane, carbon monoxide, ethylene, acetylene, etc.), under pyrolysis conditions (Table 2). A detailed analysis of FTIR signals, together with MS signals was developed in another work (Galvagno et al., 2007).

Table 3 reports the proximate and ultimate analysis of the tyres. Proximate analysis is a standard compositional analysis conducted for the determination of moisture, volatile matter, fixed carbon and ash of compounds and it is used to establish the rank of coals, to show the ratio of combustible to incombustible constituents, etc. While the volatile matter (often comprising the moisture) generally accounts for the fraction that is evolved during the thermal

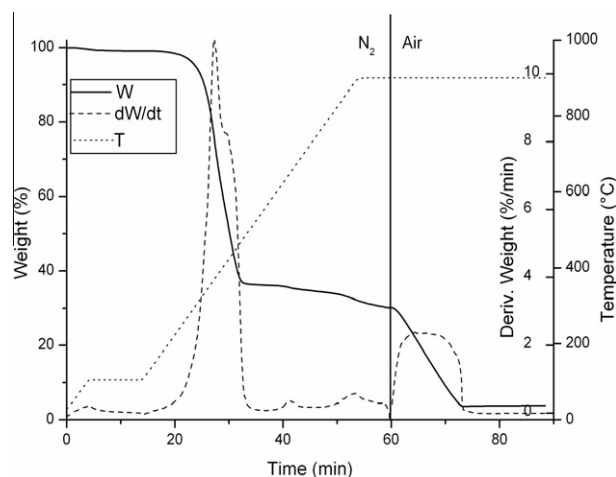


Fig. 2. Waste tyre thermogram, showing a ramp at 10 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere to 900 °C, followed by air combustion.

decomposition, the fixed carbon, together with the ash, represents the theoretical solid residue (the char fraction) of a possible pyrolysis/gasification process.

In this respect, the data show that the starting material, on a dry base, is shared for more than 65%<sub>w</sub> into the volatile fraction and for 26%<sub>w</sub> into the solid residue, together with the ash (6.8%<sub>w</sub>). Accordingly, the ultimate analysis shows a significant sulfur amount, nearly 2%<sub>w</sub>, due to the vulcanization process of the rubber, and a very high carbon content (77.3%<sub>w</sub>). The material has a high heating value, while there is no evidence of chlorine.

Table 4 reports the yields of the process fractions (char, oil, and gas) at different temperatures: the data show that the mass balance exceeds 100%, because of the introduction of the steam (Wei et al., 2007). Furthermore, as expected, rising the temperature, the gas yield progressively increases while char and oils yields decrease; the temperature effect mainly affects the condensable fraction more than the solid residue indicating an increase of the secondary cracking reactions in vapor phase (Encinar et al., 2002; Morf et al., 2002).

In regard to the gas fraction, the principal components (apart from nitrogen, which was used as the carrier gas), detected over the different trials and reported in Fig. 4, were H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and small quantities of some hydrocarbons, such as ethane, ethylene, and acetylene.

Higher temperatures clearly result in higher hydrogen concentrations; the hydrogen content rapidly increases, attaining values higher than 65%, while methane and ethylene gradually decrease over the range of the temperatures; carbon monoxide and dioxide instead, after an initial increase, show a nearly constant concentration at 1000 °C.

This situation is probably dependent on the more favorable thermal cracking and steam reforming reactions that were caused by higher temperatures, which result in the major extensions of the secondary cracking reactions into the gas fraction (Turn et al., 1998; Lin et al., 2004).

Table 1  
Operational and process parameters.

Test	Temp. (°C)	Pressure (bar)	Carrier gas flow (N <sub>2</sub> ) (l/min)	Steam/tyre ratio	Solid residence time (min)	Gas residence time (s)
T1	850	1	1.0	2	100	6.2
T2	925	1	1.0	2	100	5.7
T3	1000	1	1.0	2	100	5.3

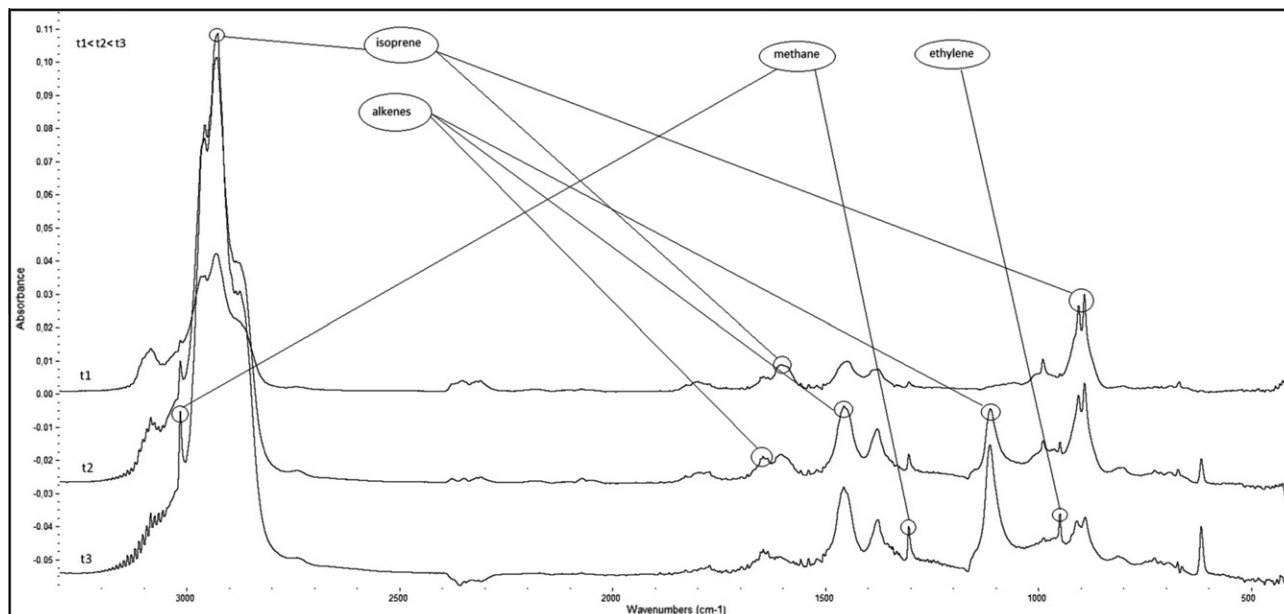


Fig. 3. FTIR spectrum of evolved gas.

Table 2

Main FTIR signals of compounds evolved by elastomers pyrolysis.

Elastomer	Compound	FTIR signals (cm <sup>-1</sup> )
NR	2-Methyl-1,3-butadiene	3101-2986-2957-1801-1603-1443-991-905-893
	2-Methyl-1-butene	3082-2974-2899-1661-1458-1077-890
	1-Pentene	3085-2966-1637-1456-999-913
	1-Hexene	3083-2936-1639-1453-994-917
	2-Methyl-1-pentene	3082-2968-1649-1455-1385-891
	2-Methyl-1-hexene	3082-2969-2939-1651-1458-1383-890
BR	Butadiene	3018-1604-1012-909
	4-Vinyl-cyclohexene	3086-3034-2937-2854-1644-1442-915
	Cyclohexene	2935
SBR	Toluene	3042-2933-1605-1497-1029-728-693
	Styrene	3080-3027-1634-1497-1421-986-909-775-695
	Benzene	3047-1482-1042-672
	Ethylbenzene	3082-2968-1649-1455-1385-891

Table 3

Proximate and ultimate analysis of starting material.

	Weight <sup>a</sup> (wt%)		Weight <sup>a</sup> (wt%)
C	77.3	Volatile	67.7
H	6.2	Fixed C	25.5
N	0.6	Ash	6.8
S	1.8		
O	7.1 (by difference)		
Density	0.8 g/dm <sup>3</sup>		

<sup>a</sup> On dry basis.

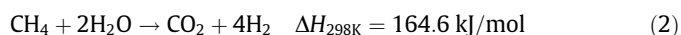
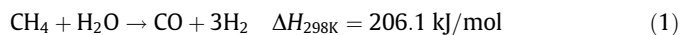
Table 4

Fractional yield.

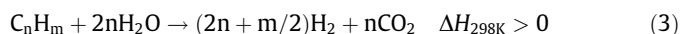
Test	Char yield (wt%)	Oil <sup>a</sup> yield (wt%)	Gas yield (wt%)
T1	43.4	27.0	34.7
T2	38.5	21.8	64.5
T3	33.3	5.3	85.9

<sup>a</sup> Oil = condensable fraction of tar and soot.

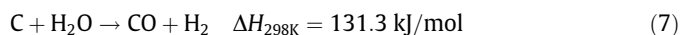
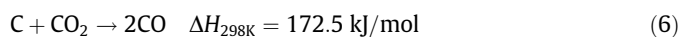
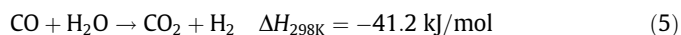
Eqs. (1) and (2) represent the steam cracking reactions for methane, the most abundant hydrocarbon in the mixture; similar reactions can be written for the other components.



Generally hydrocarbons reactions could be expressed as



Carbon monoxide and carbon dioxide abundance is influenced by the contemporary effect of the Eqs. (5)–(7):



Thermodynamical data show that the water–gas shift reaction (5), is less important at higher temperature, while the heterogeneous reactions, Boudouard reaction (6) and the carbon steam gasification (7) act on the carbon residue. Such reactions as a whole, together with the secondary cracking tar reactions, are the main factors responsible for the increase in hydrogen (Borison et al., 1989).

Table 5 reports the elemental composition (carbon, hydrogen and oxygen) of the synthesis gas, which shows that, as the temperature increases, the carbon content continuously decreases, while the oxygen content increases; the hydrogen, being the main component of the gas fraction and having a small atomic weight, is responsible for the progressive reduction of the gas density at higher temperature.

Furthermore, raising the temperature, the heating value decreases from 25.1 MJ/m<sup>3</sup> to 14.6 MJ/m<sup>3</sup>; however, on the other hand, the energy content of the total gas shows a remarkable increase (from 16.8 MJ/kg of feed to 25.0 MJ/kg of feed).

As reported in Table 6, the higher temperatures, together with the presence of the steam, strongly influence the total volume of the gas produced, and with an increase in temperature from 850 °C to 1000 °C, the gas volume per kilogram of feeding definitely triples. This aspect becomes more significant considering

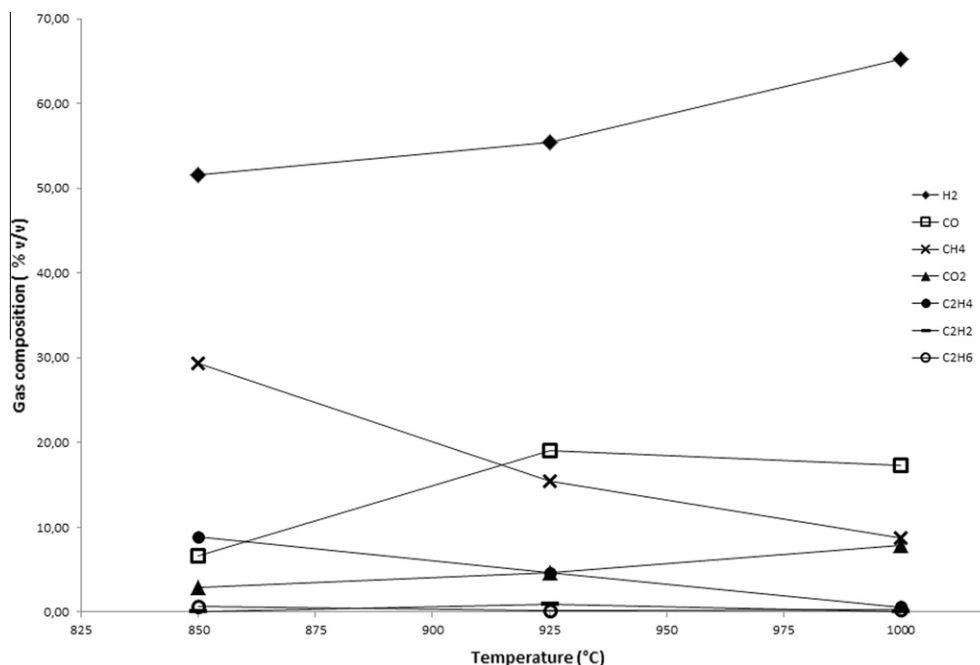


Fig. 4. Gas composition versus process temperature.

the separate contribution of the single components of the gas mixture: as it would be expected, hydrogen mainly affects the gas production at higher temperature, reaching a value of 1.12 m<sup>3</sup>/kg at 1000 °C, over a total production of 1.70 m<sup>3</sup>/kg. The progressive increase of hydrogen and carbon monoxide production is a clear indication of the major extension of the secondary cracking reactions; moreover, the methane behavior, that is the gradual decrease at higher temperature, is a compromise between the improved global gas production and the contemporary extended secondary cracking mechanisms.

Table 7 reports the proximate analysis of the char fraction at different processing temperatures; in comparison with the starting material, the char has a lower volatile content and a very high fixed carbon content in each test. It has to be noted that the fixed carbon slowly decreases with the temperature while the ash content grows, due to the effect of the reaction (7), which lowers the char yield (see Table 3) and increases the ash amount onto the solids residue (Chaudhari et al., 2001; Braekman-Danheux et al., 1998). In this regards, the appreciable organic content suggests its further exploitation as a secondary row material (carbon source, active carbon, etc.) (Nakagawa et al., 2002; González et al., 2006; Rodríguez-Reinoso et al., 1995; Ko et al., 2004).

The conversion data are reported in the last column of the table for each test; the values have been calculated according to the following formula:

Table 6

Gas composition at different temperature.

Test	H <sub>2</sub> m <sup>3</sup> /kg	CO m <sup>3</sup> /kg	CO <sub>2</sub> m <sup>3</sup> /kg	CH <sub>4</sub> m <sup>3</sup> /kg	C <sub>2</sub> H <sub>4</sub> m <sup>3</sup> /kg	C <sub>2</sub> H <sub>2</sub> m <sup>3</sup> /kg	C <sub>2</sub> H <sub>6</sub> m <sup>3</sup> /kg	Total m <sup>3</sup> /kg
T1	0.34	0.04	0.02	0.20	0.06	0.00	0.00	0.70
T2	0.64	0.22	0.05	0.18	0.05	0.01	0.00	1.20
T3	1.12	0.30	0.13	0.15	0.01	0.00	0.01	1.70

conversion = reacted organic matter/total organic matter

Holding all the other operational parameters constant, the conversion degree of the whole steam gasification process increases with the temperature.

With respect to the elemental composition (Table 8), the data show a gradual decrease in the carbon content at higher temperature, while the hydrogen content remains nearly constant. Sulfur content ranges from 1% to 2%.

Figs. 5a, 5b and 5c show for each test the distribution of carbon, hydrogen and sulfur on the different process fractions and the corresponding mass balance, with respect to their initial amount in the feed. Considering the nature of the oil fraction (tar + soot), it was impossible to perform the ultimate analysis on this fraction; for this reason its contribution was calculated by difference together with the gas cleaning sorption (CO<sub>2</sub> and COS in the scrubber). This contribution was collected as "other" in the figures. As reported, as far as the hydrogen is concerned, the minus sign expresses an over-difference that is due to the introduction of the steam, which is responsible for the increase of the hydrogen content. Carbon is appreciably present in each fraction; however, at higher temperature, the gas fraction is progressively enriched in

Table 5

Gas characterization.

Parameter	Value		
	T1	T2	T3
C (wt%)	60.2	48.9	38.1
H (wt%)	22.5	16.8	15.1
O (wt%)	17.4	34.3	48.9
<i>Gas heating value</i>			
GHV (MJ/m <sup>3</sup> gas)	25.1	19.1	14.6
GHV (MJ/kg of feed)	16.8	22.0	25.0
Gas density at n.c. (kg/m <sup>3</sup> )	0.5	0.6	0.5

Table 7

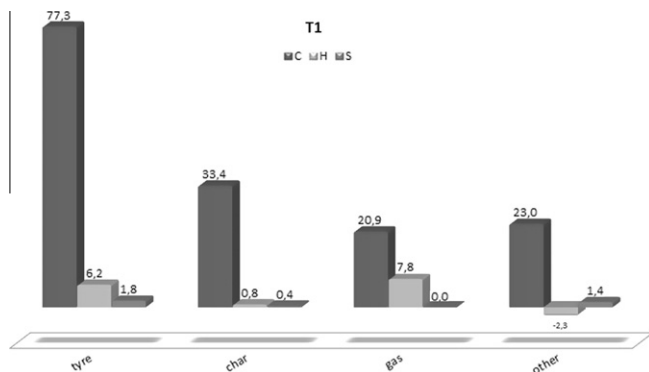
Char proximate analysis.

Test	Volatile (wt%)	Fixed carbon (wt%)	Ash (wt%)	Conversion
T1	3.10	78.90	18.00	0.62
T2	4.39	77.51	18.10	0.66
T3	5.65	71.99	21.92	0.72

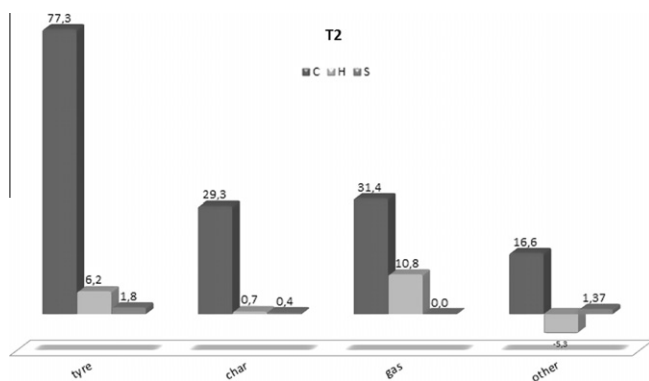
**Table 8**  
Char ultimate analysis.

Test	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O <sup>a</sup> (wt%)
T1	77.02	1.74	0.17	0.88	2.19
T2	76.23	1.88	0.19	1.12	2.48
T3	71.62	1.98	0.14	1.60	2.85

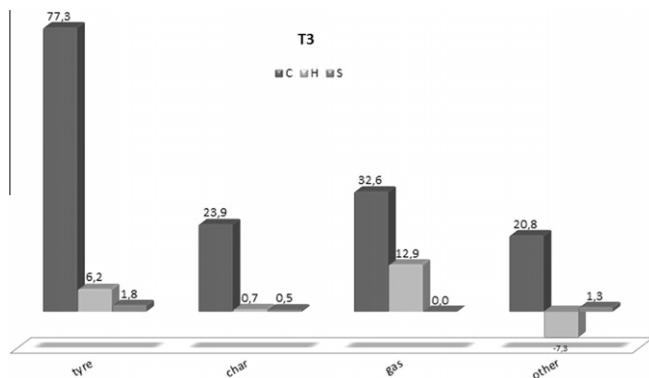
<sup>a</sup> Calculated by difference.



**Fig. 5a.** T1SGTy element mass balance.



**Fig. 5b.** T2SGTy element mass balance.



**Fig. 5c.** T3SGTy element mass balance.

carbon accordingly with the yields. Sulfur, mainly released as COS (Kagann, 1982), is almost concentrated in the volatile fraction (near 78%); the amount is nearly constant with the temperature.

## 4. Conclusions

In the present work, the steam gasification of waste tyre was performed in a series of trials, by varying the process temperature within the range of 850–1000 °C, in order to evaluate the influence of the processing temperature on the properties of the products.

The data show that the process seems promising in view of obtaining a good quality syngas, indicating that a higher temperature results in a higher syngas production (86 wt%). The syngas yield grows mainly against the condensable fraction, indicating an increase of the secondary cracking reactions in the vapor phase; moreover the char yield progressively decreases, due to the enhancement of solid–gas phase reactions with the temperature. In comparison with the biomass gasification, conducted at the same process conditions, an appreciable presence of liquid fraction (ranging from 27 to 5 wt%) is registered in the considered temperature range; in this regard, the process could be improved through the application of a catalytic tar reforming step. It is important to remark that a large amount of soot was produced during the tests, which was appreciably reduced only at high temperature (1000 °C); consequently, to prevent the plugging of the pipes, a severe filtration with ceramic wool was necessary, which rendered extremely difficult the separation between tar and soot.

When all the operational parameters are held constant, the temperature definitely affects the gas composition, in favor of a higher hydrogen production at higher temperature (up to 65% v/v) with respect to the hydrocarbon abundance; furthermore the syngas calorific value seems to be comparable to natural gas. The adopted operating conditions allow to obtain an appreciable amount of char, whose high carbon content suggest its further exploitation both as activated carbon (after the proper activation process) and as carbon source for synthesis reactions.

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