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Optimizing H₂ Production from Waste Tires via Combined Steam Gasification and Catalytic Reforming

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ABSTRACT: The disposal of waste tires represents a relevant problem within the waste management strategy of the European community: more than 300 000 000 tires are estimated to reach their end of life each year in the 27 member states of the European Union and comparable amounts are found in North America, Latin America, Asia, and the Middle East. The global total is ~1 000 000 000 and rising each year. (Source: European Tyre Recycling Association (ETRA), 2006.) It is well-known that scrap tires possess high volatiles and low ash contents, together with a heating value that is higher than coal and biomass. These properties make them an ideal material for alternative thermal processes, such as pyrolysis and gasification, which can be finalized both to energy and material recovery. Within this frame, the present work is related to experimental tests and has obtained results of a combined process of scrap tire steam gasification and syngas catalytic reforming, with the aim of exploring the possible utilization of syngas for fuel cell applications. Four catalysts have been used for the experimental tests: two natural mineral products (olivine and dolomite) and two commercial nickel-based catalysts. Experimental data show that whether olivine or dolomite is used directly into the reactor to carry out the steam gasification, the char and gas yields increase with respect to the sole tire gasification (the char production varies from 41.2% w/w without catalysts to 59% w/w and 47.9% w/w, using olivine and dolomite, respectively; the gas production varies from 60.8% w/w for the sole tire gasification to 63.5% w/w with olivine and 84% w/w with dolomite). Then, while the olivine shows a stronger effect on the char production, the dolomite seems to be more effective on the gas yield. Moreover, both the catalysts promote a higher hydrogen production, which varies from 51.6 vol % for the sole tire gasification to 65.6 vol % and 57 vol % using, respectively, dolomite or olivine, basically because of the enhanced cracking of methane and the other hydrocarbons (the methane content decreases from 27.6 vol % for the sole tire gasification to 11.3 vol % and 20.8 vol %, using dolomite or olivine, respectively). Regarding both dry and steam reforming, the experimental tests show that the catalytic step, tested by varying the temperature, the catalytic substrates, and the reactive atmosphere, promote the production of a high hydrogen-rich gas, already at the lower tested temperature. It has been seen that the stronger effect for the increase of hydrogen content is for steam reforming condition and using a commercial nickel catalyst instead of Ni/olivine: under such conditions, the hydrogen content increases, from 51.6 vol % before the reforming up to 78 vol % at 650 °C. With regard to gas production, a strong increase of the flow, mostly due to the effect of the cracking reactions, is registered as well and, more in detail, the gas production increases from 0.8 m³ kg⁻¹ fed, before the reforming, up to 1.0 m³ kg⁻¹ fed and 1.5 m³ kg⁻¹ fed, respectively, for dry and steam reforming at 750 °C and using Ni olivine catalyst, and up to 1.12 m³ kg⁻¹ fed and 1.91 m³ kg⁻¹ fed, for dry and steam reforming at 750 °C, respectively, and using a commercial Ni catalyst. The adopted operating conditions allow one to obtain an appreciable amount of char, whose high carbon content suggest its further exploitation both as activated carbon (after activation process) and as a carbon source for synthesis reactions.

INTRODUCTION

The world production of tire waste amounts to 7 million tons, 3 million of which are generated in Europe; that is 2% of the total solid waste production, and, even today, the final destination of ~13% of such an amount of waste is the landfill, with a consequent loss of high-added-value materials¹ and the relevant environmental impact.

It is well-known that scrap tires possess high volatiles and low ash content, with a heating value that is greater than that of coal and biomass. Attempts to reuse waste tires as a solid fuel have been greatly documented: waste tires have been used as a principal or secondary fuel source in the production of steam, electricity, cement, lime, paper, and steel, as well as in 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. Anyway, because of their properties, waste tires are an ideal material for thermal processes such as pyrolysis and gasification, that, unlike combustion, convert the intrinsic chemical energy of a carbon-rich material in valuable gaseous, liquid, and solid byproducts;^{2,3} however, at the moment, the experiences are limited to bench- or pilot-scale studies.^{4,5} Nevertheless, these processes are considered as promising methods for future energy systems to meet environmental requirements; furthermore, they provide one of the most

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cost-competitive means of obtaining hydrogen-rich gas or syngas from renewable resources.

Gasification is normally performed at higher temperatures (700–1400 °C) than pyrolysis and in the presence of a partially oxidative reactive atmosphere. Such a thermal treatment consists of a series of thermochemical reactions whose number, features, and performances depend on the process conditions and the gasification agent, which usually can be oxygen, steam, carbon dioxide, or hydrogen. In a way similar to pyrolysis, the first step of gasification consists of a thermal degradation where volatilized components, under the influence of temperature, are removed from the input material. The reactions that occur downward in this thermal degradation can be controlled by adjusting the operating parameters, to obtain the preferred type and yield of products, depending on the selected final utilization.

For example, synthesis gases used for the further production of liquid fuels and chemicals are composed of gaseous mixtures of carbon monoxide and hydrogen. The carbon monoxide/hydrogen ratio can be varied under different reaction conditions to yield a broad range of products.⁶ Conversely, pyrolysis does not have a reactive step; hence, its gaseous yield is produced in a smaller range and it typically cannot be used for direct fuel or chemical synthesis without further processing.

One of the disadvantages of the conventional gasification systems is the high temperature that is required for the decomposition of the feedstock and for the reforming reactions, which affect the overall energy efficiency of the process; furthermore, the removal of a significant amount of tar, soot, and acidic gases, as well as other impurities from the gas products, is also necessary, particularly when the process is oriented toward the production of a hydrogen-rich gas. To reduce the operating temperature and to promote the tar reduction, extensive studies have been performed on the catalytic pyrolysis or gasification and a comprehensive information on biomass gasification research and development has been provided by the literature.

With respect to solid wastes, several research groups have studied the catalytic gasification of these materials, which are used as feedstock to produce hydrogen for methanol⁷ or hydrogen-rich gas, which can also be converted to liquid transportation fuels using Fischer–Tropsch synthesis.⁸ With respect to the catalytic treatment of waste tire, the experiences are actually limited: in the literature, various studies are reported on the catalytic pyrolysis, which is normally used to conduct the conversion at relatively low temperature, as well as to derive oil in the boiling range of commercial fuel oil;^{9,10} furthermore, some research groups use zeolites for the catalytic conversion of pyrolytic oil into aromatic hydrocarbons.^{11,12}

To produce syngas to be conveyed in a fuel cell, such as a molten carbonate cell, a steady stream of hydrogen is required as fuel: as mentioned, that syngas usage normally requires a suitable cleaning of trace contaminants and the appropriate upgrading of the composition.^{13,14} Concerning the tar formed during gasification, catalytic tar removal from the syngas is extensively reported in the literature, at least regarding the biomass treatment.^{15–17} The presence of additives influences not only the gas composition, but also the heating value of the product gas. The use of catalytically active materials during biomass gasification promotes the char gasification, changes the product gas composition, and reduces the tar yield. Besides these, the addition of active bed materials also prevents agglomeration tendencies and subsequent choking of the bed.

The final goal of the catalyst is to accelerate the reaction rate, reduce the reaction temperature, eliminate tar in the product, and adjust the composition of the product gas. Although research on catalysts is often carried out specifically in relation to gasifier design and biomass feed type, there is still some common ground in the preparation and characterization of the catalyst. Based on their composition, Sutton et al.¹⁸ divided the catalysts into three groups: (i) dolomite catalysts, (ii) alkali metals and other metal catalysts, and (iii) nickel catalysts.¹⁸

Among the nonmetallic oxides, dolomites have been extensively investigated as biomass gasification catalysts. Dolomite is a magnesium ore with the general formula $\text{MgCO}_3 \cdot \text{CaCO}_3$ that contains ~30 wt % CaO, 20 wt % MgO, and 45 wt % CO_2 with other minor mineral impurities, such as the trace minerals SiO_2 , Fe_2O_3 , and Al_2O_3 . The use of dolomite as a catalyst in biomass gasification has attracted much attention, because it is inexpensive and abundant and can significantly reduce the tar content of the product gas from a gasifier. But it is significantly active only above 800 °C, which is not always easy to achieve in some gasification processes; furthermore, dolomite shows poor attrition resistance, which renders it better-suited for use in guard bed reactor.

With respect to dolomite, He et al.¹⁹ showed that it revealed better catalytic performance at the presence of steam: as temperature increases from 850 °C to 950 °C, tar is completely decomposed and there is a higher production of H_2 and CO. Corella and co-workers²⁰ found that the catalytic effect of the dolomite can be enhanced by increasing its Fe_2O_3 contents and/or its pore diameters. Furthermore, the comparison among dolomite, calcite (CaO) and magnesite (MgO) for the steam reforming of biomass tars shows that the order of activity is dolomite > magnesite > calcite.²¹

Hu et al. conducted apricot stone steam gasification with olivine and dolomite as downstream catalysts for the production of hydrogen-rich gas at atmospheric pressure in a fixed-bed reactor;²² the main conclusions were that both calcined olivine and dolomite are active catalysts for the steam reforming of bio-oil into H_2 -rich gas in the process of apricot stones gasification and that the catalytic activities of olivine and dolomite is improved by calcination of the catalysts at 900 °C for 4 h. For olivine, the calcination causes the disappearance of a (Mg,Fe)- SiO_3 phase and the formation of Fe_2O_3 . For dolomite, the calcination eliminates CO_2 and forms CaO-MgO , which enhances the catalytic activities of catalysts.

Alkali-metal compounds can be used directly as catalysts in the form of carbonates, or supported on other materials such as alumina.²³ Direct addition of alkali materials to biomass is done by dry mixing or wet impregnation; they catalyze the gasification reactions and are considered as effective catalysts for steam and CO_2 gasification of carbon. Since alkali metals, principally potassium and, to a lesser extent, sodium, exist naturally in biomass, their salts are normally gained from ashes of plants; for this reason, these ashes can be used as primary (in situ) or secondary (outside the gasifier) catalysts. The use of ashes as catalysts solves the problem of the handling of ash wastes and gives an added value to the gasification process by increasing the gasification rate and reducing the tar content in the produced gas. However, the major disadvantage of these catalysts is their loss of activity due to particle agglomeration.¹⁸

Nickel-based catalysts have been extensively used for the tar reforming of biomass-derived syngas, and catalytic tar cracking can be performed either during gasification or after gasification,

using a separate downstream catalytic reactor; they have a positive activity/cost balance and are commercially available, but the usage is severely limited by easy deactivation (deriving from the coke deposition, the poisoning, and the sintering of the matrix). To improve the resistance and to obtain better performances, several studies on the preparation and the testing of new nickel catalysts have been conducted, by modifying the supports and through the introduction of promoters. For example, doping with alkali metals was carried out to reduce the surface acidity, which, in turn, was expected to reduce coking and increase the activity; moreover, the maximum selectivity to H_2 and CO was reported to occur with 15 wt % Ni.^{24–28}

The addition of metallic nickel via thermal impregnation to a different support (that is, olivine) accelerates the rate of C–H and C–C bond scission. As hydrocarbons became more difficult to activate (e.g., methane is more difficult than naphthalene), a larger difference in activity is observed when comparing the olivine catalyst with and without nickel.²⁹

Several commercially available catalysts (produced by BASF, ICI-Katalco, UCI and Haldor Topsøe) also have been investigated that showed a complete removal of the tar content and the production of a H_2 -rich syngas, depending on temperature, space time, particle size, and composition of the gas.³⁰

As already mentioned, literature data concerning the catalytic gasification of waste tire are poor, despite the importance of the covered issues; for this reason, in this paper, we are reporting our experimental results on the steam gasification of waste tires, followed by the catalytic reforming of the produced syngas, using four different catalysts in two experimental configurations; in this

frame, the study, which is conducted on continuous laboratory-scale equipment, pays particular attention to the effect of catalyst on the syngas composition under dry and steam reforming conditions.

EXPERIMENTAL SECTION

Materials. Samples used for the experimental work are both commercial and natural products.

Tire samples, supplied by an Italian producer, were milled until to a maximum size of 2 mm and kept at ambient conditions. About 250 g of material was used for each gasification test.

Four catalysts have been used for the experimental tests: two natural mineral products (olivine and dolomite) and two nickel-based catalysts (a commercial steam reforming catalyst supplied by Johnson–Matthey (KATALCO 25-4M, see Table 1) and a Ni-olivine catalyst, which was kindly supplied by a research group of Strasbourg University³¹).

These catalysts were chosen because of their activity in catalytic reforming and their good tar conversion effectiveness. Furthermore, due consideration was given to the low cost of the materials and the selected experimental conditions (see the following).

Apparatus and Procedures. The schematic diagram of the experimental device is reported in Figure 1. The gasification tests were carried out on a bench-scale rotary kiln reactor, produced by Lenton (PTF 16/75/610 model) (Figure 1), while the reforming reactions were conducted in a tubular reactor inside a furnace (Lenton PTF 15/75/450) under various process conditions.

Rotary kilns 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.³²

The material was loaded into a feeder hopper with a maximum capacity of 5 L, fitted with an airtight closure system and a mechanical stirrer; during the experiments, the material was continuously fed until to the beginning of the alumina reactor by means of a screw-driver device, whose rotation was ruled by an inverter. Inside the reactor, the material rolled down the length of the kiln, thanks to a series of shields, mutually tilted at 30°, that assisted the transport and limited heat dispersions outside the

Table 1. Chemical Composition of a Commercial Nickel-Based Catalyst (KATALCO 25-4M)

parameter	value/comment
composition	
NiO	18 wt %
K ₂ O	1.8 wt %
SiO ₂	<0.1 wt %
SO ₃	<0.05 wt %
support	Ca/Al ₂ O ₃

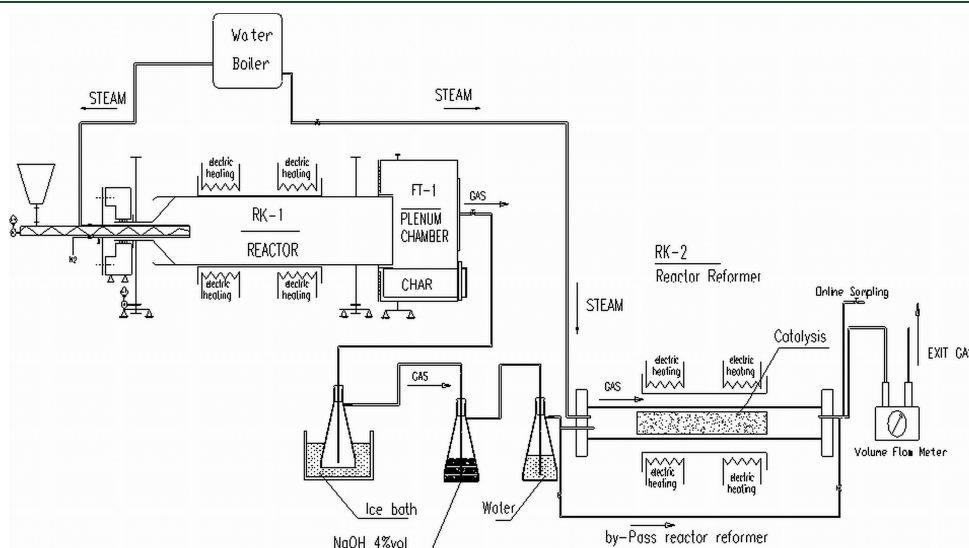


Figure 1. Bench-scale gasification and reforming system.

Table 2. Bench-Scale Plant Characteristics

parameter	value
oven heating	electric, three independent zones
maximum power	9.2 kW
maximum temperature	1600 °C
maximum working temperature	1550 °C
heating zone length	610 mm
material reactor	Al-sint
reactor length	1550 mm
inside diameter	80 mm
external diameter	94 mm
reactor volume	7.79 dm ³
heating zone volume	3.06 dm ³

refractory shell. Feeding started once the reactor reached the temperature selected for the experiment.

The kiln rotation speed was adjusted by an inverter, while reactor slope could be varied to 10°; the furnace was externally heated and three different thermocouples were provided to measure the temperature axially along the reactor.

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 before being directed toward the secondary reforming step. The abatement system first consists of an ice-jacketed condenser trap that cooled the stream further to room temperature and removed any oil particles from the gaseous products, together with the excess steam used for the tests; subsequently, the gas first bubbled into a 1 M NaOH solution, that fulfilled a basic scrubber for acid removal, then into a water-based bubbling system, that prevented any further charcoal transport; the extent of products condensation throughout the cleaning system was detected by weight difference. Before entering the reforming section, the gas flow was measured by a gas meter and analyzed (see afterward); in any case, it is important to note that, because of the efficiency of the cleaning system, the syngas entering the secondary reactor results to be tar- and sulfur-free, thus giving the chance of concentrating the catalytic reforming just on the gas conversion. All the characteristics of the experimental device are reported in Table 2.

According to Devi,³³ the tar removal methods can be categorized in two types, depending on the location where the tar is removed: either in the gasifier itself (known as the primary method) or outside the gasifier (known as the secondary method). For this reason, we tested two experimental arrangements:

- in-bed use of the catalyst (the catalyst is added directly to the feed)
- ex-bed use of the catalyst (the catalyst is located in a secondary fixed reactor for the hot gas cleaning)

Dolomite and olivine were selected as in-bed catalysts, while the two nickel-based catalysts were used for the catalytic reforming of the syngas in the secondary reactor. It is important to note that, concerning the first configuration, the performances of dolomite and olivine were evaluated by comparing their effect on the syngas characteristics with respect to the syngas obtained from the sole tire steam gasification (with no added catalyst) under the same process parameters (see Table 4, presented later in this paper).

Concerning the second configuration, the effect of the catalytic reforming efficiency on the syngas characteristics was tested at

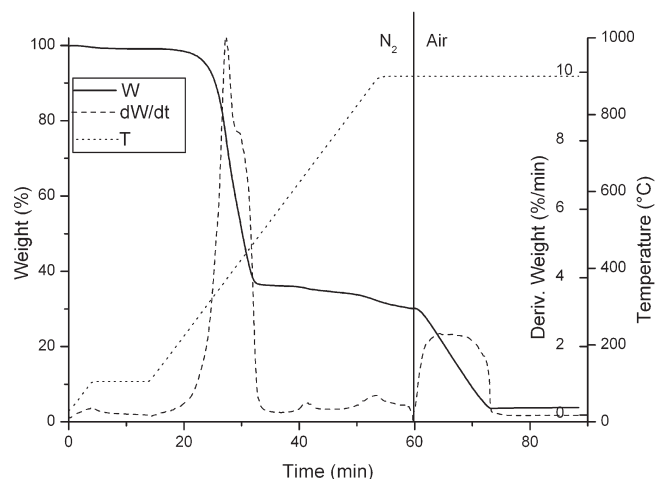


Figure 2. Waste tire thermogram, showing a ramp at 10 °C min⁻¹ in N₂ atmosphere to 900 °C, followed by air combustion.

different temperature (550–750 °C) and reactive conditions (dry or steam reforming) for both the catalysts. In this case, the equipment was constituted by a tubular reactor inside a furnace. (Lenton PTF 15/75/450) (see Figure 1), where the catalyst was compacted and where the syngas coming from the previous gasification treatment was pushed to flow.

The steam for both the gasification tests and the catalytic reforming was produced in a boiler and pumped into the reactors through a peristaltic pump. In any case, nitrogen was used as carrier gas, to create safe working conditions. Before starting the gasification experiments, the initial nitrogen flow rate was maintained at 1.5 dm³ min⁻¹ to completely purge the system until the prescribed process temperature was reached.

The gases produced were monitored online by process gas chromatography and offline by Fourier transform infrared (FTIR) analysis, performed on gas samples discontinuously collected; the gas heating value was calculated from composition data.

A TA Instruments Model TGA 2950 system, coupled with a Thermo Optek FTIR spectrometer, was used to set up the thermal process and characterize the samples, with respect to proximate analysis³⁴ (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 an inert purge gas, at a constant flow rate of 100 cm³ min⁻¹.

Proximate analyses were verified according to the Italian Technical Committee standards CTI 2/156.6 and CTI 2/156.7 (the volatiles content is calculated by burning the sample in a closed metallic pot at 850 °C for ~7 min, and the ash residue is further burned at 750 °C until a constant weight is obtained; the fixed carbon is obtained by the difference). The organic matter is the sum of the volatiles fraction plus the fixed carbon content, on a dry basis. Ultimate analysis was obtained with a Thermo Quest EA 1110 analyzer. Such analysis simultaneously gives the weight percent of carbon, hydrogen, nitrogen, and sulfur in the samples; oxygen determination can afterward be obtained by difference.

The heating value of the materials was estimated using a bomb calorimeter (IKA C5000) in adiabatic modality. Flue gas from the combustion chamber was allowed to pass through a sampling

Table 3. Proximate and Ultimate Analysis of Starting Material

Ultimate Analysis		Proximate Analysis	
element	content (wt %)*	component	content (wt %)*
C	85.2	volatiles	61.8
H	7.3	fixed carbon	33.8
N	0.4	ash	4.4
S	2.3		
O	0.5 (by difference)		
gross heating value	37.1 MJ kg ⁻¹		
density	0.8 g cm ⁻³		

* On a dry basis.

bottle filled with a NaHCO₃/Na₂CO₃ buffer solution, to be further analyzed for chlorine determination.

Online gas analysis were conducted with a gas chromatograph (Agilent, Model 3000A) that was able to provide precise analysis of the principal gas components (H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₄, C₂H₆) within 2–3 min. The instrument was equipped with two different columns working in parallel (Molsieve 5A e Poraplot Q) and used a thermal conductivity detector (TCD); the carrier gas was argon in all analyses.

RESULTS AND DISCUSSION

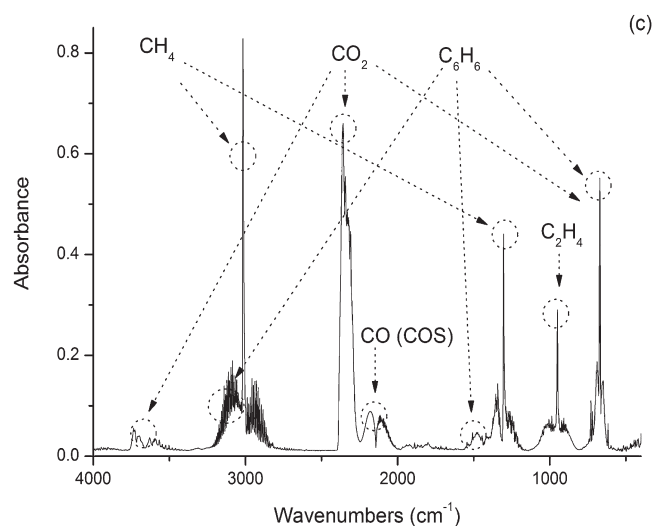
According to the decomposition profile (Figure 2), the thermal decomposition of the waste tire starts at ~220 °C and is practically complete at ~600 °C. The decomposition occurs through a series of peaks, which accounts for the simultaneous degradation of the main components of the tire, principally natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR).³⁵ The maximum degradation rates are located in the temperature range of 375 °C for NR, 445 °C for SBR, and 465 °C for BR.

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

With this respect, data reported in Table 3 show that waste tires present a high volatiles content (~60% w/w), in addition to a considerable char yield. As a consequence of the very high carbon content (see the ultimate analysis in the same table), a high fixed carbon content is observed onto the char; moreover, because of the vulcanization process of the rubber, the presence of sulfur is remarkable in the tire composition (~2.3% w/w, on a dry basis). Furthermore, the oxygen content is low, giving rise to a high heating value, while there is no evidence of chlorine.

Steam Gasification in the Rotary Kiln. Experimental tests were conducted by setting the operating conditions of the plant according to previous experimental experiences.³⁶

The flow of a material through a rotary kiln is determined by the kiln's slope and the rotational speed, as well as by the characteristics of the material being processed. The kiln is installed on a slight slope, so that the bed of solids advances by

**Figure 3.** Syngas FTIR off-line analysis.

gravity; as the kiln rotates, the material follows the rotation until it breaks the surface of the bed and tumbles down the sloping surface. The kiln residence time (t_s) is expressed by the formula³⁷

$$t_s = \frac{1.77\sqrt{\theta}BL}{SND}$$

where θ is the dynamic angle of repose (dependent on the material), L the kiln length, B the correction factor (equal to 1 for undammed kilns, >1 for dammed kilns), S the kiln slope, N the rotational speed of the kiln, and D the inside diameter of the reactor. The dynamic angle of repose of the material, which is the constant slope of the bed surface, affects the time required to transport the material through the kiln and, therefore, affects kiln residence time and is dependent on the material characteristics and the slope. The value of θ was calculated by fixing the reactor parameters (particularly S and N) and by evaluating the solid residence time under those conditions; the obtained value of 45°, corresponding to a slope of 3°, is consistent with the literature data.³⁸

The gas residence time (t_g) is calculated assuming an ideal behavior, according to

$$t_g = \frac{V}{F_T}$$

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

Under these conditions, considering the “char yield” as the ratio between the outcoming char and the incoming feedstock, and the “gas yield” as the ratio between the produced gas and the incoming feedstock, the process gives a conversion of 0.61 while the char and gas yields are equal to 41.2% w/w and 60.8% w/w, respectively.

As expected, the sum of the yields of the various fractions, compared to the incoming feedstock, exceeds 100%, because of the contribution of steam to the reaction.³⁶

The adopted experimental conditions do not allow the separate recovery of the condensable liquid fraction (tars): the liquid fraction, whose content is estimated in the range of 1%–20% w/w, results in a dispersion on the cold parts of the plant (particularly on the walls of the char tank), in addition to being

Table 4. Operational and Process Parameters of the Steam Gasification Tests

parameter	value
temperature	850 °C
pressure	1 bar
nitrogen flow	1.6 dm ³ min ⁻¹
solid residence time	15 min
gas residence time	13 s
rotational speed of reactor	2 rpm
reactor slope	3
feeding rate	1.6 g min ⁻¹
steam flow rate	2.0 g min ⁻¹

trapped in the cold trap of the cleaning system (where it is suspended in the excess condensed steam). Nevertheless, the modification of the syngas composition when using the in-bed catalysts (which will be discussed in the following) represent a clear effect of the catalytic tar removal.

The syngas produced with the steam gasification of sole waste tire, as obtained from online gas chromatographic analyses, shows a high hydrogen content together with a considerable amount of methane and C₂ and C₃ homologues. Additional FTIR off-line analysis (Figure 3) revealed the presence of benzene (and probably other aromatics) while there is no evidence of hydrogen sulfide or sulfur dioxide; the presence of steam could favor the formation of COS, whose FTIR signal is superimposed on the CO signal.

Catalytic Reforming. As already discussed, our catalytic approach was 2-fold: we alternatively applied both a primary method (by mixing the catalyst with the feed) and a secondary method (by treating the syngas downstream the gasifier, in a secondary reactor filled with the catalyst). Both the methods have been largely tested for the biomasses treatment, even at the commercial scale, and resulted to be effective for improving the tar conversion and increasing the process efficiencies. Nevertheless, poor data are available, with respect to waste tire gasification; with the aim of covering this deficiency, at least partially, we conducted a preliminary survey on waste tire catalytic gasification by testing both the methods generally employed for the catalytic gasification of biomasses and by selecting those catalysts that resulted from the literature to be used under quite similar experimental conditions, even if with different feed.^{21,30,39,40}

Dolomite is a naturally occurring mineral based on calcium and magnesium carbonates (CaCO₃·MgCO₃) whose catalytic activity is often related to the large pore size and the surface area, together with the relatively high alkaline content (K, Na). Dolomites can be of different type, depending on their origin, but they are generally considered as the most popular inexpensive catalyst for tar elimination. Olivine consists mainly of silicate minerals and it is represented by the formula (Mg,Fe)₂SiO₄; the advantage of this catalyst is the low price (similar to that for dolomite) and the high attrition resistance, compared to dolomite. The good performances of both minerals as in-bed catalysts are well-documented;^{33,41,42} the addition of dolomite or olivine can change the product distribution and they are even able to react with some contaminants (such as HCl, SO₂, PAHs, etc.), eliminating them, to some extent, from the fuel gas.

Table 4 shows the operating conditions of the process, which were kept constant with and without the catalyst. The

Table 5. Fractions Yields (Gasification with in Bed Catalyst)

	NO catalyst	Catalyst	
		olivine	dolomite
char yield (% w/w)	41.2	59.0	47.9
gas yield (% w/w)	60.8	63.5	84.0

Table 6. Syngas Composition from Tyre Gasification, with and without In-Bed Catalyst Addition

catalyst	Composition (% v/v)		
	sole tire	dolomite	olivine
H ₂	51.5	65.6	57.0
CO	6.3	10.9	8.5
CO ₂	4.7	8.3	7.0
CH ₄	27.6	11.3	20.8
C ₂ H _n	9.4	3.4	6.5
C ₂ H ₆	0.5	0.3	0.3

Table 7. Syngas Characteristics from Tyre Gasification, with and without In-Bed Catalyst Addition

parameter	unit	sole tire	dolomite	olivine
density	kg/Nm ³	0.55	0.45	0.49
gas production	Nm ³ /kg of feed	1.1	1.3	1.2
heating value	MJ/Nm ³	25.3	16.1	19.8
energy content	MJ/kg of feed	29.1	21.1	23.9

dimensions of the catalyst (6 mm), which are far different than the tire size (2 mm), render feasible the eventual mixture separation (char from catalysts) at the end of the tests by means of a sieving procedure. In addition, the complete recovery of the catalyst was verified by the proximate analysis of the char (ash data analysis).

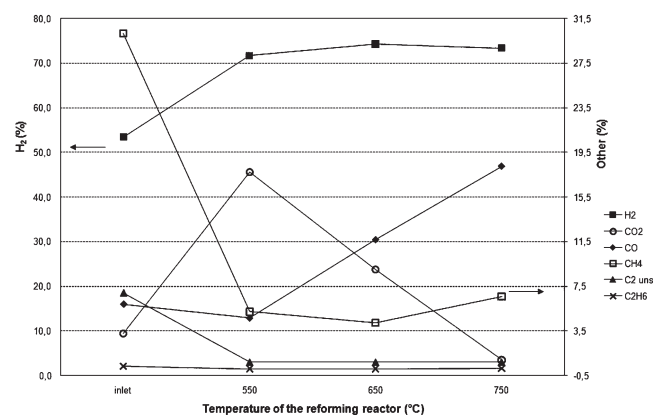
Table 5 then reports the char and the gas yields of the gasification tests with in-bed dolomite or olivine, in comparison with the sole tire gasification data. Both catalysts increase the char and gas yields, with respect to the sole tire gasification; but, while the olivine shows a stronger effect on the char production, the dolomite seems to exert a stronger effect on the gas yield. The change of the product distribution can be ascribed to the catalyst capability of influencing the volatile fraction cracking, then producing a greater amount of char and syngas and the probable reduction of the liquid fraction: this fact could have been verified with the appropriate sampling and analysis of the tar content,^{43,44} which was not feasible under the adopted experimental conditions. In any case, the modified product distribution can certainly represent an index of the increased tar conversion.

The gas composition is reported in Table 6; it could be noted that both the catalysts promote a higher hydrogen production, basically because of the enhanced cracking of methane and the other hydrocarbons.

Again, the effect is more evident for dolomite than olivine, and it reflects the reported gas yield; correspondingly, the density values (see Table 7) get smaller, because of the greater content of

Table 8. Operational and Process Parameters for Catalytic Reforming with Ni Catalysts

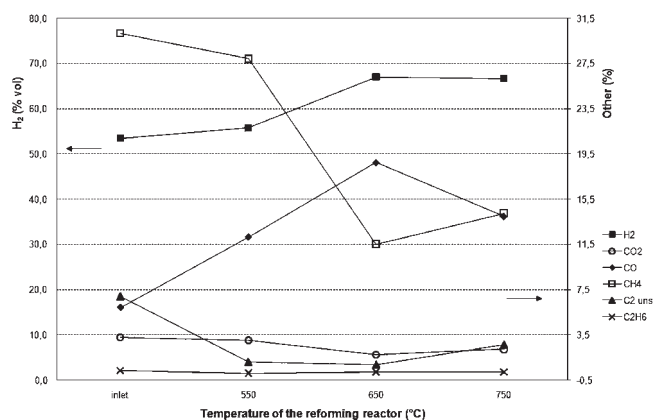
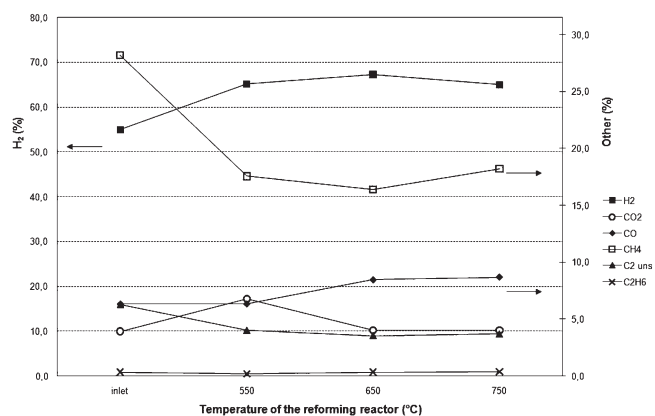
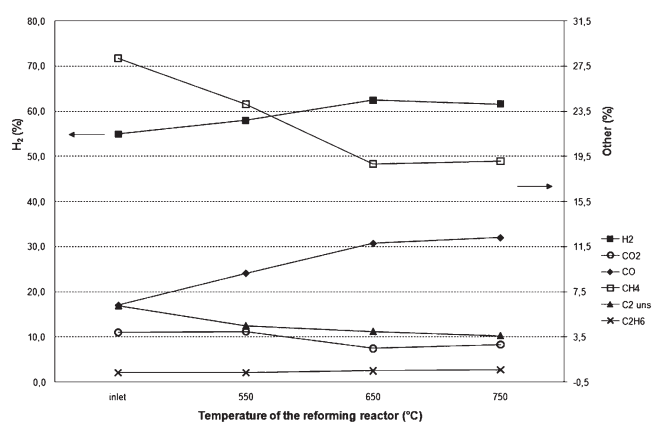
parameter	Dry Reforming			Steam Reforming		
	550 °C	650 °C	750 °C	550 °C	650 °C	750 °C
pressure (bar)	1	1	1	1	1	1
catalytic bed (g)						
Ni commercial catalyst	210	210	210	210	210	210
Ni olivine catalyst	200	200	200	200	200	200
gas flow rate (L min ⁻¹)	1	1	1	1	1	1
steam flow rate (g min ⁻¹)	0	0	0	1.5	1.5	1.5

**Figure 4.** Syngas composition after steam reforming with a commercial nickel catalyst at 550–750 °C.

light components (mainly H₂). Also, the gas production increases in the order of tire < olivine < dolomite, mainly depending on the hydrogen contribution. The gas heating values in the series decrease in a similar fashion, as a consequence of the reduction in hydrocarbons (mainly methane) content; in any case, the values are well below that of natural gas (~37 MJ/Nm³). The last set of data shows the energy content, which is a valuable index of the energy carried out from syngas per kilogram of processed material; even in this case, the index decreases in the same order.

Nickel-based catalysts are reported to be used when the flue gas needs an exhaustive clean up or polishing; furthermore, they are effective in increasing the yield of CO and H₂ and are preferred to other catalysts when the final application is the production of a H₂-rich gas. They are mainly used for their steam reforming capabilities, but their efficiency in dry conditions were also tested. Nevertheless, they are affected by the rapid deactivation, depending on the coke deposition or the sulfur poisoning; for these reasons, we decided to use them in the secondary reactor, which was fed by a highly purified syngas, to focus the attention on their performances just on the syngas reforming reactions.

The syngas catalytic reforming tests were conducted according to the experimental rig schematically shown in Figure 1; the tests were conducted by varying the catalyst, the reforming temperature, and the reactive conditions (either dry or steam reforming); operatively, the other variables (the steam/carbon ratio (in the case of steam reforming), contact time, etc.) were kept constant, as reported in Table 8.

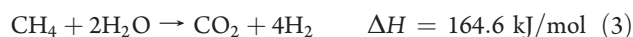
**Figure 5.** Syngas composition after dry reforming with a commercial nickel catalyst at 550–750 °C.**Figure 6.** Syngas composition after steam reforming with a Ni-olivine catalyst at 550–750 °C.**Figure 7.** Syngas composition after dry reforming with a Ni-olivine catalyst at 550–750 °C.

The following figures show the syngas composition after steam and dry reforming using a commercial nickel catalyst (Figures 4 and 5) and a Ni-olivine catalyst (Figures 6 and 7) in the examined temperature range (550–750 °C), respectively.

Table 9. Principal Syngas Characteristics

	Ni-Olivine Catalyst				Commercial Nickel Catalyst			
	raw	550 °C	650 °C	750 °C	raw	550 °C	650 °C	750 °C
Steam Reforming								
<i>F</i> (L/min)	0.86	0.99	1.19	1.57	0.7	1.4	1.9	1.7
gas prod (m ³ /kg of fed)	0.82	0.94	1.13	1.50	0.80	1.57	2.13	1.91
<i>r</i> (kg/m ³)	0.47	0.45	0.38	0.40	0.49	0.52	0.43	0.37
HHV (MJ/m ³)	21.72	18.72	17.90	19.22	24.12	12.32	13.15	14.82
energy prod (MJ/kg of fed)	17.79	17.65	20.29	28.74	19.30	19.38	28.07	28.31
Dry Reforming								
<i>F</i> (L/min)	0.86	0.86	0.86	1.05	0.7	0.9	1.2	1
gas prod (m ³ /kg of fed)	0.82	0.82	0.82	1.00	0.80	1.01	1.35	1.12
<i>r</i> (kg/m ³)	0.47	0.48	0.41	0.42	0.49	0.47	0.42	0.41
HHV (MJ/m ³)	21.72	21.19	19.78	19.67	24.12	20.50	16.18	17.74
energy prod (MJ/kg of fed)	17.79	17.36	16.20	19.67	19.30	20.73	21.82	19.93

The fundamental involved reactions are summarized below:



Reactions 1 and 2 are prevalent under steam reforming conditions, while reaction 4 affects the gas composition mainly under dry conditions. The equations were referenced to methane, which is the most abundant hydrocarbon in the mixture, but similar equations can be also considered for each hydrocarbon in the volatiles fraction.

Data show that the catalysts used promote a high hydrogen-rich gas production, both in dry and steam reforming; the maximum percentage of hydrogen is detected under steam reforming conditions, particularly with a commercial nickel catalyst (74%). At 650 °C, the catalysts show the higher activity within the considered range. With respect to the steam reforming, as the temperature increases, slight decreases of both H₂ and CO₂ concentrations and increases of CO concentration are observed, because of the reverse water-gas shift reaction effect.⁴⁵

With regard to the dry reforming, the temperature increase from 650 °C to 750 °C does not give any noticeable effect on the syngas composition, other than a slight decrease of the overall reforming effect, probably due to the coking of the catalyst, which could promote different reaction paths. Under these conditions, the methane conversion passes from 53% at 650 °C to 45% at 750 °C.

Data show that, under real conditions, the commercial nickel catalyst is more effective than the Ni-olivine catalyst, with regard to the syngas reforming.

Table 9 resumes the principal syngas characteristics for the considered catalysts within the range of the examined conditions.

Generally, the reforming has a remarkable effect on the gas production, mostly due to the effect of the cracking reactions. Such an effect is stronger under steam reforming conditions and using a commercial nickel catalyst instead of Ni-olivine. The best results, with regard to the gas production (hydrogen content),

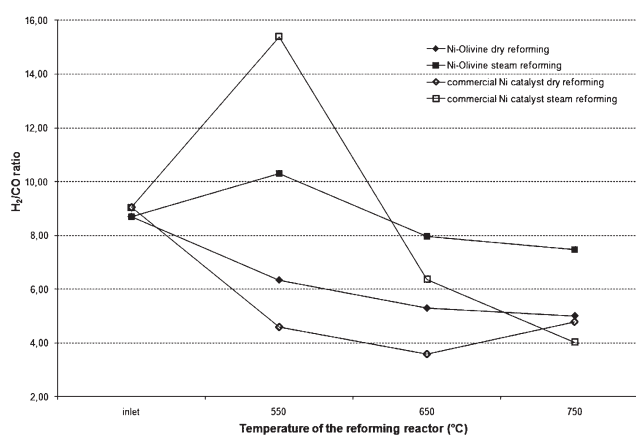


Figure 8. H₂/CO ratio of the syngas under different catalytic reforming conditions, versus temperature.

were obtained at 650 °C, where the methane conversion is highest and obtains a value of 78 vol %.

In term of the energy exploitation of the process, the two last rows of Table 9 report the heating values and the energy content of gas for 1 kg of feeding; the first ones are quite low, well below that of natural gas (~37 MJ/Nm³). The second parameter generally grows with temperature. Even in this case, the best results are achieved under steam reforming conditions.

The H₂/CO ratio is an useful indicator for the suitable application of the flue gas. The values concerning the syngas under dry and steam reforming conditions are reported in Figure 8.

Syngas with a H₂/CO ratio of >2 is favorable for producing hydrogen for ammonia synthesis or for fuel cell application,^{46,47} whereas synthesis gas with a H₂/CO molar ratio in the range of 1–2 is highly desirable as feedstock for Fischer–Tropsch synthesis for the production of transportation fuels.^{48,49} As shown in Figure 8, the H₂/CO ratio for tire syngas, in any case, is >3.5, indicating its potential use as a fuel cell supply. The maximum value is reached under steam reforming conditions for both catalysts, but the commercial nickel catalyst seems to potentially show the best performances in influencing the gas composition, with really strong differences between the dry and

steam reforming conditions. Furthermore, the effect is more pronounced at the lower tested temperature; it is probably dependent on the unfavorable CO conversion, according to the reverse effect of the water-gas shift reaction (which is exothermic).

CONCLUSIONS

Steam gasification of scrap tires seems to be a promising process, for the purpose of obtaining a good-quality syngas. In order to evaluate the catalytic effect on tire waste steam gasification, two different experimental arrangements have been tested under real conditions: one by adding the catalyst (olivine and dolomite) directly to the feed (in bed), and another by using a secondary (ex-bed) catalytic stage (Ni/olivine and Ni/Al₂O₃/CaO JM KATALCO) under steam and dry reforming conditions.

The two in-bed catalysts, commonly reported in the literature as tar cracking catalysts, increase the char and gas yields, in comparison to the sole tire gasification; the gas production increases in the order of tire < olivine < dolomite, and it is mainly due to the hydrogen contribution.

Ex-bed catalysts promote a high hydrogen-rich gas production, under both dry and steam reforming conditions; a commercial nickel catalyst is more effective than the Ni-olivine catalyst, with regard to syngas reforming. Particularly, under steam reforming conditions, the maximum hydrogen content is reached at 650 °C with a commercial nickel catalyst (74 vol %).

Under the considered range of conditions, the reforming process enhances the gas production, mainly increasing the hydrogen content. The effect is wider under steam reforming conditions and using a commercial nickel catalyst instead of Ni-olivine.

Although the modification of the syngas composition when using the in-bed catalysts represents a clear effect of the catalytic tar removal, the adopted experimental conditions do not allow the separate recovery of the condensable liquid fraction (tars); therefore, they have not been quantified. In fact, the resulting liquid fraction is dispersed on the cold parts of the plant (particularly on the walls of the char tank), in addition to being trapped in the cold trap of the cleaning system (where it is suspended in the excess condensed steam). For this reason, we are planning to conduct further experiments aimed at quantifying the tar produced under the different experimental conditions that have been investigated (sole tire gasification and in-bed catalytic gasification).

A global process consisting of gasification/reforming/CO-shift produces a suitable fuel for molten carbonate cells, because of the high H₂/CO ratio that has been reported. The adopted operating conditions allow one to obtain an appreciable amount of char, whose high carbon content suggests its exploitation both as an activated carbon source (after activation process) and a carbon source for synthesis reactions.

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