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Energetic valorization of waste tires



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ABSTRACT

Significant high levels of available waste tires in Brazil, which reached approximately 473 thousand tons in 2015, offer an attractive potential for their use as fuel in advanced thermal conversion processes. Technologies for energetic valorization of waste tires were reviewed and two alternatives based on updraft gasification in a modified reactor design were proposed. First of all, a large-scale updraft gasifier on IGCC (Integrated Gasification Combined Cycle) was considered for the gasification of the derived fuel from waste tires, capable to produce between 10.8 and 16.1 MJ of electric energy per kg of derived fuel from waste tires fed to the reactor. The second alternative considered a small-scale updraft gasifier feeding an internal combustion engine, coupled to an electricity generator for the production of up to 8.2 MJ of electric energy per kg of derived fuel from waste tires in Brazil, solving their disposal problems, creating jobs, reducing negative disposal environmental impacts in landfills, and increasing distributed generation of electricity.

1. Introduction

Environmental concerns, oil price instability, economical and geopolitical issues motivate the development of new energy generation technologies. Sustainable use of energy resources is necessary for the proper management of the planet's natural resources and reduction of environmental pollution. Thus, obtainment of renewable fuels is an issue among current challenges. This should be done at affordable costs with economically feasible applications, in order to reduce pollutant emissions, including NO_x , CO_2 , particulate matter (PM), and C_xH_y .

Tire disposal is a worldwide problem, aggravated along with growing vehicle fleets. Tires must be properly disposed to reduce their impact on the environment; however, disposal occurs through incineration most of the time, which is the fastest and easiest discarding procedure. Tire incineration produces a large number of emissions, including a broad set of hydrocarbons, and halogen-chlorinated compounds (chlorinated methanes, dioxins, and PCBs -polychlorinated biphenyl) [1]. This also produces pyrolytic oil, which contains toxic chemicals and heavy metal compounds capable of causing adverse health effects.

Studies stated that water pollution caused by runoff derived from tire fires can last up to 100 years [2]. In addition, toxic incineration exhausts from waste tires are far more mutagenic than from welldesigned and properly operated coal-fired plants emissions [3].

Disposal of tires in landfills is environmentally harmful, since they tend to return to the surface and break layer covers, damaging the land settlement in the long term and their rehabilitation [3].

Estimates regarding the number of waste tires annually generated in Brazil range between 17 and 20 million units, 6 million only in the state of São Paulo state; the number of accumulated units within inappropriate deposits is estimated to be at least 100 million [4]. According to CEMPRE [5]- Business Commitment for Recycling, nonpassive tire recovery has negative value, i.e., waste tires carry costs for new tire dealers who eventually pay for residue disposal.

Concerns related to contamination associated with tire disposal led to the search for reuse technologies of discarded tires. Thus, energetic valorization of tires began along with the introduction of their use as a raw material in building construction, in asphalt surfacing processing, and in the footwear industry, among other applications [6].

2. Tire production and waste tire disposal

The estimate growth for the worldwide tires demand, about 4.3 percent per year, reached 2.9 billion units in 2017, while waste tire disposal in 2015 reached nearly 1 billion units [7].

According to the Brazilian Pneumatic Industry Association [3], production of tires in 2014 by the Brazilian industry totaled 70.8 million units, which was a small reduction compared to 2013, a year in which the historical record was achieved by the sector. In addition, 12.4 million units were exported in 2013, a slight growth of 0.6% in total manufactured tires; and 7.0 million tires were imported. Table 1 presents the number of tires produced in the 2006-2014 period.

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Table 1

Number of tires produced in Brazil in the 2006–2014 period [3,8].

	Production by Categories (Million of units)									
	2006	2007	2008	2009	2010	2011	2012	2013	2014	
Cargo	6.9	7.3	7.3	6	7.7	7.448	7.138	8.231	7.894	
Van	5.9	6	5.8	5.6	7.9	8.470	8.267	9.904	8.860	
Drive car	28.9	28.8	29.6	27.5	33.8	32.568	30.406	32.554	33.266	
Motorcycle	11.4	13.8	15.2	13	15.2	16.078	14.519	15.041	15.642	
Agricultural	0.688	0.83	0.903	0.679	0.917	0.793	0.807	0.928	0.873	
Others	n.a	n.a	n.a	n.a	n.a	0.109	0.107	0.103	0.118	
Industrial	0.508	0.462	0.716	0.963	1.6	1.396	1.360	2.072	2.069	
Airplane	0.051	0.061	0.047	0.0418	0.06	0.060	0.054	0.052	0.050	
Total	54.347	57.253	59.566	53.783	67.177	68.933	64.670	70.898	70.786	

n.a: not available.



Fig. 1. Behavior of the Brazilian tire production in the 2006–2014 period [3,8].

Main export destinations included Argentina, United States, Colombia, and Mexico. Due to a competitiveness loss regarding Brazilian products and reduction of imports from MERCOSUR, direct exports from tire factories have been reduced by an average of 3% per year since 2010, ranging from 25.1% of total Brazilian production in January 2010 to 18.0% in 2014. Fig. 1 shows the behavior of the Brazilian tire production in the 2006-2014 period.

The observed behavior regarding Brazilian tire production presented a sustained increase, except in 2009 and 2012. A significant reduction of tire production in those years was a reflection of the global economic crisis [9–11].

2.1. Waste tire generation and disposal

The tire life cycle generally consists of five main stages, comprising of raw materials extraction, production, consumption (use), waste tire collection, and processing for recycling or disposal, depending on local conditions of each country or region where they are produced or sold [12].

Waste tire generation in 2013 by region was: USA, 4.4 million metric tons [13]; Europe, 3.4 million metric tons [17]; Japan, 1.02 million metric tons [14], Russian Federation, 1 million metric ton [15], and Brazil, 365 thousand tons [3,16], with 3.31 million metric tons produced in the rest of the world. Fig. 2 shows the volume distribution of waste tire generated in 2013 worldwide.

The Brazilian Pneumatic Industry Association [3] invested R\$ 105 million in 2015 to recycle tires from 834 collection points across the country. This value was higher than the amount spent in 2014 (R\$ 99



Fig. 2. Waste tire volume generation worldwide in 2013 [12-14,20].

million), when 89 million units were collected. 445 thousand tons of waste tires were collected in 2014, which was in amount 10.1% higher in comparison to that collected in 2013. Since the waste tire collection by manufacturers began in 1999, 3.11 million tons of waste tires were collected and disposed of properly, which was the equivalent of 623 million passenger tires. Tire manufacturers have already invested R\$ 724 million in the program until March 2015, equivalent to US\$ 207 million. Fig. 3 shows the mass of waste tires recycled in Brazil, in the 2000-2015 period.

The recollected waste tire amount increased steadily during the last 5 years, but it remained below 85% of the total waste tire generated.





Recollection and correct disposal in the country are still unsolved issues. The mass of waste tires in 2015 without a proper disposal were around 83,500 t, which represent 2.99 PJ of available gross energy.

3. Disposal routes for waste tires

Incorrect disposal of waste tires can lead to rainwater accumulation, creating favorable conditions for propagation of disease-carrying pests. Auto-ignition of large tire piles is also possible, polluting groundwater and air. When disposed in a landfill, lighter-end gases are released during the decomposition process. Such gases can build up within the tire interior, gradually forcing it to "float" to the surface. This affects the landfill design integrity, and some tires might not remain buried, causing environmental problems, as presented above.

Reuse is currently the best option for waste tire recycling. Around 40% of the tire rubber forms the tread, leaving 60% in the waste tire after tread was worn out. Retreading aims reuse the housing, permitting the reutilization of the tire through the addition of a new tread. This process reduces the rubber use for the "new" tires, and also reduces the production costs.

Recycling of tires to create a new product is another route for waste tire disposal. Through this process, cut up or shredded waste tires are completely used. Recycled tires are used for the production of a diversity of new products like: liquids reservoirs, mats, high performance roads base, playground cover, and sports fields, among others.

Currently, the most common disposal procedure for used tires in Brazil is its use as an alternative fuel for the cement production, which in 2014 accounted for 69.7% of the total. The second most regular destination is granulated manufacturing and rubber powder for use in rubber products, rubber or asphalt, accounting for 17.8% of the allocation. Lamination [3], in which 6.0% of the waste tires collected as raw material is used, is applied for shoe soles manufacturing, inland pipelines, among others. Fig. 4 shows the tire life cycle.

Energetic valorization of waste tires is not recycling; however, it is a valuable use of waste tires, different to dumping them in landfills, due to their high energetic content. The energetic valorization routes will be discussed in the next section.

3.1. Energetic valorization of waste tires

Tires have a mixed conformation, formed by carbon black, elastomer compounds, and steel, as well as different other organic and inorganic constituents. Fig. 5 shows a diagram of waste tire average composition.

Rubbery materials are main tire components. They thermoset polymers, included in the arrangement of C_xH_y , with fibrous elements [18]. Automobile tires are principally a combination of NR (natural rubber) and SR (synthetic rubber), like BR (butyl rubber) and SBR (styrene–butadiene copolymer) [19]. Shulman [20] notes that NR comes from the Hevea tree, while SR is in general obtained from petroleum-derived products. NR has exceptional flexible properties and it is a tire critical element.

Through analyses of different of rubber compounds, different results are reported for proximate and elemental analysis, as shown on Table 2 and Table 3. In order to obtain the average element content of tires, to be analyzed by parts.

High heating value was estimated by using average elemental compositions reported in Table 3 and the Modified Dulong Eq. (1), which is largely better applied for fuel with high carbon to hydrogen content, such as tire derived fuels (TDF) on moisture and ash-free basis [37].

$$HHV = \left[78.31C + 359.32\left(H - \frac{O}{8}\right) + 22.12S + 11.87O + 5.78N\right]$$

0.0041868 (MJ/kg) (1)





The HHV was determined to be 35.86 MJ/kg, which is close to the experimental values of Cooper et al. [38] (37.79 MJ/kg) and Clark et al.. [39] (36.05 MJ/kg).

TDF fuel is compact and it has a consistent composition with low moisture content. These are characteristics beneficial to the fuel user. Due to their high energetic density, used tires are widely used as a fuel

Table 2	
Proximate analysis for waste tire rubber by several authors [21-30)] .

Reference	Volatile (wt %)	Moisture (wt %)	Fixed Carbon (wt%)	Ash (wt %)
[21]	67.3	0.5	28.5	3.7
[22]	61.61	1.72	22.66	14.01
[23]	58.8	-	27.7	3.9
[24]	62.32	1.31	26.26	10.29
[25]	61.9	0.7	29.2	8.0
[26]	93.73	0.54	-	5.3
[27]	59.3	-	27.6	3.5
[28]	58.7	-	33.6	7.7
[29]	66.5	0.8	30.3	2.4
[30]	68.7	0.4	23.3	7.6

 Table 3

 Elemental analysis of waste tire rubber by several authors [21–27,29–36].

Reference	C (wt%)	N (wt%)	H (wt%)	0 (wt%)	S(wt%)	Ashes
[31]	74.2	0.3	5.8	4.7	1.5	13.5
[22]	81.24	0.49	7.36	8.92	1.99	-
[23]	74.2	0.3	5.8	4.7	1.5	13.5
[24]	74.4	0.21	6.96	5.02	1.6	10.21
[25]	86.7	0.4	8.1	1.3	1.4	2.9
[26]	81.16	0.47	7.22	2.07	1.64	7.44
[27]	74.2	0.3	5.8	5.1	1.5	13.1
[21]	83.8	0.4	7.6	3.1	1.4	3.7
[32]	73.8	0.44	5.3	0.11	1.71	17.8
[29]	85.8	0.4	8.0	2.3	1.0	2.4
[30]	81.3	0.3	7.3	-	1.5	1.4
[33]	82.63	0.36	7.5	-	1.69	-
[34]	86.7	0.3	6.9	1.0	1.9	3.3
[35]	86.6	0.5	8.1	2.2	0.8	-
[36]	86.4	0.5	8.0	3.4	1.7	2.4

in thermoelectric generation, in co-combustion coal-fired boilers, and oil production.

However, these applications cause concerns due to high levels of pollutant emissions. Waste tire incineration and combustion are the most polluting energy conversion routes for waste tires. According to the United States Environmental Protection Agency [39,40], tire combustion releases approximately 6% of burned fuel mass, considering solid particles and volatiles.

3.2. Incineration

Incinerators can directly employ waste tires as fuel. Direct combustion of waste tires in incinerators has advantages, among them: low cost for power-production costs, high energy recovery, and lower environmental impacts when compared to landfill disposal. Among disadvantages that can be listed are: no material recuperation, higher capital investment, necessity of exhaust gas cleaning process, higher CO_2 emission and operating costs. Additional researches are needed to reduce the environmental impact associated with this process, especially those related to emissions of polycyclic aromatic hydrocarbons (PAH) [22].

3.3. Combustion

Another technology for waste tire energy valorization is to burn them for power generation. In such cases, tires are burned in boilers for high-pressure steam production, which is introduced into a steam turbine coupled to a generator for electricity generation.

The combustion process could be accomplished in fixed or fluidized bed conditions. Successful waste tire combustion experiments in fluidized-bed reactors were reported [41,42], being the most effective process for waste tire management. However, this is relatively expensive due to high operating costs and considerable feedstock preparation.

Rotary kiln combustion allows waste tires combustion with different sizes at reasonably low operating costs, although disadvantages of combustion in rotary kiln combustors encompass the requirement of implementation of technologies for particulate filtration and for emissions controls in the effluent gas. The environmental impact from this process needs additional research, especially regarding to the generation of PAH (polycyclic aromatic hydrocarbons) in the exhaust gases. In 1998, Carraso et al. [43] reported that energy retrieval from waste tires when used as fuel in cement industries, satisfy environmental standards. The effects of using of waste tires as fuel in cement production was evaluated by Giugliano et al. [44]. Combustion in grate kilns is also an alternative, which is economically justified, especially for large-sized plants [22]. Studies of waste tires combustion emissions have been performed by several authors. The amount of toxic emissions from combustion depends upon the employed technology and the process operational.

When coal and waste tire combustion were compared, NO_x emissions from tires were observed to be 3 to 4 times inferior to those from coal emissions, and SO_2 emissions were similar. CO and PAH presented higher concentrations from waste tires than from coal, but relative quantities of PAH indirect compounds were comparable in the effluents for both fuels [45].

Mastral et al. [42] reported that, with the increment of temperatures, the amount of released polycyclic aromatic hydrocarbons, is reduced in the fluidized-bed combustion of used tires. Lemieux et al. [46] studied the emissions of toxic compounds in air by open combustion

of several waste materials. Results show that PAH emissions were higher after the polymers combustion, requiring the implementation of technologies for particulate filtration and for emissions controls in the effluent gas.

3.3.1. Waste tire combustion

Brazil employs approximately 70% of 400 thousand tons of waste tires collected as an alternative fuel in twenty four cement production facilities, which became the main use of this refuse [8,16]. As a large energy consumer, this industry has been making efforts to develop energy saving techniques and to diversify the fuels used. It has cooperated in the development of a technique for waste tire utilization as an auxiliary fuel for cement production. Thus, the established system has properly met the needs of the tire industry in economically disposing large numbers of used tires, reducing the pollution impacts to the environment and the amount of fuel used by the cement industry.

Conventional cement-burning fuels are known to be gas, oil, and pulverized coal, which are blown into the kiln by burners, atomized with air, and then burned rapidly. However, the tire material is elastic and its pulverization is meticulous. In addition, it is extremely costly to break it to the necessary size for pneumatic transport. Therefore, it was necessary to develop a method which allowed feeding of larger dimensions into a kiln. This technique is economically attractive by finding the maximum permissible size for complete burning in several types of kilns. Since tires do not contain deleterious components to the cement quality, there is no quality change caused by feeding tires, as proven from long term experience in checking the final product quality, with tire combustion residues not found in the finished cement.

A recent Life Cycle Assessment (LCA) has been carried out to compare waste tire combustion in cement kilns against different recycling streams [47]. LCA is a tool to estimate impacts associated to a product, service or system from a point of view, that includes all possible environmental impacts.

The units employed are entitled *person equivalents (PE)*, covering the impact of the treatment over a tonne of used tires in relation to the impact triggered by a person over the period of a year.

Results evaluate the savings when used tires are recycled instead of burned. Processes such as mineral resource use and nitrification in water, where recycling has a negligible advantage, are disregarded. Between 0.07 and 0.31 PE are saved per tonne of waste tires recycled instead of incinerated [47].

3.4. Pyrolysis

Employment of waste tire as fuel in advanced thermal-conversion processes with low contaminant emissions is a very promising alternative in the current market, which allows the energy use of such wastes at affordable costs and reductions of environmental impact regarding waste tire disposal [48–50].

Processes of pyrolysis could be categorized according to applied pressure as vacuum, atmospheric and fast or slow according to the heating rate. Some advantages of a pyrolysis process are low energy requirements, simple devices for volatile product condensation, and high liquid yield [51,52].

Pyrolysis processes reduce solid carbonaceous residues, condensable fraction (pyrolytic-oil), and non-condensable fraction of gases. The mass distribution of each phases are determined by operation parameters, as temperature profiles, pressure, heating rate, fuel dimensions, heating system, catalysts, among others [49,53].

Pyrolysis is an efficient method to recycle waste tires, and it recently has gained a renewed attention because of its advantages to solve used tires disposal problems [31]. Apart from the possibility of carbon black recovery, the volatile compounds released have the potential of renewable energy recovery. Their liquefaction to a liquid fuel is noteworthy, because they can be easily manipulated, transported and stored, permitting high flexibility for power applications. In fact, waste tire pyrolysis oil is fully miscible with petroleum diesel and blends of both fuels are used in some experimental studies, fueling existing compression ignition engines [54–56].

Pyrolysis reaction can be classified as [57] a) primary pyrolysis reaction (250–520 °C), b) secondary pyrolysis of volatiles compounds (600–800 °C), and c) char gasification with CO₂, H₂O, and O₂ (750–1000 °C). Pyrolysis experiments of waste tires at temperatures ranging 300 and 720 °C were conducted by Williams et al.. [58], with rates of heating between 5 and 80 °C min⁻¹. The conversion rate peak, for tire samples (Table 4), was observed to occur at approximately 600 °C. Laresgoiti et al. [59] state that temperature increments over 500 °C do not influence char and gas yields, but temperature variations effects sensibly the final gas composition.

The energy for pyrolysis, defined as pyrolysis enthalpy or pyrolysis heat, is the required energy to increase the feedstock temperature from ambient temperature to the reactional temperature, as well as the energy to carry out the pyrolysis reactions (reaction enthalpy) [64,65]. According to Dodds [66], the net energy balance for waste tire pyrolysis suggests that the energy recovery ranges between 75% and 82% of the tire combustion heat. Laird et al. [67] stated that the pyrolysis energy efficiency includes the main process products as a function of marketability [67].

Waste tire pyrolysis provides promising results for plants at both pilot and industrial scale with distinct process technologies. As for industrial scale plants, the Waste Tire to Fuel Oil Pyrolysis Plant implemented by Huaying Energy Group stands out. It is capable to process 3-10 t/day of waste tires, rubber, medical waste, or municipal solid waste (MSW) [68]. In this plant, tire pyrolysis involves high temperatures from 400 to 450 °C, in oxygen deficiency conditions. During the pyrolysis process, waste tire components decompose into pyrolysis oil, pyrolysis gas, steel wire, and carbon black. Distribution of products from such Waste Tire to Fuel Oil Pyrolysis Plant is: 45% pyrolytic oil, 30% carbon black, 15% steel wire, and 10% combustible gas.

The Beston Group from China also developed a Pyrolysis Plant for Waste Tires, with process capacity of 10 t/day [69]. The rotary reactor in this plant is horizontal, with a combination of direct and indirect heating, and a 50% pyrolytic oil yield rate.

Brazil still does not have an industrial scale pyrolysis plant, but there are several ongoing research projects. The São Bernardo do Campo Industrial Engineering Faculty (FEI) developed research projects for evaluation of properties related to condensate fuel derived from waste tire pyrolysis [69]. This project verified the feasibility of using the resulting compound from waste tire pyrolysis as an alternative fuel to petroleum, since its chemical composition is similar to diesel used in vehicles. Partial project results indicate that the bio-oil product from tire pyrolysis has ideal combustion properties and viscosity, for use as a fuel, and it is within the range allowed by Brazilian fuel legislations. Thus, its production and consumption is feasible considering the economic and environmental points of view.

Frigo et al.. [70] also evaluated the option of using oil derived from tire pyrolysis on Diesel engines. The pyrolytic oil was obtained by thermo-mechanical cracking conducted between 300 and 500 °C. Pyrolytic oil fuel properties were analyzed through standard methods for: heating value, viscosity, density and flash point. These properties were comparable to those of Diesel Fuel (DF) used in commercial vehicles, but with a considerably higher sulphur content and lower cetane number. In addition, yields and composition of remaining pyrolysis products were analyzed, in order to evaluate their potential re-uses. Fig. 6 shows the experimental apparatus used in this research.

An experimental investigation was conducted using a 440 cm³ single-cylinder Diesel engine fed with two blends of tire pyrolysis oil (TPO) and DF: one blend composed by 20% TPO and 80% of DF volume basis (TPO20) and the other composed by 40% TPO and 60% of DF volume basis (TPO40). The reported results were checked with those using only DF. Engine performance, which was evaluated at different engine speed and loads, showed that TPO20 does not generate significant differences in engine performance, when compared to DF; while TPO40 leads to general worsening of engine combustion characteristics [70].

According to Frigo et al. [70], lubricant oil analysis performed at the end of the experiments showed a certain contamination level. No significant mechanical problems were observed during the experiments. Kapura et al. [71], evaluated the possible use of a pyrolytic oil from used tire pyrolysis on diesel engines. Fig. 7 shows the pilot plant employed for waste tire pyrolysis.

Effects were evaluated regarding the addition of small amounts of an ignition improver to a tire derived fuel diesel blend on combustion, performance, and emission parameters of a small powered, direct injection (DI) diesel engine. A 40% light fraction pyrolysis oil (LFPO) obtained from a pilot tire pyrolysis plant, blended with 60% diesel fuel, was used as test fuel. 40LFPO cetane number was lower in comparison to diesel. Four different samples of 40LFPO-Diethyl ether (DEE) blends were tested in a single cylinder, four-stroke, air cooled, direct injection (DI) diesel engine, with a 4.4 kW developing power at 1500 rpm. Investigation results showed that the ignition was delay reduced with the 40LFPO blend as the percentage of DEE increased. 4% DEE addition allowed higher performance and lower emissions than other experiments at full load. NO emission was lower by nearly

Influence of process conditions on char, liquid, and gas yields presented by several authors [24,25,36,58-63].

Reference	Temperature (°C)	Pressure kPa	Heating Rate (°C/min)	Sample sizes	Liquid (wt. %)	Gas (wt.%)	Solid (wt.%)
[58]	300-720	101	5-50	-	55	10	35
[59]	400-700	101	15	20-30 mm	28-40	7–9	43-53
[60]	400-700	101	15	20 mm	30-43	2.4-4.4	47-63
[25]	350-700	101	5-20	0.2-1.6 mm	55	4-11	37-40
[61]	440-570	1.3 - 28	_	3.8 cm ³	50-60	3.2-11.9	30.6-53.4
[62]	400-460	101	_	2-20 mm	51	16.6	32.5
[24]	200-600	101	_	20 mg	28-42	30-53	14-28
[36]	450-600	101	_	-	53-58	5-9	37-38
[63]	25-500	0.8-28	15	-	62	1-3	35-36



Fig. 6. Experimental apparatus used for waste tire pyrolysis [70].



 Reactor; 2- Electric motor; 3- Sealing elements; 4- Flexible connection; 5- Oil separator; 6-Heavy oil tank; 7- Damper; 8, 12- Condenser; 13- Cooling tower; 14- Smooth inspect mirror; 15- Light oil tank; 16- Water sealing and gas recycling system; 17- Gas burner; 18- Pump; 19-Control panel.

Fig. 7. Pilot plant for waste tire pyrolysis [71].

25% in comparison to diesel operation at full load.

Several studies of waste tire pyrolysis have been conducted to evaluate the influence of operating parameters like heating rate, temperature, pressure, as well as solid and volatiles residence times on product yields and its properties, using different pyrolysis reactor types.

The main problem of large-scale applications to drive the pyrolysis process is an efficient heat transfer for an uniform temperature distribution [65,72]. This is an important obstacle for large plants which impairs its promotion, as well as its economic and technical feasibility. Furthermore, products from the pyrolysis of used tires are physico-chemically more complex than products from alternative thermochemical conversion processes of this waste, such as gasification or combustion. This fact is also responsible for waste tire pyrolysis not having gained enough interest by the industry as a well-known process, like combustion. Furthermore, some authors [61,73–77] agree that the market shortage for liquid and solid fractions from waste tire pyrolysis obstructs the expansion of the process to industrial levels. Murillo et al. [78] indicated that the pyrolysis of this waste is technically and environmentally feasible; these authors also note that the economic sustainability of the process strongly depends on the possible uses of its derived products. Gasification appears as an alternative process with several advantages over waste tire combustion and pyrolysis.

3.5. Gasification

fuel molecules. It has a goal to transfer the energy contained in the fuel to a producer gas, with minimum loss of energy. Char and ash are also produced in this process [79], which takes place in sub-stoichiometric conditions with controlled oxygen supply, likewise the pyrolysis process [80]. Gasification can be highly efficient, achieving cold gas efficiency values between 60 to 70%, and carbon conversion of 98 to 99%. It is a feasible alternative for the energetic valorization of waste tires [81]. Studies of waste tire gasification at laboratory scale in fluidized bed gasifiers show the possibility of employing this technology for energy valorization [82–88]. The main disadvantage for large-scale application is the fuel size required for fluidized bed gasification, which ranges between 0.5 and 2 cm [82-84.86.87]. According to experiments conducted by Leung et al. [82], several gasification process parameters are directly influenced by the particle dimensions, including bed temperature, secondary reactions temperature, product gas composition, gas yield, gas heating value, products distribution (gas, tar, and char), volatile release ratio, fixed carbon conversion ratio, and energy recovery ratio. For better results, particles size must be lower than 1 mm [82].

Among commercial gasification technologies, plasma gasification is the main technique used for waste tire gasification [89].

3.6. Plasma gasification

The plasma gasification process converts waste tires into commercially feasible products using dynamic plasma physics. Waste tires pass through an electric field within a plasma-processing chamber without oxygen. Thus, gasification of waste tire components occur in an extremely high temperature atmosphere (1300 °C).

Such extreme heating process without oxygen is different from incineration, and it does not generate a problem with exhaust emissions produced when the waste ignites. In comparison to incineration, plasma gasification creates syngas, which can be used to generate a multitude of valuable products, including electricity, liquid fuels, ethanol, and fertilizers. The material introduced into this process is detoxified and its volume is reduced by a factor of 20 to 1. The only byproduct of the process is an inert ash.

3.6.1. Syngas processing and cleaning

Syngas processing and a regenerative cleaning phase begins when syngas exits the reactor. Complete decomposition of any organic structure occurs because the synthetic gas is circulated through the plasma field several times. The synthetic gas leaks into the reactor and comes out clean. The syngas immediately passes through a cooling water and lime bath to lower the temperature below 80 °C. The cooling bath scrub removes any remaining particulate material. Then the syngas is fed through the pipeline to a diesel generator through the air intake manifold. This process is mechanically controlled and can be adjusted to optimize power output and to control the process speed.

The GUASCOR group is a leader of this innovative technology. In 2010, a plant started up in order to diminish the impact of waste tires through its Enviroil subsidiary at As Somozas (La Coruña). According to the group, a worldwide leader in the development of technologies for generating electricity from renewable sources and reducing environmental impact, the gasification plant solves a serious environmental problem in achieving effective recycling of tires to replace the current landfill storage.

This facility has a processing capacity of 12000 t per year, which is equivalent to the annual output of used tires throughout Galicia. Additionally, since it is a modular floor, the installation may even double this treatment capacity if demand requires it.

Among some benefits from waste tire plasma gasification, it is possible to mention the following:

- Almost no residue is left after the process (< 5% inert ash).
- It eliminates the use of landfills.

 Higher efficiency in energy conversion materials is achieved in comparison to traditional incineration systems and power generation by combined cycle.

Despite being the most applied technology, some disadvantages must be mentioned for waste tire gasification:

- Its implementation requires high initial investment.
- It has high electricity consumption.
- Requires periodic maintenance.
- Elevated operation costs.

Due to these reasons, some alternatives to the gasification technology for energetic valorization of waste tires are required. Updraft gasification has demonstrated effectiveness for high gasification efficiency of carbonaceous materials.

3.7. Waste tire updraft gasification

After analyzing commercially available gasification technologies and their working principles, the updraft gasification for energetic valorization of waste tires was proposed, using a technology of lower cost in comparison to plasma gasification. With some process modifications, it could help to mitigate the impact of improper disposal of waste tires.

Updraft gasifiers transform waste tire components in carbon black, steel and base oil, as well as a large volume of gas, that can be used as fuel after cleaning, for power generation and similar applications mentioned for the plasma gasification syngas.

Such gasifiers are the best mobile bed gasifiers, suited to the design on an industrial scale. They may reach 20 MW thermal power and are less sensitive to changes in moisture content and fuel geometry [89]. However, heavy hydrocarbon formation in the gasification process within these reactors, known as tars, is a significant challenge for implementation of this technology on industrial applications [90]. Tars can also disable catalysts in the subsequent reforming process, such as the Fisher-Tropsh process. If tar is completely removed, the gas will be able to be used in gas turbines or in internal combustion engines, and it can be used as a feedstock for the synthesis of other compounds [91]. Overall reactor efficiency increases due to high carbon conversion rates and low outlet temperature of the gasifier product gas. The updraft reactor in Denmark Harboøre plant is a good example of high efficiency equipment [92–95].

The proposed reactor design for the gasification of waste tires [Fig. 8b] has a modification in the gasification stages with respect to the common configuration [Fig. 8a] of updraft gasifiers, specifically in the

reactor feeding position for raw materials. In this design, the raw fuel is fed through a conduit located in the reactor base over the grid. This modification ensures a strong tar decrease in the produced gas [96].

Shredded waste tires are forced up and introduced into the reactor base; a microwave sensor constantly measures the bed height. There are two entrances for gasifying agent in this design. The first entrance is located in the reactor base through the grid, as common in this kind of reactor; the second is located in the mid-section of the reactor structure.

In the modified gasifier design, pyrolysis and reduction within the drying zone are in inverted relative positions in the combustion region and this is common for updraft gasifiers. As the feed material flows upwards from the base section, it reacts with gases moving upward, as shown in Fig. 8b.

In this configuration, gas produced in a de-volatilization zone is forced to go through the oxidation zone before leaving the reduction precinct. Such configuration is based on experiments with downdraft reactor projects, for which the gas has low tar content. This reaction path produces a tar reduction in the producer gas, in comparison to other modified updraft flow gasifiers [97–99]. In this manner, most tars formed during pyrolysis (composed of oxygenated organic compounds) are burned and cracked in a process named flaming pyrolysis [79]. Flame temperatures are between 1000–1400 °C, but flame pyrolysis occurs in particle interstices between 500 and 700 °C. In this way, the major part of tars is burned, providing energy for coal pyrolysis and gasification [79]. Cracking of this tar produces CO, H_2 , and light hydrocarbons [98,99]. Table 5 shows a comparison among analyzed gasifiers.

According to gasifier comparisons (Table 5), implementation of waste tire gasification using the updraft gasifier proposed design, instead of plasma gasification or fluidized bed gasification, will allow small-scale energetic valorization of this residue at lower cost and high efficiency.

3.8. Alternatives to application of technologies for waste tire energy valorization

Based on those technologies analyzed, some alternative solutions for energetic valorization of waste tires are proposed. The first proposed alternative considers a large-scale updraft gasifier with a modification exposed on Section 3.7 and an IGCC for generation of energy using waste tires gasification. With this configuration (Fig. 9), the clean gas produced in the gasification island feed a gas turbine for electricity production and uses the heat from exhaust gases to produce steam in the Heat Recovery Steam Generator (HRSG), with the function of producing energy.



Fig. 8. Updraft gasifier: (a) Traditional configuration [90], (b) Modified reactor [96].

Table 5

Gasifier type co	omparison, v	with each typ	e ranked from •	(poor) to •••• (good)	Adapted from	IREMA	[100]	and E4tech	101	١.
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Reactor type	Feedstock tolerance	Development status	Scale up potential	Costs
Updraft BFB CFB Plasma	 Dimensions < 10 cm, up to 50% moisture, high ash % composition Between 50 and 150mm, 10-55% moisture, care with ash Dimensions < 20mm, 5-60% moisture, care with ash No specific requirements 	 Integration and large scale experience, large industrial players Past heat & power applications, modest scale up, some BTL interest Extensive heat & power expertise, research & scale up, but few developers, particularly for BTL Several developers, many power applications, early stage of scale-up 	 Up to 40 MW reactors and plants possible Several large projects planned Several large projects planned Only small scale, modular systems 	 High efficiency. Relative low inversion cost Possible higher gasifier capital costs and lower efficiency Possible higher gasifier capital costs Very high capital costs, low efficiency

A feeding system, a gasifier, and a gas cleaning system compose the gasification island. The electricity generation efficiency in this configuration ranges between 30% and 45% [103] (i.e. for each kg of TDF, it is possible to produce between 10.8 and 16.1 MJ of electric energy), and the capacity of processing waste tires will be a function of the gasifier size in the gasification island.

The second proposed alternative considers small-scale updraft gasifiers and contemplates an internal combustion engine, powered by producer gas, coupled to an electricity generator. In this configuration (Fig. 10), the producer gas is generated in the gasification island by a modified updraft gasifier (Section 3.7).

The producer gas is fed to an internal combustion engine for electricity production. In this configuration, heat from the exhaust gas could also be used for hot water production [104]. A feeding system, a modified updraft gasifier, and a gas cleaning system compose the gasification island. Electricity generation efficiency in this configuration could reach 23.43% [104] (i.e. for each kg of TDF, it is possible to produce up to 8.2 MJ of electric energy) and the capacity of processing waste tires will be a function of the gasifier size or the number of gasifiers in the gasification island.

In both configurations proposed for waste tires, the main pretreatment objective is to separate the steel from tires, as well as reduce particle sizes for their introduction in the gasification island. Final fuel size dimensions will depend of the gasifier technology.

Is also possible to use the producer gas in both configurations, for production of second-generation fuel through the Fischer Tropsch process.

3.9. Advantages of waste tire energy valorization by updraft gasification

Updraft waste tire gasification have a wide applicability, mainly due to its feasibility as a fuel. This waste significantly affects the environ-



Fig. 10. Simplified scheme of a waste tire gasification plant and internal combustion engine, powered by producer gas, to generate electricity.

ment, with conventional treatments by combustion and incineration techniques releasing high amounts of pollutants.

Considering the negative impact caused by used tire combustion, its incineration or landfill disposal, as well as the complexity of waste tire pyrolysis products from the physicochemical point of view in comparison to products from combustion and gasification, it is important to point out the advantages of using this waste as a fuel in modified updraft gasifiers.

There are other advantages besides the proper gasification in cogeneration plants:

Technical advantages: less complexity of implementing the updraft gasification technology in comparison to implementation of plasma gasification.

Strategic advantages: It will be possible to decentralize power generation next to consumption points. The proposal would increase generation and can complement hydroelectric generation in the dry season in the specific case of Southeast and Midwest regions of São Paulo, Brazil, where several plants are located. Fischer Tropsh fuel products can be used as a complement to fossil fuels, in the transport



Fig. 9. Simplified scheme of a waste tire gasification plant integrated to a combined cycle system (IGCC).

sector and different production processes.

Economic advantages: It will be used as a fuel, increasing the energy supply in power plants and increasing profits from surplus sales.

Social benefits: Job generation in the plants used for energetic valorization of waste tires.

Environmental advantages: Reduction of landfill volume and waste amount. CO_2 emissions will be reduced, as well as other pollutant products from burning tires, along with their deposition in the open air.

4. Final considerations

The main route for waste tire disposal in Brazil is its use in the cement industry as secundary fuel, and a low percentage in the rubber modified asphalt production. This study proposed two alternatives for energetic valorization of waste tires based on updraft gasification in a modified reactor design, due to the advantage of the gasification process. The first alternative considers a large-scale updraft gasifier with a modified design in IGCC for the gasification, capable to produce between 10.8 and 16.1 MJ of electric energy per kg of waste tire fed to the reactor. The second alternative considers an updraft gasifier small-scale to feed an internal combustion engine, coupled to an electricity generator for the production of up to 8.2 MJ of electric energy per kg of waste tire. It is also possible to employ the producer gas for production of second-generation fuel by the Fischer Tropsch process.

Implementation of these technologies will allow energetic valorization of waste tires in Brazil, solving disposal problems regarding this waste, creating jobs, reducing negative environmental impacts related to landfill disposal, and increasing generation of distributed electricity distributed.

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References

- Lew G. Preliminary test data from the modesto energy company evaluation test. California Air Resources Board, Review Draft, Sacramento; February 1990.
- [2] Andrade HS. Scrap tires: possible reuse alternatives. Course conclusion work (Graduation in Economics) – Federal University of Santa Catarina, Brazil; 2007 [in Portuguese].
- [3] ANIP. National association of the tire industry. Reciclanip. Available at: (www.reciclanip.com.br/?cont=ecopontos_oquesao). [accessed 12.06.15].
- [4] ABRELPE. Overview of solid waste in Brazil. Available at: (www.abrelpe.org.br). [accessed 23.06.15]. [in Portuguese].
- [5] CEMPRE Business commitment for recycling. Available at (www.cempre.com. br), [accessed 10.11.15].
- [6] Lagarinhos CAF, Tenório JAS. Tire recycling: discussion of the impact of Brazilian politics. Engevista 2009;11(1):32–49.
- [7] World Tires, Industry Study 3105. The Freedonia Group; 2014.
- [8] Lagarinhos CAF. Reciclagem de pneus: análise do impacto da legislação ambiental através da logística reversa. PhD Thesis 291 p.- Escola Politécnica da Universidade de São Paulo USP. São Paulo: Departamento de Engenharia Metalúrgica e de Materiais; 2011.
- [9] Coleman N, Feler L. Bank ownership, lending, and local economic performance during the 2008–2009 financial crisis, J Monet Econ. vol. 71; April 2015, p. 50– 66. http://dx.doi.org/10.1016/j.jmoneco.2014.11.001.
- [10] Piqueira JRC, Mortoza LPD. Brazilian exchange rate complexity: financial crisis effects. Commun Nonlinear Sci Numer Simul. vol. 17(4); April 2012, p. 1690–95. http://dx.doi.org/10.1016/j.cnsns.2011.08.031.
- [11] Aloui R, Aïssa MSB, Nguyen DK. Global financial crisis, extreme interdependences, and contagious effects: The role of economic structure. J Bank Financ. vol. 35(1); January 2011, p. 130–41, http://dx.doi.org/10.1016/j.jbankfin.2010.07. 021.
- [12] Van Beukering PJH, Janssen MA. Trade and recycling of used tires in Western and Eastern Europe. Resour Conserv Recycl 2001;33(4):235–65.
- [13] U.S. Scrap tire management summary. Rubber Manufacturers Association, 2014. Available at: (www.rma.org/scrap-tire/scrap-tire-markets/).
- [14] Tyre Industry of Japan 2014. The Japan automobile tyre manufacturers association, Inc.; 2014. Available at: (www.jatma.or.jp/).
- [15] Yankovoy D, Bederov L, Ladygin K, Stompel S. All about tire recycling. Available

at: (www.i-pec.ru/).

- [16] RECICLANIP; 2015. Available at: (www.reciclanip.org.br).
- [17] ETRMA. End of life tyres a valuable resource with growing potential 2014 edition. Available at: (www.etrma.org/uploads/Modules/Documentsmanager/ 20150408-statistics-booklet-2014-final-%28modified%29.pdf).
- [18] Leung DYC, Wang CL. Kinetic study of scrap tyre pyrolysis and combustion. J Anal Appl Pyrolysis 1998;45:153-69.
- [19] Martinez JD, Puy N, Murillo R, Garcia T, Navarro MV, Mastral AM. Waste tyre pyrolysis – A review. Renew Sustain Energy Rev 2013;23:179–213.
- [20] Shulman VL. Tyre recycling, RAPRA review reports, vol. 15(7). UK; 2004.
- [21] Min Lee J, Soo Lee J, Rae Kim J, Done Kim S. Energy, vol. 20(10); 1995. p. 969– 76.
- [22] Juma M, Koreňová Z, Markoš J, Annus J, Jelemenský Ľ. Pyrolysis and combustion of scrap tire. Pet Coal 2006;48(1):15–26.
- [23] Rodriguez IM, Laresgoiti MF, Cabrero MA, Torres A, Chomon MJ, Caballero B. Fuel Process Technol 2001;72:9–22.
- [24] Chang YM. Resour Conserv Recycl 1996;17:125-39.
- [25] González JF, Encinar JM, Canito JL, Rodríguez JJ. J Anal Appl Pyrolysis 2001;58-59(1):667-83.
- [26] Chen JH, Chen KS, Tong LY. J Hazard Mater 2001;84(1):43–55.
- [27] Laresgoiti MF, Caballero BM, de Marco I, Torres A, Cabrero MA, Chomón MJ. J Anal Appl Pyrolysis 2004;71:917–34.
- [28] Atal A, Levendis YA. Comparison of the combustion behaviour of pulverized waste tyres and coal. Fuel 1995;74(11):1570-81.
- [29] Williams PT, Bottrill RP. Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil. Fuel 1995;74(5):736–42.
- [30] Orr EC, Burghard JA, Tuntawiroon W, Anderson LL, Eyring EM. Compressing waste rubber tire material and coal. Fuel Process Technol 1996;47(3):245–59.
- [31] Rodríguez I, Laresgoiti MF, Cabrero MA, Torres A, Chomon MJ, Caballero B. Pyrolysis of scrap tires. Fuel Process Technol 2001;72(1):9–22.
- [32] Arion A, Baronnet F, Lartiges S, Birat JP. Characterization of emissions during the heating of tyre contaminated scrap. Chemosphere 2001;42(5–7):853–9.
- [33] Lanoir D, Trouvé G, Delfosse L. Waste Manag 1997;17(8):475-82.
- [34] Senneca O, Salatino P, Chirone R. Fuel 1999;78(13):1575-81.
- [35] Roy C, Darmstadt H, Benallal B, Amen-Chen C. Fuel Process Technol 1997;50(1):87–103.
- [36] Cunliffe AM, Williams PT. J Anal Appl Pyrolysis 1998;44(2):131-52.
- [37] Buckley TJ, Domalski ES. (Discussion by Rigo HG), Evaluation of data on higher heating values and elemental analyses for refuse-derived fuels. In: Proceedings of the 13th Biennial ASME Solid Waste Processing Conf., Philadelphia, PA, 1988, p. 16–24
- [38] Cooper CD, Kim B, MacDonald J. Estimating the lower heating values of hazardous and solid wastes. J Air Waste Manag Assoc 1999;49(4):471-6.
- [39] Clark G, Meardon K, Russe D. Burning tires for fuel and tire pyrolysis: air implications. US Environmental and Protection Agency. EPA-450/3-91-07-December 1991.
- [40] Marchiori H. Tire Use Feasibility Study as Fuel in Power Generation. Final report.pp 2007;58.
- [41] Teng HS, Chyang CS, Shang SH, Ho JA. Characterization of waste tire incineration in a prototype vortexing fluidized-bed combustor. J Air and Waste Manag Assoc 1997;47(1):49–57.
- [42] Mastral AM, Callen MS, Garcia. T. Fluidized Bed Combustion (FBC) of Fossil and Nonfossil Fuels. A comparative study. Energy Fuels 2000;14(2):275–81.
- [43] Carraso. F, Berdin N, Oningue Y, Heitz M. Environmental impact of the energy content recovery of scrap tires in a cement kiln. Environmental Technology 1998;19(5):461-74.
- [44] Giugliano M, Cernuschi S, Ghezzi U, Rosso M. Experimental evaluation of waste tires utilization in cement kilns. J Air Waste Manag Assoc 1999;49(12):1405–14.
- [45] Levendis YA, Atal. A, Carlson J, Dunayevskiy Y, Vouros P. Comparative study on the combustion and emissions of waste tire. Environ Sci Technol 1996;30(9):2742–54.
- [46] Lemieux PM, Lutes CC, Santoianni DA. Emissions of organic air toxics from open burning: a comprehensive review. Prog Energy Combust Sci 2004;30:1–32.
- [47] Genan Business & Development A/S. Comparative life cycle assessment of two options for waste tyre treatment: material recycling vs. co-incineration in cement kilns. Executive summary; 2009.
- [48] Pedroso DT, Kaltschmitt M. Dichrostachys cinerea as possible energy crop facts. Biomass Convers Biorefin 2012;2:41–51.
- [49] Williams PT. Pyrolysis of waste tyres: a review, Waste Manag. vol. 33(8); August 2013, p. 1714–28, ISSN 0956-053X. http://dx.doi.org/10.1016/j.wasman.2013. 05.003.
- [50] Van de Beld L. Cleaning of hot producer gas in a catalytic, reverse flow reactor. Final Report For: Novem (EWAB Program, Report no. 9605) and European Commission (AIR Program, AIR-CT93-1436); 2001.
- [51] Martinez JD, Murillo R, Garcia T, Veses A. Demonstration of the waste tire pyrolysis process on pilot scale in a continuous auger reactor. J Hazard Mater 2013;261:637–45.
- [52] Antoniou N, Zabaniotou A. Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery. Renew Sustain Energy Rev 2013;20:539–58.
- [53] Quek, A., Balasubramanian, R. Liquefaction of waste tires by pyrolysis for oil and chemicals—a review, J Anal Appl Pyrolysis. vol. 101; May 2013, p. 1–16. http:// dx.doi.org/10.1016/j.jaap.2013.02.016.
- [54] Murugan S, Ramaswamy MC, Nagarajan G. Assessment of pyrolysis oil as an energy source for diesel engines. Fuel Process Technol 2009;90(1):67–74.
- [55] Ilkiliç C, Aydin H. Fuel production from waste vehicle tires by catalytic pyrolysis

and its application in diesel engine. Fuel Process Technol 2011;92(5):1129-35.

- [56] Ayanoğlu A, Yumrutaş R. Production of gasoline and diesel like fuels from waste tire oil by using catalytic pyrolysis, Energy, vol. 103; 15 May 2016, p. 456–68. http://dx.doi.org/10.1016/j.energy.2016.02.155.
- [57] Li S-Q, Yao Q, Chi. Y, Yan. J-H, Cen K-F. Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor. Ind Eng Chem Res 2004;43:5133–45.
- [58] Williams PT, Besler S, Taylor DT. Fuel 1990;69:1474.
- [59] Laresgoiti MF, de Marco I, Torres A, Caballero B, Cabrero MA, Chomón MJ. J Anal Appl Pyrolysis 2000;55:43–54.
- [60] Berrueco C, Esperanza E, Mastral FJ, Ceamanos J, García- Bacaicoa P. J Anal Appl Pyrolysis 2005;73:65–73.
- [61] Pakdel H, Pantea DM, Roy C. Production of dl-limonene by vacuum pyrolysis of used tires. J Anal Appl Pyrolysis 2001;57:91–107.
- [62] Mahmood M, Barbooti TJ, Mohamed AA, Hussain FO Abas. J Anal Appl Pyrolysis 2004;72:165–70.
- [63] Roy C, Caumia B, Caumia BD. Resour Conserv Recyl 1990;4:203.
- [64] Daugaard DE, Brown RC. Enthalpy for pyrolysis for several types of biomass. Energy Fuel 2003;17:934–9.
- [65] Martínez JD, Puy N, Murillo R, García T, Victoria VN, Mastral AM. Waste tyre pyrolysis – a review, Renew Sustain Energy Rev. vol. 23; July 2013, p. 179–213, ISSN 1364-0321. http://dx.doi.org/10.1016/j.rser.2013.02.038.
- [66] Dodds J, Domenico WF, Evans DR, Fish. LW, Lassahn PL, Toth. WJ. Scrap tyres: a resource and technology evaluation of tyre pyrolysis and other selected alternative technologies. US Department of Energy Report EGG-2241 1983; 1983.
- [67] Laird DA, Brown RC, Amonette JE, Lehmann J. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioprod Biorefin 2009;3:547-62.
- [68] Huayin Energy Group. China. Waste tire to fuel oil pyrolysis plant; 2015. Available at: (www.huayinenergy.com)
- [69] Beston Group, China. Pyrolysis plant for waste rubber; 2015. Available at: (www. bestongroup.net/auto/47.html)
- [70] Frigo S, Seggiani M, Puccini M, Vitolo S. Liquid fuel production from waste tyre pyrolysis and its utilization in a Diesel engine. Fuel 2014;116:399–408.
- [71] Kapura T, Murugan S, Patel SK. Evaluation of a DI diesel engine run on a tire derived fuel-diesel blend. Journal of the Energy Institute, ISSN 1743-9671; 2015. http://dx.doi.org/10.1016/j.joei.2015.07.004.
- [72] Cypres R, Bettens B. Production of benzoles and active carbon from waste rubber and plastic materials by means of pyrolysis with simultaneous post cracking. In: Ferrero GL, Maniatis K, Buekens A, Bridgwater AV, editors. Pyrolysis and Gasification. Elsevier; 1989. p. 200–29.
- [73] Clark C, Meardon K, Russell D. Scrap tire technology and markets. US Environmental Protection Agency Pacific Environmental Services: 1993.
- [74] Bouvier JM, Gelus M. Pyrolysis of rubber wastes in heavy oils and use of the products. Resour Conserv Recvcl 1986;12:77–93.
- [75] Roy C, Chaala A, Darmstadt H. The vacuum pyrolysis of used tires. End-uses for oil and carbon black products. J Anal Appl Pyrolysis 1999;51:201–21.
- [76] Jang JW, Yoo TS, Oh JH, Iwasaki I. Discarded tire recycling practices in the 97: Cypres, R.; Bettens, B. Production of benzoles and active carbon from waste rubber and plastic materials by means of pyrolysis with simultaneous post cracking. In: Ferrero GL, Maniatis K, Buekens A, Bridgwater AV, editors. Pyrolysis and gasification. Elsevier; 1989. p. 209–29 United Sates, Japan and Korea. Resources, Conservation and Recycling 1998; 22: p. 1–14.
- [77] Chan OS, Cheung WH, McKay G. Preparation and characterization of demineralized tyre derived activated carbon. Carbon 2011;49:4674–87.
- [78] Murillo R, Aranda A, Aylo´n E, Calle´n MS, Mastral AM. Process for the separation of gas products from waste tire pyrolysis. Ind Eng Chem Res 2006;45:1734–8.
- [79] Reed TB, Siddhartha GA. Survey of biomass gasification, 2nd ed., The National Renewable Energy Laboratory and the Biomass Energy Foundation Inc, Golden CO; 2001.
- [80] Mendiburu AZ, Carvalho JA, Coronado CJR. Thermochemical equilibrium modeling of biomass downdraft gasifier: stoichiometric models. Energy

2014;66:189-201.

- [81] Basu P. Combustion and gasification in fluidized beds. Taylor & Francis; 2006. p. 355–7.
- [82] Leung DYC, Wang CL. Fluidized-bed gasification of waste tire powders, Fuel Process Technol. vol. 84(1–3); 15 November 2003, p. 175–96. http://dx.doi.org/ 10.1016/S0378-3820(03)00054-7.
- [83] Karatas H, Olgun H, Engin B, Akgun F. Experimental results of gasification of waste tire with air in a bubbling fluidized bed gasifier, Fuel, vol. 105, March 2013, p. 566-71. http://dx.doi.org/10.1016/j.fuel.2012.08.038.
- [84] Song BH, Kim SD. Gasification of tire scrap and sewage sludge in a circulating fluidized bed with a draft tube. Studies in Surface Science and Catalysis, vol. 159. Hyun-Ku Rhee, In-Sik Nam, Jong Moon Park [Editors]. Elsevier B.V.; 2006.
- [85] Donatelli A, Iovane P, Molino A. High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Exp Numer Investig Fuel, vol. 89(10), October 2010, p. 2721-8. http://dx.doi.org/10.1016/j.fuel.2010.03.040.
- [86] Ibrahim F, Elbaba P, Williams T. High yield hydrogen from the pyrolysis-catalytic gasification of waste tyres with a nickel/dolomite catalyst, Fuel, vol. 106; April 2013, p. 528-36. http://dx.doi.org/10.1016/j.fuel.2012.12.067.
- [87] Gang X, Ming-Jiang N, Yong C, Ke-Fa C. Low-temperature gasification of waste tire in a fluidized bed, Energy Convers Manag. vol. 49(8); August 2008, p. 2078– 82. http://dx.doi.org/10.1016/j.enconman.2008.02.016.
- [88] Portofino S, Donatelli A, Iovane P, Innella C, Civita R, Martino M, Matera DA, Russo A Cornacchia G, Galvagno S. Steam gasification of waste tyre: influence of process temperature on yield and product composition, Waste Manag. vol. 33(3); March 2013, p. 672–8. http://dx.doi.org/10.1016/j.wasman.2012.05.041.
- [89] Worley M, Yale J. Biomass gasification technology assessment, Consolidated Report 2012. National Renewable Energy Laboratory (NREL)-SR-5100-57085; 2012.
- [90] Basu P. Biomass gasification and pyrolysis, practical design. Academic Press; 2010. p. 460.
- [91] Heidenreich S, Foscolo PU. New concepts in biomass gasification. Prog. Energy Combust Sci 2014:1–24.
- [92] Paisley MA, Litt RD, Creamer KS. Gasification of refuse-derived fuel in a high throughput gasification system. Energy Biomass Waste 1991;14.
- [93] van der Meijden CM, Veringa HJ, Rabou LPL. The production of synthetic natural gas (SNG): a comparison of three wood gasification systems for energy balance and overall efficiency. Biomass Bioenergy 2010;34(3):302–31.
- [94] Skouloua V, Mariolish N, Zanakish G, Zabaniotoua A. Sustainable management of energy crops for integrated biofuels and green energy production in Greece. Renew Sustain Energy Rev 2011;15:1928–36.
- [95] Samolada MC, Zabaniotou AA. Energetic valorization of SRF in dedicated plants and cement kilns and guidelines for application in Greece and Cyprus. Resour Conserv Recycl 2014;83:34–43.
- [96] Pedroso DT, Machin EB, Silveira JL, Nemoto Y. Experimental study of bottom feed updraft gasifier. Renew Energy 2013;57:311–6.
- [97] Mc Conville A. New Coal Facilities-Overcoming the Obstacles, IEA Coal Research, Gemini House, lo-18 Putney Hill, London SW15 6AA, IEAPERI 26; 1996.
- [98] Taylor LT. Bottom feed updraft gasification system, United States Patent 5607487; 1997.
- [99] Michel-Kim H. Apparatus for producing generator gas and activated carbon from solid fuels, United States Patent 5089030; 1992.
- [100] IREMA. International Renewable Energy Agency. Biomass for power generation. Renewable energy technologies: cost analysis series. Volume 1: Power Sector Issue 1/5, 2012 (www.irena.org)
- [101] E4tech. Review of technology for the gasification of biomass and wastes; 2009.
- [103] Larson ED. Biomass gasification systems for electric power, cogeneration, liquid fuels, and hydrogen. GCEP biomass energy workshop. Stanford University; 2004, April.
- [104] Pérez NP, Machin EB, Pedroso DT, Roberts JJ, Antunes JS, Silveira JL. Biomass gasification for combined heat and power generation in the Cuban context: energetic and economic analysis. Appl Therm Eng 2015;90.