A critical review on Acacia gasification and mix Acacia/Tires co-gasification, and their energy assessments

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Abstract

This paper presents a study that compares the energetic potential of the syngas and the properties of sub-products (chars analysis and tars measurements) originated from the gasification of acacia (an invasive vegetable species in Portugal) and co-gasification of acacia and tires with a mix of 20 wt%. The gasification tests were performed on an AllPowerLabs PP20 Power Pallets - 20kW gasifier, which results from a combination of a downdraft type reactor fixed bed, with an electric power generator and an electronic control unit. The tests were performed at 800 ºC and the collection of gas was carried out when the equipment was stabilized (about two hours to three hours from the start of the tests), as well as the collection of chars and tars at the end of the each test (when the equipment was stopped and cold). The results of the study demonstrated the great potential of both experiments (gasification and co-gasification at 800 ºC) with these materials, where they present similar results for the synthesis gas, both near 4 MJ/Nm3. However, in terms of the composition of chars and tars measurement, they differ slightly but with advantage for the gasification of acacia alone.

Keywords: biomass; thermal gasification; fixed bed; calorific power

Introduction

Issues related to the scarcity of fossil natural resources, the rising prices of fuels derived and the high emissions of greenhouse gases, have increasingly encouraged research and adoption of new technological strategies for energy production from renewable sources. A number of programs and legislation such as the European 20-20-20 objectives have been developed with the aim of consolidating these actions in order to promote environmental and economic sustainability (European Commission, n.d.).

Forest biomass residues are an abundant resource rich in hydrocarbons that exhibit an enormous potential for energy recovery from heat generation processes, without however affecting the environmental balance and guaranteeing sustainability of resources for future generations.

Several studies have demonstrated the feasibility of gasification of forest residues for the production of a gas with good heat properties. Materials such as pine, wood, sawdust and straw have been tried (Niu et al., 2016: 1) (Long et al., 2013: 36). As acacia is an invasive species with a significant presence in the Portuguese territory, with a strong reproductive capacity and that inhibits the balanced growth of the remaining flora, it is possible to produce a high amount of residues of this species during the control operations and that have a considerable potential for energy and material recovery by application of the gasification process (Brito et al., 2013; 59).

The habits of consumption associated with the modern lifestyle lead to the inevitable production of waste and its management and this is a huge problem on a global scale. The option of dumping landfill seems to be a disused solution in developed countries at present, as most landfills have already reached the limit of their capacity and also the existence of new technologies for waste recovery.

In 2015 in Portugal the production of this waste was 17827.01 tons. Thus in recent years, thermal conversion techniques such as combustion and gasification have gained a great deal of interest in energy recovery from non-recycled waste. Therefore, it is of great importance the systematic investigation of waste of flaked tires as fuel for combustion and gasification processes (Demirbas A. 2000; 6:19-40).

Thus, this work intends to compare the composition and properties of the gas and the biochars generated from the gasification of acacia residues and co-gasification of acacia and tires at 800 º C, in a down-flow fixed bed gasifier, were investigated. To determine the extent to which they can be valued at both energy and material use levels in new applications.

Methodology

Materials

This work was performed with acacia chips, provided by a forestry operator. The acacia chips underwent mechanical and manual sorting in order to select particles with dimensions between 1 cm and 4 cm, suitable for this type of reactor. For the co-gasification tests of acacia and tires it was necessary to carry out the mechanical screening to separate only bits between 1 cm and 4 cm compatible with the operation of the Ibert reactor. After sorting by size, a manual sorting was carried out in order to avoid the introduction of pieces of rubber with wires in the reactor, as this would render the reactor unusable.

Equipment

In this work, proximate and ultimate analyzes were carried out to characterize the residues, with determination of calorific value, moisture, volatile and ash contents, and elemental analyzes. Gasification tests were also carried out in order to analyze the quality of the biomass and waste as fuel with particular analysis in the gaseous emissions produced.

The equipment used to carry out the tests and the chemical analyzes of the products, were a Thermal Analyzer ThermoFisher Scientific Flash 2000 CHNS-O Analyzer, to determine the levels of C, S, N, O and H present in the chemical structure); a Calorimeter IKA C200, to determine the higher heating value (HHV); a PerkinElmer STA 6000 thermogravimetric analyzer, to obtain the immediate analysis of the samples (moisture, volatile matter, fixed carbon and ash content) as well as the loss of mass profile as a function of temperature rise; a X-ray Fluorescence Analyzer (XRF) Thermo Scientific Niton XL 3T Gold ++, to identify and quantify the elements in the inorganic fraction of the samples); a Varian 450-GC gaseous chromatograph with TCD detector, used for the identification and quantification of gaseous constituents CO, CO_2, H_2, CH_4 and light hydrocarbons present in the synthesis gas.

For the gasification and co-gasification tests, the PP20 Power Pallets - 20kW gasifier from AllPowerLabs as used, which is a combination of imbert style downdraft fixed bed reactor, an electric power generator and an electronic control unit. The equipment is composed of a storage hooper of biomass, where it is simultaneously made to dry through the recirculation of the hot gases produced in the reactor. The biomass is supplied from the top while the air moves downwards, being preheated through contact with the walls of the reactor. Ash collection is carried out in a separate tank in the lower zone of the reactor, while the synthesis gas produced passes through a cyclone to remove fine particles. The gas is conducted to the biomass hooper in order to dry it (as already mentioned) and is subjected to a new filtration by a filter composed of biomasses of various granulometries, and from here can be collected for analysis or directly injected into the generator. The condensates are collected in this filter. (Figure 1)

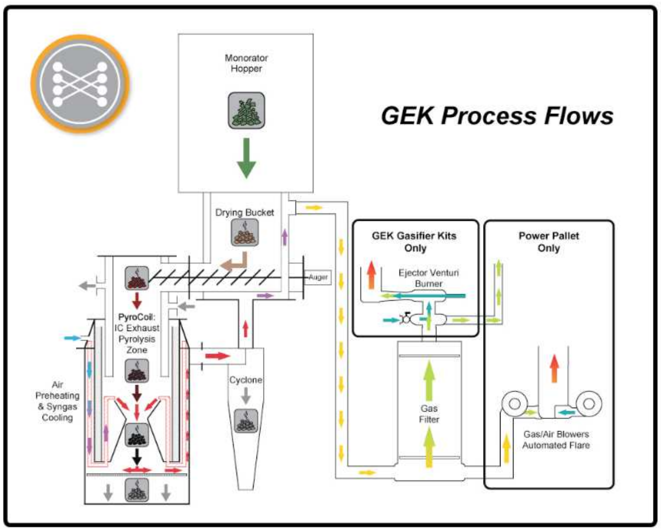

Figure 1 – Gasification unit schematic.

Analyses of the properties and composition of the biomass

The biomass was analyzed by the following parameters: HHV (determined in the calorimeter on a wet basis), elemental analysis (verified with the elemental analyzer), and immediate analysis. Immediate analysis (moisture content, volatile matter and fixed carbon combined with ash) was performed on the thermogravimetric analyzer using a nitrogen flow of 20 mL/min to inert the atmosphere, and a temperature growth rate of 20°C/min. The contents of each type of matter were determined from the thermogravimetric profile (variation of sample mass vs. temperature), taking into account the inflection points of the mass derivative in order of time.

Gasification and co-gasification tests

The gasification tests were carried out in series due to reactor specifications and for efficient analysis of multiple parameters. That is, at the end of each test, the reactor was deactivated and cooled to perform the maintenance and measurement of raw material consumption, as well as its by-products (chars and condensates). This experiment was based on two assays (gasification and co-gasification), with duplicate replication of each, at a temperature of approximately 800°C with duration of 8 hours. In the case of the co-gasification a mixture of 80 wt% of acacia and 20 wt% of tires was made, since it is considered the ideal to work with this type of reactor. With higher percentages of tires, there were problems of biomass admission in the reactor and problems of oxidation of the biomass itself at this temperature. During the tests, the values of temperature and pressure in the upper and lower parts of the reactor (i.e. oxidation and reduction zones, respectively), pressure in the biomass particle filter, inlet air flow and finally the amount of biomass consumed during the test were monitored. The gas samples were withdrawn from the biomass particle filter into suitable bags with the help of a vacuum pump, one when the gasification process was stabilized (zero or near zero temperature variation) and another at the end of the process, before the equipment is closed. The chars were captured in the bottom of the reactor and in the cyclone filter, which was downstream of the reactor. The condensates were collected at the bottom of the biomass particulate filter. Table 1 shows the gasification conditions considered.

Table 1 - Gasification conditions used in the various tests.

Parâmeters	Unit	Test			
		Gasification (acacia)		Co-Gasification (80% acacia + 20% tires)	
		1	2	3	4
Oxidation Temperature	(ºC)	808	810	802	803
Reduction Temperature	(ºC)	524	508	574	571
Filter Pressure	(mbar)	-107,1	-117,07	-129,35	-141,98
Oxidation Pressure	(mbar)	-7,47	-10,02	-19,98	-24,9
Reduction Pressure	(mbar)	-42,34	-51,03	-37,36	-39,49
Biomass Flow	(kg/h)	7,2	7,4	5,1	4,9
Inlet Air Flow	(m^3/h)	18	18	24	24

Analysis of the composition and properties of the gas

Analysis of the synthesis gases was determined by gas chromatography. Each bag containing the synthesis gas was analyzed using a peristaltic pump to inject the samples, where the components were separated through a set of specific columns using helium and nitrogen as entrainment gases. Two thermal conductivity detectors allowed later to detect the several species that were quantified through the evaluation of their areas.

Analysis of the composition and properties of the chars

For each chars sample obtained, the mass and the total volume were determined, as well as the HHV on a wet basis, the composition of the inorganic fraction, the thermogravimetric profile and the immediate analysis. The HHV was measured in duplicate in the calorimeter and the final value was calculated from the average of the measurements made. The masses of the samples used in the test ranged from 0.3 to 0.4 g. The composition of the inorganic fraction was determined by X-ray fluorescence emission using XRF. The tests were performed in triplicate and each lasting 180 s, and the final fraction of each oxide was calculated from the mean of the values obtained experimentally. The thermogravimetric profile (mass reduction as a function of temperature) was determined using the thermogravimetric analyzer, considering a nitrogen atmosphere with a gas inlet flow of 20 mL / min. The apparatus has been programmed to perform a temperature increase rate of 20 ° C / min, within a range of 30 to 995 ° C. The initial masses of the samples were between 8 and 10 mg. The immediate analysis (moisture, volatile matter and fixed carbon + ash contents) was estimated from the graphs of the thermogravimetric profile and the mass derivative in order of time, using simultaneously the location of the inflection points of the last curve.

Results and Discussion

Analysis of the composition and properties of the biomass

The elemental, immediate and HHV analyzes for acacia are shown in Table 2. Figure 2 presents the thermogravimetric profile of acacia and tires, where it is possible to observe a rapid degradation of cellulose among 300-400 ºC in the case of acacia and of the polymeric structure among 400-500 ºC in the case of tires. The calculated HHV (17 MJ / kg) and the elemental analysis are similar to the results reported by other studies (S. Sarker, 2014 and Dinh Quoc Viet, 2015). The same HHV is in the range obtained for coal (14.6 MJ / kg to 26.7 MJ / kg (Manara & Zabaniotou, 2012: 2570)), which reveals potential for energy production.

Table 2 - Properties of the acacia.

Parâmeters		**Units**	**Value**
HHV		(MJ/kg)	17
Instantaneous analysis	Moisture	(% mass)	14,2
	Volatil	(% mass)	49,7
	Fixed Carbon	(% mass)	32,1
	Ashes	(% mass)	4
Elemental Analises	Nitrogen	(% mass)	0,3
	Carbon	(% mass)	44,1
	Hidrogen	(% mass)	5,6
	Sulfur	(% mass)	0
	Oxigen	(% mass)	49,9

Results for proximate analysis (dry basis) are also near to the previously mentioned studies. The elemental, immediate and LHV analyzes for tires are shown in Table 3.

The HHV calculated for the tires (38MJ / kg) was twice that of the acacia. These same results are similar to those reported by other studies (U.P.B. Sci. Bull., Series D, Vol. 74, Iss. 4, 2012). This value is so high that tires could be a risk for equipment not prepared to withstand fuels with such a high calorific value. Biomass energy production equipment usually has a recommended limit of 18 MJ / kg for LHV.

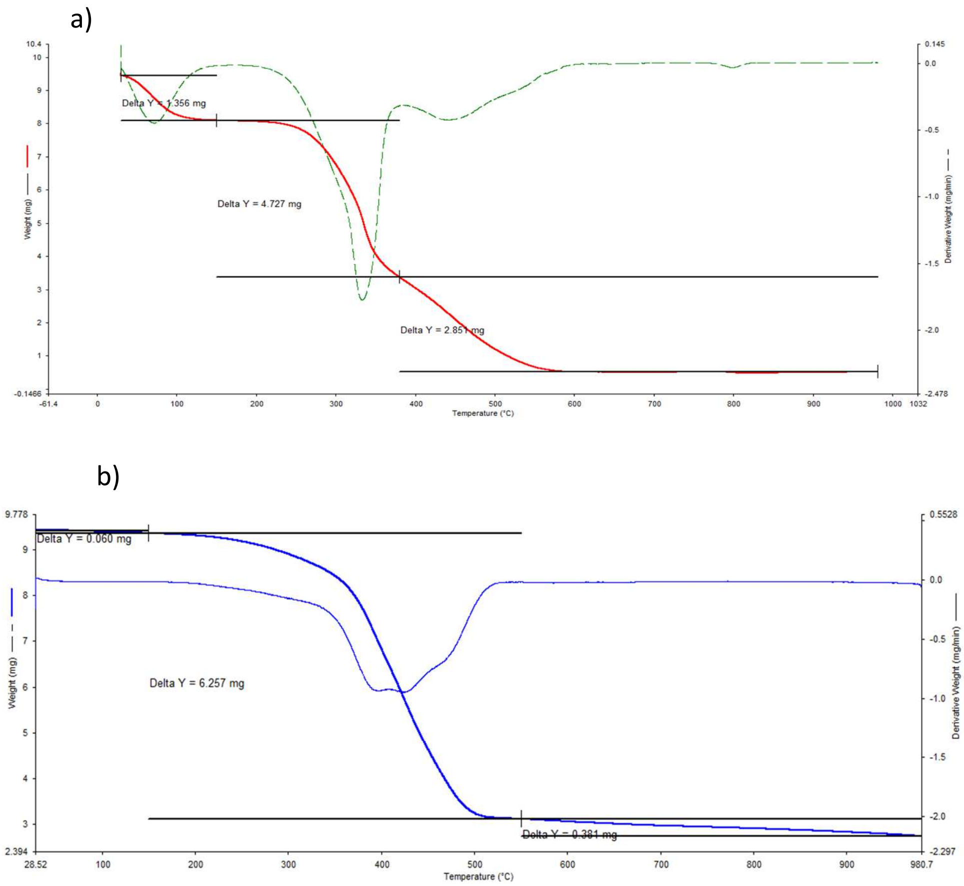

Figure 2 - Thermogravimetric profile of a) acacia and b) tires.

Table 3 - Properties of the tires.

Parâmeters		**Units**	**Value**
LHV		(MJ/kg)	38,6
Immediate analysis	Moisture	(% mass)	0,8
	Volatil	(% mass)	64,5
	Fixed Carbon	(% mass)	29,6
	Ashes	(% mass)	5,1
Elemental Analises	Nitrogen	(% mass)	0
	Carbon	(% mass)	75,5
	Hidrogen	(% mass)	7,1
	Sulfur	(% mass)	5,6
	Oxigen	(% mass)	11,8

The energetic difference between acacia and tires, despite the difference in materials, can be justified by the greater amount of moisture and oxygen present in the acacia compared to the tires, which for its turn has a much higher carbon concentration and lower humidity.

Analysis of the composition and properties of the gas

Table 4 shows the volume production, compositions and lower heat value (LHV) of the gases and condensates produced from acacia gasification.

Table 4 - Production and composition results of condensates and generated gases from the gasification of acacia.

Parameter / Product		Units	Test Acacia	
			1	2
Temperature		(°C)	808	810
Condensates		(cm^3/h)	8,6	8,6
Gases	CO_2	(% volume)	13,31	12,4
	Ethylene	(% volume)	0,28	0,45
	Another Gases	(% volume)	0	0
	Ethane	(% volume)	0	0
	Acetylene	(% volume)	0	0,19
	H_2S	(% volume)	0	0
	N_2	(% volume)	63,99	70,46
	CH_4	(% volume)	4,35	1,74
	CO	(% volume)	11,26	8,42
	H_2	(% volume)	6,8	6,32
LHV of the Gas		(MJ/Nm^3)	3,83	2,69

A first analysis shows that the gas produced is relatively rich in carbon monoxide (with percentages ranging from 8% to 11%), molecular hydrogen (6%), methane (2% to 4%) and traces of ethylene (less than 0.5%), and these last four gases are the main ones that contribute effectively for the global calorific value. The rate of condensate production is relatively low in both tests.

The analysis of the results obtained with the acacia biomass allowed verifying that, at a temperature of 808° C, the LHV of the gas was about 4 MJ/Nm^3. The main components of the synthesis gas (H_2, CO, CH_4 and CO_2) underwent changes with increasing temperature and residence time inside the reactor. The variation of LHV between the two tests was justified by the increase of nitrogen in the gas and by the lower presence of CO and H_2, in the test at 810 ° C, which caused an energetic decrease.

Table 5 shows the volume productions, compositions and lower heat value (LHV) of the gases and condensates produced by the co-gasification of acacia and tires. The data presented in the co-gasification are similar to those of gasification, in terms of the calorific value of the gas and its components, but in the evaluation of production of condensates, the tests show that there is four times more production of this liquid. These results may suggest that the co-gasification temperature must be increased in order to attenuate the generation of condensates.

Table 5 - Production and composition results of condensates and generated gases from the co-gasification of acacia and tires.

Parameter / Product		Units	Test Acacia and Tires	
			3	4
Temperature		(°C)	803	802
Condensates		(cm^3/h)	38	38
Gases	CO_2	(% volume)	10	8,1
	Ethylene	(% volume)	0,4	0,2
	Another Gases	(% volume)	0	0
	Ethane	(% volume)	0	0
	Acetylene	(% volume)	0	0
	H_2S	(% volume)	0	0
	N_2	(% volume)	54,3	61,2
	CH_4	(% volume)	3,6	3,4
	CO	(% volume)	10	5,9
	H_2	(% volume)	6,8	3,6
LHV of the Gas		(MJ/Nm^3)	3,48	2,45

The analysis of the results obtained with the mixture of acacia and tires allowed verifying that, at a temperature of 803 ° C, the LHV of the gas was about 3.5 MJ/Nm^3, which was similar to the result found for acacia alone. The variation of LHV between the two tests is justified by the lower presence of CO and H_2, in the test at 802°C, which caused an energy content decrease. This situation also happened with the gasification of acacia alone. As noted, both tests are very similar in terms of energy obtained from the gases. LHV tends to increase with the decrease of the equivalence ratio, due to the higher nitrogen content inside the reactor. It was also found that CO_2 remains constant throughout the tests, which suggests that the combustion reactions also increase, as can be seen by the decrement of CO:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad (1)$$

A more detailed evaluation shows clearly in the tests of elemental analysis that the tires contain a very high carbon content compared with acacia. The amount of unburnt carbon is given, along with the processing conditions, by the reactivates of the carbon with H_2O (g) and CO_2. In this context, two reactivity parameters that provide relevant information on the unburned carbon would have to be evaluated: the temperature of the start of coal gasification and the rate of gasification at the test temperature. This can be a possible justification that, with the mixture of acacia/tires, the calorific value of the gas goes down, and there is also a lot of material unburned inside the reactor at the end of the test (Straka, 2009).

Composition and properties of biochars produced

The HHV values of the biochars resulting from the gasification and co-gasification tests are specified in Table 8.

Table 8 - Composition and HHV values of the produced biochars.

Testes	Temperature (ºC)	Mass (g)	Volume (cm³)	Density (g/dm³)	HHV (MJ/kg)
Acacia Gasification	808	64,98	283,72	229	15,2
	810	63,44	277		13,37
Acacia/Tires Co-gasification	802	231,05	1008,84		5,5
	803	221,3	966,27		5,9

The results demonstrate that biochars produced during acacia gasification have a high caloric value (about 15 MJ/kg), unlike the ones produced during the co-gasification process (about 5 MJ/Kg) and which makes them uninteresting in terms of energy use. This difference can be explained by the composition of both biomasses, where the amounts of volatiles and ashes present in the tires are higher compared with acacia: during the thermal conversion processes, the volatiles will be the first substances to be consumed and the ashes will always remain in more quantity than the carbon at the end.

For the case under study, the HHV obtained in gasification (15 MJ/kg) is within the range where the fossil fuels are fitted (14.6 MJ/kg to 26.7 MJ/kg (Manara & Zabaniotou, 2012: 2570)). It would therefore be interesting to try a steam gasification of these chars for the production of a synthesis gas in order to evaluate their calorific content, as had been proposed in other works using chars from sludge, rapeseed and miscanthus (Sattar Et al., 2014: 276). It would also be relevant to determine the nitrogen content present in the biochars, which could give rise to pollutants such as NOx after the respective gasification in order to determine the necessity to install a gas purifier at the outlet of the gasifier (e.g. filters catalysts with platinum and TiO_2, or addition of aqueous solutions of ammonia in the gas stream).

The thermogravimetric profiles of the biochar samples obtained under the different tests are shown in Figure 3. It is possible to infer an abrupt reduction in the mass of acacia among 650-750 ºC that does not happen in the case of the mixture acacia/tires possibly due to sinergetic effects.

Figure 4 presents the results for immediate analysis of biochars for comparison. Both tests show similar moisture contents. In terms of volatile matter and fixed carbon there is a significant difference. This last aspect corroborates what was previously mentioned, where it is difficult to oxidize the large amount of carbon that exists in the tires and, therefore, the volatile matter is more easily consumed (Straka, 2009). The low moisture content suggests the possibility of direct combustion of the biochar to obtain energy without the application of a drying pre-treatment and the consequent additional energy consumption. From a qualitative point of view, high fixed carbon + ash and low volatile matter and moisture content are in harmony with other studies conducted on other lignocellulosic residues, such as rice husk (Shackley et al., 2012: 53).

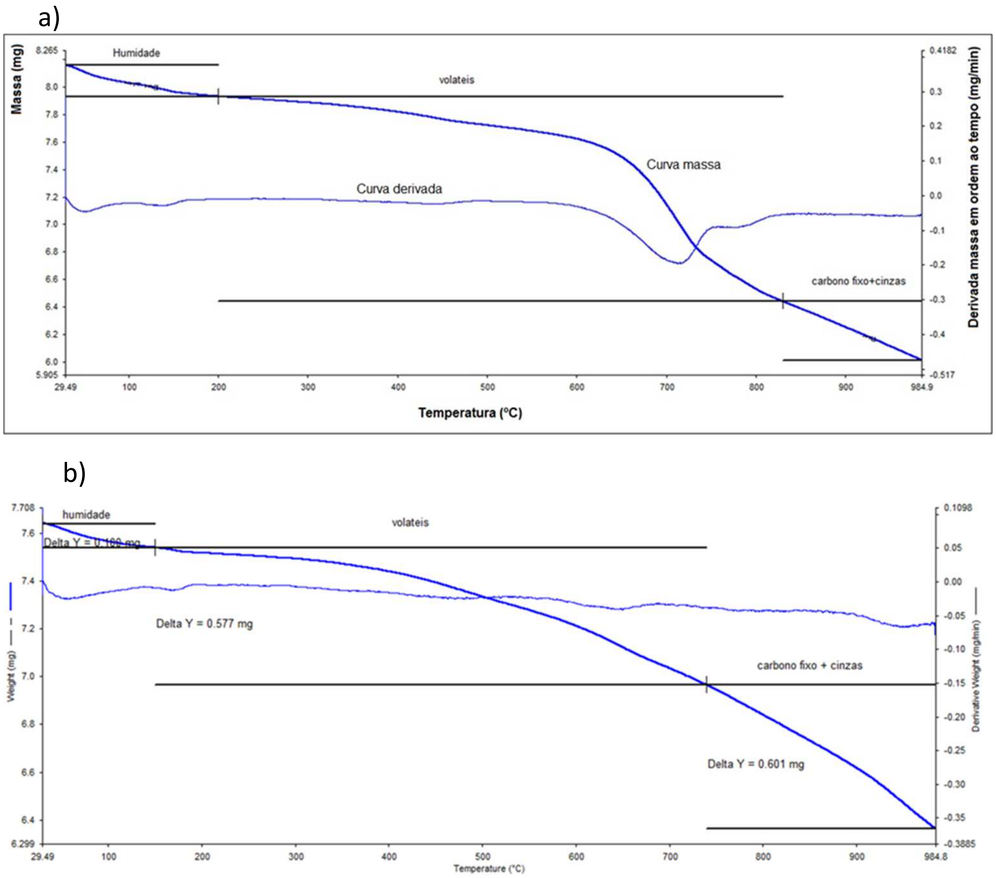

Figure 3 - Thermogravimetric profile of a) acacia b) acacia/tires chars.

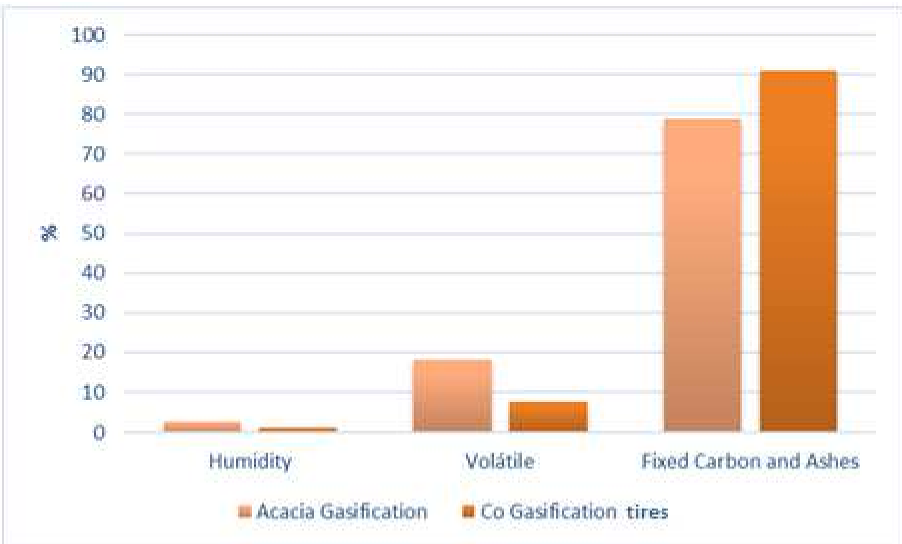

Figure 4 – Thermogravimetric profile comparison.

Figures 5 and 6 shows the inorganic fraction of the ashes obtained in both tests.

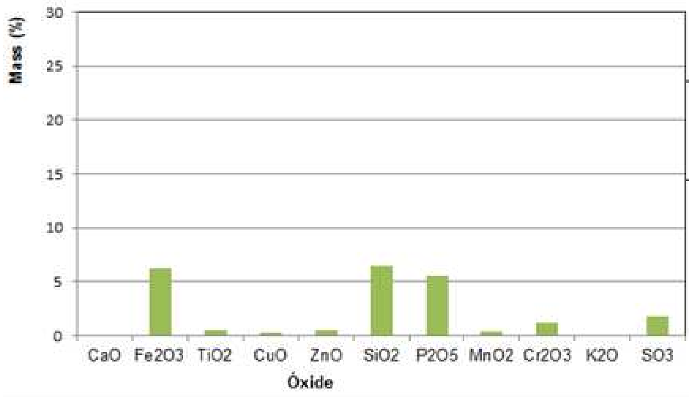

Figure 5 –Inorganic analyses of acacia ashes (XRF).

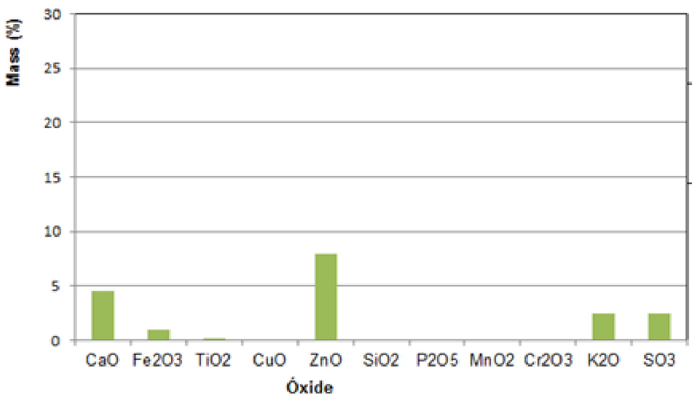

Figure 6 –Inorganic analyses of acacia/tires ashes (XRF).

The inorganic study of the ashes shown a great difference that exists in their composition. While acacia ashes have a high phosphorus and iron content, ashes of acacia/tires have a high zinc, potassium and sulfur contents. The massive amount of Fe and P and other micronutrients in trace amounts, namely Zn and Cu, suggests the use of biochars as fertilizer for agricultural soils in the case of acacia (Jha et al., 2010: 1222). The excess of Fe may also catalyze the decomposition of the tars formed during gasification, so it would be of interest to conduct gasification tests using these biochars as catalysts (Shen, 2015: 287). On the contrary, ashes of acacia/tires show a significant amount of Zn (a heavy metal) that may prevent their use as a fertilizer or cement additive.

Conclusions

In the present study, the thermal gasification of acacia and co-gasification of acacia (80 wt%) and tires (20 wt%) were analyzed in a fixed downdraft bed at 800 ºC.

The study carried out at 800 º C tends to favor the thermal cracking reactions and the increase of the concentration of carbon monoxide, which will increase the calorific value of the synthesis gas.

In addition, this work has demonstrated the feasibility of transforming waste or energy crops and highly polluting waste into valuable, hydrogen-rich gas and other products that are highly relevant in terms of heating power and are of interest to the chemical industry. It also showed that the thermal gasification unit performed very well during the tests.

The optimum gasification condition for the production of a synthesis gas with the highest LHV occurred with acacia at 808 ºC, reaching a value of 3.83 MJ / N m^3 with contents of H_2, CO and CH_4 of 6.8 vol%, 11.26 vol% and 4.35 vol%, respectively.

For the co-gasification of acacia/tires the most relevant value of LHV was obtained at a temperature of 803 ºC, reaching a value of 3.48 MJ / N m^3 and with levels of H_2, CO and CH_4 of 6.8 vol%, 10 vol% and 3,6 vol%.

The inorganic and immediate composition of the biochars are quite different for the tests performed. It can be affirmed that the higher levels of Fe and P (in the case of acacia) enable them for soil fertilization operations and possibly as catalysts during the decomposition of tars. However, it would be relevant to determine the nitrogen content present to qualitatively assess the emission of the NOx pollutant during the energetic recovery by gasification as well as the actual quantities of nutrients that would be deposited in the soil through the agricultural valorization of these by-products.

For similar massic flows of biomass, it seemed than mono-gasification of acacia is more favorable compared with co-gasification of acacia/tires since both produce a syngas with similar calorific values but the former generates less condensates and biochars, which is an advantage for a process that aims to maximize the production of the gas fraction for energy valorization.

As suggestions for future work on biochar recovery, it is proposed a study of the area and surface porosity in order to ascertain the characteristics as adsorbent of contaminants in effluents, or the use as a catalyst during the gasification to improve H_2 production.

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