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Elemental Composition and Flue Gas Emissions of Different Components from Five Semi-Arid Woody Species in Pyrolysed and Non-Pyrolysed Material

Maginot Ngangyo Heya¹, Rahim Foroughbakhch Pournavab¹, Artemio Carrillo Parra^{2,*}, Volker Zelinski³  and Lidia Rosaura Salas Cruz⁴ 

¹ Facultad de Ciencias Biológicas (FCB), Universidad Autónoma de Nuevo León (UANL), Av. Universidad s/n Cd. Universitaria, San Nicolás de los Garza 66451, Nuevo León, Mexico; nheyamaginat@yahoo.fr (M.N.H.); rahimforo@hotmail.com (R.F.P.)

² Instituto de Silvicultura e Industria de la Madera (ISIMA), Universidad Juárez del Estado de Durango (UJED), Boulevard del Guadiana #501, Ciudad Universitaria, Torre de Investigación, Durango 34120, Mexico

³ Faculty of Resource Management, University of Applied Sciences and Arts (HAWK), Büsgenweg 1A, D-37077 Gottingen, Germany; volker.zelinski@hawk.de

⁴ Facultad de Agronomía (FA), Universidad Autónoma de Nuevo León (UANL), Francisco Villa s/n, Col. Ex-Hacienda “El Canadá”, Escobedo 66050, Nuevo León, Mexico; biolidiasalas@yahoo.com.mx

* Correspondence: acarrilloparra@ujed.mx; Tel.: +52-1-618-180-9912

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Abstract: Biofuels are sustainable alternatives to fossil fuels. However, they must comply with energy efficiency requirements and contribute to environmental protection. This study was focused on elemental composition (carbon, hydrogen, nitrogen, sulphur and chlorine) of different plants' components (stems, branches, twigs and leaves) from pyrolysed (charcoal) and non-pyrolysed samples of five semi-arid trees: *Acacia berlandieri*, *A. wrightii*, *Ebenopsis ebano*, *Havardia pallens* and *Helietta parvifolia*. Carbon fluctuated from 80.77% to 89.30% in charcoal and 44.99% to 49.70% in non-pyrolysed biomass, and hydrogen ranged from 2.38% to 2.69% in charcoal and 5.89% to 6.62% in non-pyrolysed biomass. Nitrogen accounted for 0.39%–0.65% (branches) and 0.32%–0.64% (stems) in charcoal, and the ranges for non-pyrolyzed material were 2.33–4.00% (leaves), 1.06%–1.76% (twigs), 0.21%–0.52% (branches) and 0.15%–0.28% (stems). Considerably higher concentrations of sulphur compared to chlorine were found, with increasing values for both elements from the base of trees to the leaves. Non-pyrolysed samples were characterized by 68.05 mg/kg–769.16 mg/kg (stems), 118.02 mg/kg–791.68 mg/kg (branches), 225.11 mg/kg–1742.25 mg/kg (twigs) and 374.73 mg/kg–6811.52 mg/kg (leaves) for sulphur, and 117.86 mg/kg–528.08 mg/kg (stems), 109.18 mg/kg–464.15 mg/kg (branches), 905.47 mg/kg–4205.19 mg/kg (twigs) and 2799.68 mg/kg–5072.76 mg/kg (leaves) for chlorine. In charcoal, the concentration ranges for sulphur were 47.54 mg/kg–376.95 mg/kg (branches) and 42.73–292.20 mg/kg (stems) and 139.34 mg/kg–419.68 mg/kg (branches) and 177.39 mg/kg–479.16 (stems) for chlorine. The study has shown that pyrolysis increased the amount of carbon and decreased the amount of hydrogen. Coincidentally, the amount of nitrogen, chlorine and sulphur could be decreased significantly by pyrolysis which means an improvement of the fuel considering the flue gas emissions. Besides the influence of the type of combustion plant and the influence of the source of biofuel, the treatment has a significant influence on the amount and composition of flue gases emitted in the combustion.

Keywords: biofuels quality; pyrolysis; sulphur and chlorine; elemental analysis; semi-arid woody species

1. Introduction

Energy produced from biomass is a sustainable alternative in the long-term perspective to petroleum to lower emissions of carbon dioxide (CO₂) and sulphur oxide (SO_x), as well as nitrogen oxides (NO_x) [1,2]. In addition, it reduces energy dependence and contributes to increased employment in rural areas and technological development. For now, governments resume the momentum to the development of biofuels [3] to partially replace fossil fuels and nuclear energy in four different markets: the generation of electricity, thermal applications, transportation fuels and energy services [4].

However, a decade after its implementation, the official reports of the United Nations (UN) and Non-Governmental Organizations (NGOs) exposed serious unforeseen consequences to the increase in the international production and consumption of biofuels [5], which raises further questions about the social, economic and environmental benefits or harms of large-scale production. As a by-product of fuel combustion [6], flue gas is composed of Greenhouse Gases (GHG) that consist of CO₂, N₂, oxygen (O₂) and water (H₂O), sulphur dioxide (SO₂), nitrogen oxides (NO_x) and hydrogen chloride (HCl), entailing negative effects on the environment [7]. Therefore, burning biomass is a precursor of significant amounts of short-living global warming substances, such as black carbon, and also significantly contributes to ozone formation by photochemical reactions among its precursor VOCs and NO_x [8].

Faced with this situation, the prevention and control of pollution have gained particular importance [9], therefore there has been great variation in fuel quality requirements which are no longer only the result of considerations about the evolution and design of engines and technologies, however are mainly a consequence of the growing concern for environmental protection. Nowadays, pyrolysis, a thermal treatment of organic material, is getting attention for its lower emissions of air pollutants [10,11], and it additionally provides an opportunity of transforming materials of low-energy density into bio-fuels of high-energy density, while at the same time recovering highly-valued chemicals [12,13].

Carbon, hydrogen, oxygen and nitrogen are the main constituents of natural organic as well as inorganic components found in solid and liquid fuels [14]. These elements are involved in the oxidation reactions and can therefore define the calorific potential of biofuels. However, for the control of pollution resulting from the combustion of biomaterials, the sulphur and chlorine contents are parameters that indicate the quality of fuels causing problems both to the equipment itself as well as to the environment and health [15]. Emissions of NO_x, HCl, SO_x and particles and the performance of boilers depends mainly on physical and chemical properties of the biomass including moisture, ash content, Cl, S and N [16].

In accordance with the above concerns, it is important to know the potential impacts related to the use of biofuels on the environment in the coming years. To do that, it is necessary to look at the interactions between chemical biomass characteristics and flue gas emissions in order to establish their identity, their purity and their potential effect on the environment. The aim of this study was to determine the elemental composition and emission of sulphur, chlorine and nitrogen of different components from five semi-arid tree species in pyrolysed and non-pyrolysed conditions.

2. Materials and Methods

2.1. Study Area

The research was conducted in experimental plantations that were 30 years old at the Forest Sciences Faculty field of the Nuevo Leon Autonomous University (UANL) at Linares. The plantation is located at north latitudes 24°47' and west longitudes 99°32' in the altitude of 430–450 m at the Sierra Madre Oriental, Mexico [17]. According to Köppen classification [18], modified by García [19], the climate conditions in this region are classified as semi-arid and sub-humid of type (A) C (Wo), presenting two rainy seasons in summer and autumn and a dry season from April to November.

2.2. Selection of Species and Sampling Design

The tree species were selected according to their importance value index, determined by frequency and abundance, based on the work of Cabral and Treviño [20]. The selected species are: *Acacia berlandieri* Benth (Mimosaceae), *A. wrightii* Benth. (Mimosaceae), *Ebenopsis ebano* (Berl.) Barneby (Mimosaceae), *Havardia pallens* (Benth.) Britton & Rose. (Mimosaceae) and *Helietta parvifolia* (Gray.) Benth. (Rutaceae).

The sampling consisted of three plots per tree species for a total of 15 plots with the dimensions 10 × 10 m. In each plot, there were about 25 trees with a distance of 3 m among them, of which one tree that was without any visible defects and representative of the community was cut down and separated into stems, branches, twigs and leaves, forming two groups of samples: group 1 for the purpose of treatment by pyrolysis, consisting of stems and branches; group 2 for the physical and chemical analysis of the untreated material, consisting of stems, branches, twigs and leaves.

Samples of group 1 were cut to 2 cm length and were placed in a climatic chamber at 65% of relative humidity and 20 °C temperature until constant weight to homogenize their moisture content (MC) at 12% before submitting them to pyrolysis at 650 °C for three hours, according to Briseño-Urbe et al. [21]. The product obtained (charcoal), classified as “pyrolysed biomass”, was milled and screened through an ultra-centrifugal mill (mark RESTCH, model ZM 200) at 425 µm particles size for further analysis.

The second group of samples was splintered, outdoor dried and ground in a Wiley machine (Model 4 Bench, 115 V, 50/60 Hz). The sawdust obtained (non-pyrolysed biomass) was screened using different sieves, and the fraction containing particles from 40 mesh (425 µm) to 60 (250 µm) was used for the chemical analysis [22].

2.3. Biofuels Elemental Characterization

The amounts of carbon, hydrogen and nitrogen of the studied solid biofuels were evaluated through elemental analysis which was carried out according to the standard EN 15,103. Specifically, 5 mg to 10 mg of the dried and milled sample was placed in a tin boat, weighted to the nearest 0.01 mg and folded into an airtight ball. Then, the material was combusted at 1050 °C in a CHN analyzer, type Vario EL III, from Elementar GmbH. During the combustion, the organic material was converted to CO₂, H₂O and N₂, and was carried by helium (He) through different absorption columns to the thermal conductivity detector to evaluate nitrogen (N), carbon (C) and hydrogen (H) contents. Nitrogen reaches directly to the detector, while two absorption tubes kept water and CO₂ until releasing them by warming the columns successively.

2.4. Sulphur and Chlorine Determination

For the analysis of sulphur and chlorine, the samples were decomposed according to the standard EN 15,289 using a calorimeter (IKA C 7000) for the combustion of pellets made from about 1 g of each sample through a laboratory press. The resulting residues were recovered and diluted in 100 mL of distilled water.

Sulphur and chlorine were determined through an Ion chromatograph, type Basic IC plus 883 from Metrohm Deutschland GmbH, according to EN 15,289. The method consisted of passing the fluid through a cationic and/or anionic exchanger which allows the replacement of cations with the hydrogen ion (H⁺) and anions with hydroxyl ion (OH⁻). Separation of the analytes sulfate and chloride was done with a Metrosep A Supp 5–150/4 column. The retention times are given in Figure 1, showing the sufficient selectivity.

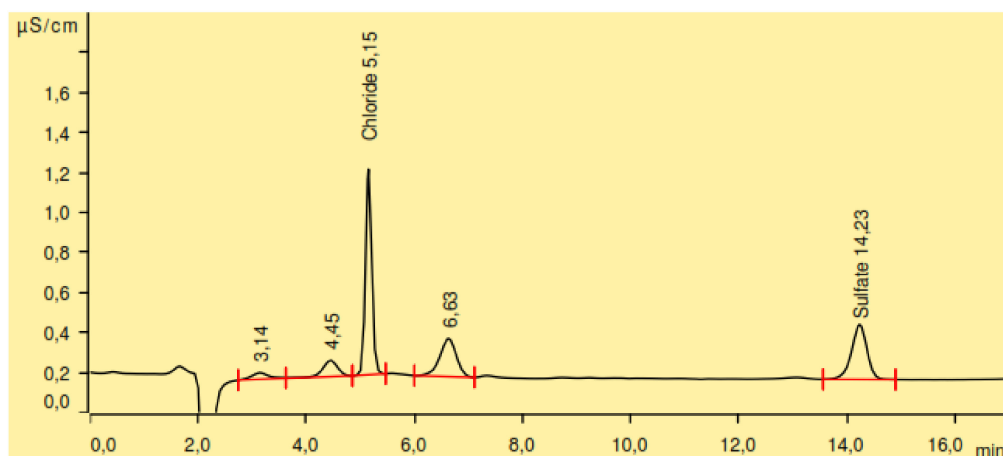


Figure 1. Selectivity and retention time of SO_4^{2-} and Cl^- in a standard solution.

2.5. Statistical Analysis

The data significance was determined at $\alpha = 0.01$ through a one-way analysis of variance with four levels: stems, branches, twigs and leaves. All statistical analyses were done with the Statgraphics program, version 7.0 (Statgraphics Technologies, Inc., The Plains, Virginia, USA).

Since the elemental analysis values were percentages, they were transformed using the arcsine sum of square function [23]. Then, the Kolmogorov-Smirnov normality tests were applied for all the variables. The experimental design was randomly complete blocks, performing the multiple comparison Tukey's tests where significant differences among treatments were detected at 95% confidence level ($p = 0.05$) [24]. Simple regressions were used to determine relationships between the sulphur and chlorine and the main elemental constituents of the forest biomass was analyzed (Carbon, Hydrogen and Nitrogen) both in pyrolysed and non-pyrolysed conditions, using simple linear models of Equation (1):

$$y = ax + b. \quad (1)$$

3. Results

3.1. Carbon, Hydrogen and Nitrogen in Pyrolysed and Non-Pyrolysed Material from Different Components of Semi-Arid Tree Species

The contents of carbon, hydrogen and nitrogen showed significant statistical differences ($p < 0.05$) for all the studied species. The carbon amount ranged from 80.77 to 89.30 % in charcoal (pyrolysed biomass) and from 46.32% to 49.70 % for the same components (stems and branches) in non-pyrolysed biomass, while twigs and leaves presented slightly lower amounts of carbon in the ranges of 46.39%–47.21% and 44.99%–47.43%, respectively (Table 1).

Table 1. Amounts of the major elements carbon, hydrogen and nitrogen in different components from five semi-arid woody species in pyrolysed and non-pyrolysed material.

		Non-Pyrolysed Biomass				Pyrolysed Biomass	
		Stems	Branches	Twigs	Leaves	Stems	Branches
		[%]	[%]	[%]	[%]	[%]	[%]
Carbon	<i>H. parvifolia</i>	49.29 ± 0.66	48.80 ± 0.28	46.39 ± 0.85	44.99 ± 0.87	84.81 ± 1.23	85.89 ± 0.83
	<i>E. ebano</i>	49.70 ± 0.44	48.14 ± 0.83	47.14 ± 0.81	46.09 ± 0.52	84.54 ± 0.92	83.19 ± 1.09
	<i>A. berlandieri</i>	47.21 ± 0.69	46.32 ± 0.71	47.21 ± 0.95	47.17 ± 0.24	84.17 ± 0.45	80.77 ± 0.23
	<i>H. pallens</i>	47.79 ± 0.72	48.35 ± 0.94	46.93 ± 0.56	46.74 ± 0.08	81.99 ± 0.33	82.76 ± 0.77
	<i>A. wrghtii</i>	48.92 ± 0.65	47.96 ± 0.22	46.92 ± 0.59	47.43 ± 0.19	85.84 ± 1.25	89.30 ± 1.37
Hydrogen	<i>H. parvifolia</i>	6.41 ± 0.12	6.51 ± 0.15	6.32 ± 0.17	6.20 ± 0.23	2.55 ± 0.05	2.54 ± 0.11
	<i>E. ebano</i>	5.89 ± 0.13	6.17 ± 0.19	6.27 ± 0.09	6.55 ± 0.08	2.38 ± 0.09	2.42 ± 0.07
	<i>A. berlandieri</i>	6.26 ± 0.17	6.31 ± 0.17	6.34 ± 0.24	6.37 ± 0.09	2.49 ± 0.17	2.51 ± 0.04
	<i>H. pallens</i>	6.39 ± 0.04	6.62 ± 0.21	6.55 ± 0.07	6.54 ± 0.09	2.69 ± 0.02	2.61 ± 0.09
	<i>A. wrghtii</i>	6.17 ± 0.03	6.37 ± 0.04	6.46 ± 0.05	6.40 ± 0.14	2.62 ± 0.14	2.69 ± 0.08
Nitrogen	<i>H. parvifolia</i>	0.27 ± 0.05	0.21 ± 0.03	1.06 ± 0.15	2.33 ± 0.33	0.64 ± 0.02	0.52 ± 0.11
	<i>E. ebano</i>	0.24 ± 0.05	0.39 ± 0.13	1.73 ± 0.22	3.21 ± 0.14	0.48 ± 0.03	0.65 ± 0.12
	<i>A. berlandieri</i>	0.15 ± 0.05	0.52 ± 0.45	1.39 ± 0.01	4.00 ± 0.09	0.39 ± 0.07	0.51 ± 0.05
	<i>H. pallens</i>	0.28 ± 0.08	0.34 ± 0.09	1.76 ± 0.15	3.12 ± 0.03	0.57 ± 0.04	0.52 ± 0.06
	<i>A. wrghtii</i>	0.15 ± 0.05	0.21 ± 0.05	1.34 ± 0.16	2.58 ± 0.06	0.32 ± 0.08	0.39 ± 0.02

For hydrogen, the ranges 2.38%–2.69% were registered for charcoal and 5.89%–6.62% for the corresponding components (stems and branches) in non-pyrolysed biomass (Table 1), indicating more carbon in charcoal than in non-pyrolysed biomass and less hydrogen in charcoal than in non-pyrolysed biomass. The amounts of hydrogen for twigs and leaves were in the range of 6.20%–6.55%, which is similar to the amounts found in stems and branches for the non-pyrolysed samples. The change of carbon and hydrogen amounts showed the opposite behavior of trough treatment by pyrolysis when considering the same components.

The amount of nitrogen showed highly significant statistical difference ($p < 0.001$) among the species as well as between the components. In the non-pyrolysed biomass samples, nitrogen showed decreasing amounts from leaves with 2.33%–4.00% and 1.06%–1.76% for twigs, down to 0.21%–0.52% in branches and stems with 0.15%–0.28%. The highest value was found in leaves of *Acacia berlandieri*. The pyrolysed biomass showed amounts of 0.39%–0.65% for branches and 0.32%–0.64% for stems.

3.2. Chlorine and Sulphur in Pyrolysed and Non-Pyrolysed Biomass

There were significant statistical differences ($p < 0.05$) among species and highly significant differences ($p < 0.01$) among plants' components, showing very high concentrations of sulphur compared to chlorine, with increasing values from the base of plants to the leaves. In the pyrolysed biomass (charcoal), the concentrations of sulphur ranged from 47.54 mg/kg to 376.95 mg/kg (branches) and 42.73 mg/kg to 292.20 mg/kg (stems). The concentrations for chlorine were in the ranges of 139.34 mg/kg–419.68 mg/kg (branches) and 177.39 mg/kg–479.16 mg/kg (stems), as Figure 2 shows. For the non-pyrolysed material, concentrations were in the ranges of 68.05 mg/kg–769.16 mg/kg (stems), 118.02 mg/kg–791.68 mg/kg (branches), 225.11 mg/kg–1742.25 mg/kg (twigs) and 374.73 mg/kg–6811.52 mg/kg (leaves) for sulphur, and 117.86 mg/kg–528.08 mg/kg (stems), 109.18 mg/kg–464.15 mg/kg (branches), 905.47 mg/kg–4205.19 mg/kg (twigs) and 2799.68 mg/kg–5072.76 mg/kg (leaves) for chlorine. Compared to chlorine concentrations in twigs and leaves, significantly higher concentrations of sulphur were found.

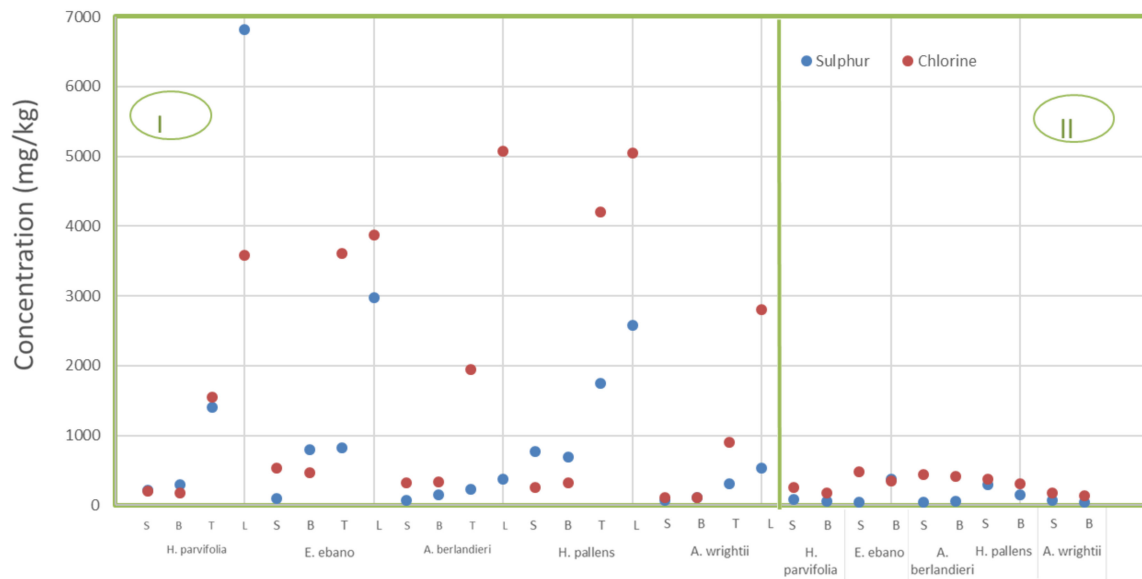


Figure 2. Sulphur and chlorine concentrations from non-pyrolysed (I) and pyrolysed biomass (II) from different components of semi-arid woody species (S = Stems, B = Branches, T = Twigs, L = Leaves).

3.3. Correlations between Carbon, Hydrogen and Nitrogen and the Elements Sulphur and Chlorine in Solid Biofuels before and after Treatment by Pyrolysis

The correlations between the elements chlorine and sulphur and carbon, hydrogen and nitrogen are given for non-pyrolysed biomass (Figure 3) and for pyrolysed material (Figure 4), indicating statistically significant correlations ($p < 0.05$) at 95% confidence level, as presented in Table 2.

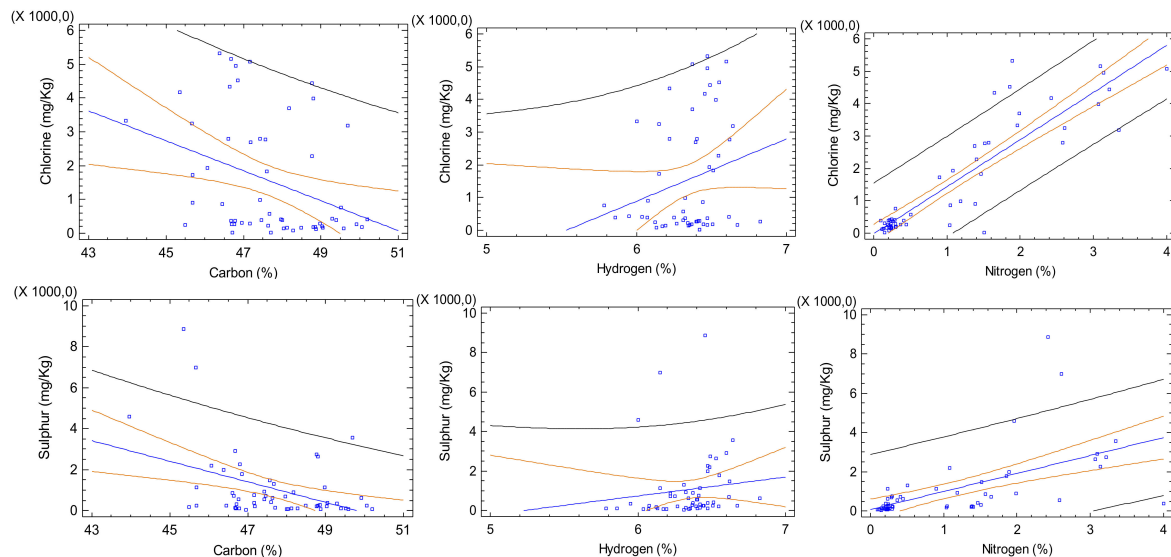


Figure 3. Linear regression between chlorine/sulphur and carbon, hydrogen and nitrogen in semi-arid woody species without treatment by pyrolysis, at confidence intervals ($p < 0.05$).

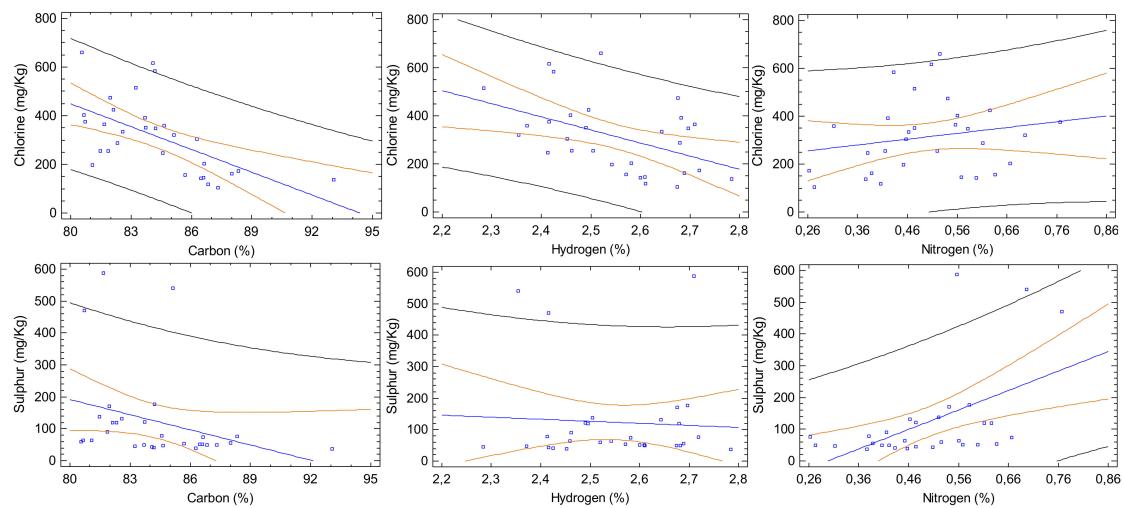


Figure 4. Linear regressions between chlorine/sulphur and carbon, hydrogen and nitrogen in semi-arid woody species after treatment by pyrolysis, at $p < 0.05$ confidence intervals.

Table 2. Correlations between chlorine/sulphur and carbon, hydrogen and nitrogen contents.

		Dependent Variable	Independent Variable	Linear Regression	Correlation Coefficient	R-Squared	p-Value
Non-pyrolysed biomass	1	Chlorine	Carbon	Chlorine = $22660.7 - 442.8 \times \text{Carbon}$	-0.35	12.28	0.0087 *
	2	Chlorine	Hydrogen	Chlorine = $-10511.2 + 1900.54 \times \text{Hydrogen}$	0.23	5.20	0.0941
	3	Chlorine	Nitrogen	Chlorine = $-20.6675 + 1455.23 \times \text{Nitrogen}$	0.90	80.59	0.0000 **
	4	Sulphur	Carbon	Sulphur = $24991 - 501.86 \times \text{Carbon}$	-0.41	16.76	0.0019 *
	5	Sulphur	Hydrogen	Sulphur = $-4989.95 + 954.51 \times \text{Hydrogen}$	0.12	1.39	0.3907
	6	Sulphur	Nitrogen	Sulphur = $76.59 + 917.61 \times \text{Nitrogen}$	0.58	34.04	0.0000 **
Pyrolysed biomass	7	Chlorine	Carbon	Chlorine = $2947.89 - 31.24 \times \text{Carbon}$	-0.59	34.43	0.0007 *
	8	Chlorine	Hydrogen	Chlorine = $1702.6 - 544.50 \times \text{Hydrogen}$	-0.46	21.44	0.0100 *
	9	Chlorine	Nitrogen	Chlorine = $192.56 + 242.70 \times \text{Nitrogen}$	0.20	3.84	0.2995
	10	Sulphur	Carbon	Sulphur = $1458.54 - 15.84 \times \text{Carbon}$	-0.31	9.66	0.0945
	11	Sulphur	Hydrogen	Sulphur = $288.58 - 64.83 \times \text{Hydrogen}$	-0.06	0.33	0.7623
	12	Sulphur	Nitrogen	Sulphur = $-182.55 + 613.08 \times \text{Nitrogen}$	0.52	26.75	0.0034 *

* statistically significant at 95% confidence level; ** highly significant at 95% confidence level.

Chlorine and sulphur show high correlations to nitrogen ($p = 0.0000$) in the non-pyrolysed biomass (Equations (3) and (6) in Table 2). The correlation coefficients of 0.90 and 0.58 indicate a relatively strong correlation between sulphur and nitrogen and a moderately strong correlation between chlorine and nitrogen, respectively. The R-Squared statistic indicates that the model as fitted explains 80.59% of the variability for sulphur and 34.04% for chlorine.

There were significant correlations ($p < 0.05$) between chlorine/sulphur and carbon (Equations (1) and (4), Table 2) in non-pyrolysed biomass, sulphur and nitrogen (Equation (12), Table 2), chlorine and carbon/hydrogen (Equations (7) and (8), Table 2) in charcoal (pyrolysed biomass). However, the correlation coefficients of -0.35 and -0.41 indicate a relatively weak correlation between chlorine and carbon and sulphur and carbon, respectively, in non-pyrolysed biomass. For the pyrolysed biomass, relatively weak correlations for Cl/C, Cl/H, S/N were also found since the correlation coefficients were -0.59, -0.46 and 0.52, respectively.

Since the p -value is greater or equal to 0.05, there is no statistically significant correlation at 95% confidence level (Equations (2), (5), (9)–(11), Table 2). In these cases, there is too low variability, with the R-Squared statistic ranging from 0.33 to 9.66.

4. Discussion

4.1. Carbon, Hydrogen and Nitrogen in Pyrolysed and Non-Pyrolysed Forest Biomass

The species and the components of the trees from which the fuel originates influences the composition of the charcoal, in accordance with Marcos [25], who highlighted that tree species with higher content of carbon will yield charcoals with higher contents of fixed carbon and higher calorific values, resulting in more efficient combustion. Hydrogen is found in biomass on the water structure, producing humidity or constituting the silicates mineral matter [26], allowing it to determine water produced during the combustion.

The range of nitrogen concentrations for charcoal from 0.32 to 0.65% compared to the range for non-pyrolyzed material (0.15%–0.52%) showed that treatment by pyrolysis of the biomass leads to an increase of nitrogen content on a mass basis of the resulting material. The nitrogen content of the fuel is related to the nitrogen oxides emissions. Compared to fossil fuels, the effect of the nitrogen amounts from biomass on the environment is negligible [27,28]. However, during solid biofuel combustion, NO_x emissions caused the main environmental impacts [29]. According to Hu et al. [30], the NO_x emissions will increase with an increasing nitrogen content. High nitrogen content is detrimental, since NO_x emissions would be produced, which is of great concern for the environmental measures that are being taken in the evaluation of new fuels.

The proportion of all these elements affects the biofuels quality, according to Raju et al. [31], both from an energy efficiency perspective and for environmental protection reasons. Vapor released is formed mainly of hydrogen and oxygen molecules that react, resulting in gas synthesis, principally H₂, CO and CO₂, which produce methanol ammonia as well as other products [27].

4.2. Sulphur and Chloride in Pyrolyzed and Non-Pyrolyzed Forest Biomass Combustion

The findings show that forest biomass contains sulphur, especially in less or not lignified structures, such as twigs and leaves. As well as other ions, sulfate-ions resulting from combustion have adverse effects on equipment, reducing its effectiveness and, consequently, its life time [32], therefore it is not advantageous to use twigs and leaves as fuels. Wood is considered to be a low-sulphur fuel, in accordance with Abdoli et al. [33], who obtained the sulphur content of different solid biomass, from 95 mg/kg of stored sawdust up to 525 mg/kg from fresh logging residues, highlighting that sulphur releases sulphur oxides (primarily Sulphur dioxide) estimated at about 10.8 g/GJ.

The sulphur contents obtained for pyrolysed biomass were less than those from the same components (stems and branches) in non-pyrolysed biomass. However, the values obtained in both cases are not considerable, corroborated by Alakangas et al. [34], who state that SO₂ emissions are typically low during wood combustion due to low sulphur concentration in forest biofuels and particularly in some wood products such as chips and barks because of relatively high concentrations in ashes.

As stated by Valantinavičius and Vonžodas [29], SO₂, SO₃, alkali and earth-alkali sulphates are formed by sulphur of solid biofuels. During the flue gas cooling in combustion plant boilers, SO_x can form sulphates that condense on heat exchanger surfaces, fine fly ash particles, or also can directly react with fly ash particles accumulated on heat exchanger surfaces (sulphation). It was shown that the ashes from wood chip or bark combustion contain about 40–70% or 60–90% of the sulphur from the fuels [35].

Sodium as well as magnesium sulfates display an abrasive effect, making their high contents undesirable [36,37].

As regards to chlorine, its content was lower than sulphur content in all cases. The major elements as well as minor elements constitute the ash components which, together with chlorine and sulphur, are relevant for ash melting point, deposit formation, fly ash and aerosol emissions, ash deterioration/corrosion and utilisation/disposal. Alkali chlorides with low melting point and some aluminosilicates may reduce the ash melting point of biofuels [38]. Melting point reduction may

cause slag formation or sintering, obstructing air flow inside the combustion equipment, reducing plant availability and lifetime. Also, melts of fly ash particles produce hard deposits in the furnace walls or heat exchanger tubes. Alkali and heavy metal salt as mixtures of alkali chlorides and sulphates containing Zn and Pb chlorides accelerated the formation of hard deposits because of sticky fly ash particles [35].

4.3. Correlations Between Carbon, Hydrogen and Nitrogen and the Elements Sulphur and Chlorine in Solid Biofuels before and after Treatment by Pyrolysis

During combustion, the organic matter of the fuel is mainly oxidized to CO₂ and H₂O gases, and nitrogen is entirely converted into N₂ and nitric oxides (NO_x, [NO, NO₂]) [29]. In China, for example, coal combustion is mainly responsible of the air pollutant emissions: CO₂ (85%), SO₂ (90%) and NO_x (70%) [39]. However, CO₂ emissions from biomass combustion are considered as CO₂-neutral concerning the greenhouse gas effect, assuming a sustainable utilization [40]. Therefore, there are needs of alternative energy sources to reduce environmental pollutions that could be caused by sulphur and nitric oxides to improve air quality.

In order to achieve an efficient combustion with low amounts of these undesired gases, Obernberger et al. [35] mentioned that the combustion and equipment technologies as well as the type of biofuels used must be taken into consideration. Looking to the size and type of the combustion application, this has an important influence on the requirements concerning fuel quality and finally on the emissions resulting from the combustion. On small-scale applications, the technologies include wood-stoves, fire place inserts, heat-storing stoves and boilers for wood fuels like logs, pellets and chips [35], all of which are equipped with relatively simple flue gas cleaning or without any filter system, resulting in a need for high quality fuel. Bigger combustion plants are more often equipped with sophisticated filter systems and they are able to use less quality fuel.

The carbon content affected nitrogen content so that the forest biofuels with more carbon content help to reduce the sulphur/chloride content as well as the nitrogen amount, consequently reducing the SO_x and NO_x emissions. In a similar study, Jiancheng et al. [41] showed that mixing wood with coal decreases the sulphur content of fuel, which reduced SO_x emissions and improves combustion conditions.

Guardado et al. [42] found a very close correlation between fixed carbon and volatile material, stating that the greater the content of volatile matter, the lower the fixed carbon concentration and vice versa; a higher fixed carbon amount will produce more ash content. In other research, a model is proposed for the strategic management of the sustainable production of charcoal, which is based on the evaluation of ecological indicators and the mathematical-economic model as a tool that provides the basis for the planning of charcoal production [43]. In general, it can be said that charcoal is an excellent alternative as a fuel because it is an environmental friendly product and is scarce of substitute products [44]. Nevertheless, it is essential to perform and promote management strategies by selecting the appropriate species in order to produce charcoal that meets the industrial requirements [45].

5. Conclusions

The main elemental components of the studied forest biomass were carbon and hydrogen, however with different proportions in pyrolysed (charcoal) and non-pyrolysed material. Charcoal contains on average 1.75 times more carbon, however 0.40 less hydrogen than non-pyrolysed biomass. However, the forest biomass also contains small amounts of nitrogen, found more in charcoal than in non-pyrolyzed components. The proportions of all these elements affects the biofuel quality in relation to energy efficiency and environmental protection. The proportions of their amounts depending on the wood species, the tree components and, above all, the treatment, e.g., by pyrolysis, influences the characteristics of a fuel. The content of chlorine and sulphur were very variable, with values from few to hundreds of milligrams per kg. Therefore, it is important to look for the best alternatives to reduce environmental pollutions that could be caused by sulphur and nitric oxides to

improve air quality. Mixing wood with charcoal is recommended to decrease the flue gas emissions, especially from sulphur, resulting in reduced SO_x emissions and improved combustion conditions.

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