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Ash content and chemical elements in 10 clones of *Hevea* by scanning electron microscopy and energy dispersive spectroscopy SEM/EDS

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Abstract: The process of generating energy through biomass is a viable alternative for the industrial sector. There are infinite materials that can be used in energy conversion. However, the generation of waste from conversion (ash) is one of drawbacks. Therefore, the objective of this study was to determine ash contents and identify semi quantitatively the main chemical elements in the wood ash progenies of 10 clones of rubber tree [*Hevea brasiliensis* (Willd. Ex Adr. De Juss.) Muell-Arg. by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) analyses. *Hevea brasiliensis* presented low ash content, a favorable characteristic for energy conversion, being favorable in the conversion of biomass into energy. Thus, by ash analysis it possible to identify fundamental chemical elements that can be used in agriculture calcium, potassium, magnesium, and phosphorus. Including soil correction, and low levels of toxic elements, allowing new approaches of this product in the segment.
Keywords: Energy, Biomass, Use of ashes.

Introduction

Scanning electron microscopy along with dispersive energy spectrometry (SEM/EDS) are elementary microanalysis techniques widely applied in the physical and biological sciences, engineering, technology, and forensic investigations (Goldstein et al., 2003). Scanning electron microscopy (SEM) analysis allows the identification and quantification of elements by characteristic peaks generated from the electrons for all biomass constituent (Newbury; Ritchie, 2012).

The ashes (inorganic material) of the wood corresponds to mineral components present in the vegetables, which vary between species and individuals of same species. Silva et al. (1983) mention that ash percentage for forest biomass is mainly affected by physiological age, tree size, soil type and nutritional characteristics of each species. There are studies that highlight wood, since it presents higher proportions of certain elements in its constitution (Rocha, 2011).

Garcia et al. (2014) reports thar main problem with the energy application of biomass is the clogging of burning equipment caused by the deposition of combustion residues.

Blunk et al. (2005) reports that incrustations occur when the contents are retained on heat exchangers of boilers, generating losses. According to Nakashima et al. (2014), the main mineral residues of ash are calcium, potassium, iron, silicate materials and other mineral oxides.

Mineral elements are crucial in the development of vegetables and their importance is well known. In trees, their quantities vary with species, soil availability, individual needs and other minor factors. They act physiologically on leaves, but are found in all organs and tissues, since they are absorbed from soil and carried through the trunk to the canopy, participating in plant metabolism (Fredo, 1999).

The chemical structure of wood is comprehensive and diversified from several cross-links of great importance for wood since they aid in preservation and properties of woody materials (Abreu et al., 2006). However, there are variations in the chemical, physical and anatomy composition of wood, vary between species and specimens (Trugilho et al. 1996).

Hevea brasiliensis (Willd. ex A. Juss.) Müll. Arg (Euphorbiaceae) is considered the main source of natural rubber in the world, constituting, among others, a product of great economic importance in the pneumatic industry, contributing with 75% of the world production (Bicalho et al. 2008). The state of São Paulo represents 60% of the national production, standing out as the largest producer in Brazil APABOR-(São Paulo association of producers and processors of natural rubber, 2017). There are few studies that address the chemical properties of rubber tree ash.

The growing generation of ash is a reality that is currently under discussion, as the use of biomass is expected to increase in the next years. Thus, research on the chemical composition and determination of ash contents becomes a possibility to reuse the material (Voshell et al. 2018).

Therefore, the aim of this study was to determine the percentage of ash and characterization of the chemical composition by SEM/EDS of 10 progenies clones of rubber tree.

Methods

Sampling

Wood samples (discs from base trunk) of Rubber tree were collected from 30 trees, three of each clone progeny in the municipality of Selvíria, Mato Grosso do Sul State (20°20′S, 51°24′W, elevation 350m). Rubber tree trial plantation was established in 2006 at a spacing of 3 × 3 m from seeds of free-pollinated clones (of IAC 40, IAC 41, IAC 326, IAC 311, IAC 301, IAN 873, GT1, PB 330, Fx 2261, and RRIM 725). Soil in the experimental area was classified as Red Latosol, a clayey texture (Santos et al. 2018).

In the laboratory, discs were cut into small longitudinal splinters. Then, the samples were ground in a micro-knife mill Willey type, being transformed into powder, classified using sieves of 20, 40 and 60 mesh, being the fraction from the 40-mesh sieve used for laboratory determination.

Ash contents

The ash content was determined according to ASTM D1102-84 (2013). The samples (1 g) were weighed in crucibles previously calcined at a 750°C for 30 minutes. Then, they were taken into a muffle, model 0212 for 6 hours at 600°C.

After the predetermined treatment time, the crucibles containing ashes were cooled in a desiccator for 40 minutes and weighed on an analytical scale from Shimadzu AUY220. The ash content was calculated according to (1).

$$Tac = \frac{Pac - Pc}{Pdr}.100 \qquad Eq.1$$

Where:
T_{ac} = Ash content [%]; P_{ac} = Mass of ashes + mass of the crucible; P_c = Crucible mass; P_{dr} = Mass of the dried sample.

Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS)

The ashes of the materials collected after the muffle stage were analyzed by scanning electron microscopy for a structural and semi quantitative characterization of the chemical elements present in samples. The assays were conducted with a Hitachi scanning electron microscope, model TM3000, coupled with a dispersive energy spectroscopy (EDS) probe responsible for obtaining the elementary microanalyses. The samples were fixed on a metal support on double- sided carbon adhesive tape. The applied acceleration voltage was 15 kV.

The elements identification in the graphs originated from EDS was made following a pre-stipulated pattern for intensity. Only peaks greater than or equal to the count of 0.4 cps/ev (counts per second per electron volt) were considered over the entire spectrum from 0 to 10 keV (kilo-electron-volt). Values under this intensity parameter were not considered, despite the presence of these elements in the samples.

Statistical analysis

For the ash contents of each of the 10-clone progeny, a descriptive analysis was initially performed. Then, a normality test was performed to observe data distribution and comparison between clone progeny, being a parametric analysis of variance applied. In the case of significant difference, Tukey test was applied to identify pairs determinants of differences. Results with $p<0.001$ were considered significant, all statistical analyses were performed in SigmaPlot-version 12.3.

The statistical test for SEM/EDS analyses of each progeny clone wood chemical composition was not applied because it is a semiquantitative analysis, aimed only to quantify the percentage of each element present in the ashes.

Results and Discussion

Ash contents ranged from 0.42% (IAC-301) to 1.49% (IAC-311). According to Schoninger and Zinelli (2012), it is ideal that the wood applied for energy purposes presents in ash content ranging from 1 to 3 %. Thus, according to results, ash contents are within the recommended range (Table 1).

Eucalyptus species are widely used for energy, due to its adaptive conditions. In a study developed by Juizo et al. (2017), with nine *Eucalyptus* species, the ash content varied between 0.35 to 0.58%. The rubber tree clones progeny presented values above the *Eucalyptus*, however it is not a restrictive characteristic for biomass, since the percentages are within standard range.

According to Vamvuka and Kakaras (2011), the elemental content of forest waste ash tends to present high amounts of silicon oxides, calcium, potassium and phosphorus and lower amounts of magnesium oxides, which was not observed in the present study, once that amount of magnesium detected was higher than the amount of phosphorus. Thus, based on the EDS analyses oxygen, calcium, carbon, and magnesium are predominant in all images, while sulfur, phosphorus and potassium are less abundant (table 1).

Table 1. Ash contents and main chemical elements detected by SEM/EDS in 10 progenies of rubber tree clones.

	Progenies of Clones									
	IAC40 ill. [wt.%]	IAC41 ill. [wt.%]	IAC326 ill. [wt.%]	IAC311 ill. [wt.%]	IAC301 ill. [wt.%]	Fx2261 ill. [wt.%]	GT1 ill. [wt.%]	IAN873 ill. [wt.%]	PB330 ill. [wt.%]	RRIM725 ill. [wt.%]
Ash	1.08b	0.87cd	0.86cd	1.49e	0.42a	1.08b	1.38e	1.03bc	0.74d	0.75d
Oxygen	46.90	48.69	4913	45.02	44.13	51.43	50.76	50.08	45.89	48.05
Calcium	27.68	24.09	20.82	19.22	16.57	18.20	20.77	17.90	17.87	23.37
Potassium	12.61	14.05	13.15	16.73	15.74	12.69	13.35	9.52	14.21	11.37
Magnesium	8.05	9.02	10.39	13.06	11.58	11.67	11.02	18.26	10.32	12.98
Phosphorus	2.66	2.47	5.01	4.24	6.37	4.11	3.13	3.09	5.68	3.41
Sulfur	0.97	0.85	1.02	0.87	3.60	0.98	0.77	0.72	4.31	0.77
Sodium	0.54	0.81	0.39	0.67	0.78	0.67	0.16	0.29	1.27	0.01
Aluminium	0.41	0.01	0.08	0.14	0.63	0.24	0.03	0.13	0.29	0.04
Silicon	0.18	0.01	0.01	0.06	0.60	0.01	0.01	0.01	0.16	0.01
Total	100	100	100	100	100	100	100	100	100	100

ill= illegitimate (progeny obtained free pollination clone).

It was not possible to identify significant amounts of silica, a conflict since it is a residual material, this result is possibly due to low association of material with external contaminants from soil (Tomeleri, 2019). In general, chemical elements present in ashes of different progenies of rubber tree clones indicate satisfactory energy yield of the burning process, resulting in low total ash contents composed mainly by inorganic elements similar to those identified in the literature for this biomass of forest origin.

In ashes chemical components analyses can observe the presence of metals and oxides, fact already described in the literature. Caustic alkalis and oxides such as Ca, Mg, K and P are related to the increase in pH (Wons et al., 2018). Another important factor to evaluate ashes composition is associated to their melting characteristics. Thus, it is possible to predict how the scale and corrosion of boiler will occur. Some elements that have been identified as problematic in this aspect, such as alkaline metals: sulfur, sodium, aluminum and silicon in low quantities (Table 1), making the process of combustion less harmful to furnaces and not contributing to formation of fouling in the furnaces.

Components that fit in alkaline metals at low combustion temperatures ranges between 500-550ºC (Nunes et al. 2016) may result in the process of converting biomass into energy depreciation in the boiler, impairing the energy performance of the biomass that is intended to be used for power generation (Magdziarz et al., 2018).

Among the advantages in use of ash in agriculture it is possible to highlight its use as a soil pH corrector, since ashes have alkaline pH (Ahmaruzzaman, 2010). In addition, the soil alkalinization can be associated to release by ashes in the soil of Ca2+ ions, Na+, Al3+ and OH ions. Also, ash can be used to improve water retention capacity due to increasing the micro porosity of the soil with the disposal of ash.

Thus, the ashes of each rubber tree progenies clones have potential to be used in agriculture, because it presented nutritional elements to improve soil micro porosity and can be used for this corrective purpose. The elements in larger quantities stood out under the surface of the ashes in clones of rubber tree clone progenies

Conclusions

The low ash content observed among the 10 progenies of clones of rubber tree it was observed a great potencial to be used as a bioenergetic source. In the study of ashes

chemical composition was possible to observe low levels of heavy metals in all studied clones, a factor that can expand the possibilities of using this material, mainly for soil correction.

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