Physicochemical Characterization of Waste from Vegetal Extracts Industry for Use as Briquettes

Maíra O. Palm, Cintia Marangoni, Ozair Souza, Noeli Sellin

***Abstract*—**Wastes from a vegetal extracts industry (cocoa, oak, Guarana and mate) were characterized by particle size, proximate and ultimate analysis, lignocellulosic fractions, high heating value, thermal analysis (Thermogravimetric analysis – TGA, and Differential thermal analysis - DTA) and energy density to evaluate their potential as biomass in the form of briquettes for power generation. All wastes presented adequate particle sizes to briquettes production. The wastes showed high moisture content, requiring previous drying for use as briquettes. Cocoa and oak wastes had the highest volatile matter contents with maximum mass loss at 310 ºC and 450 ºC, respectively. The solvents used in the aroma extraction process influenced in the moisture content of the wastes, which was higher for mate due to water has been used as solvent. All wastes showed an insignificant loss mass after 565 °C, hence resulting in low ash content. High carbon and hydrogen contents and low sulfur and nitrogen contents were observed ensuring a low generation of sulfur and nitrous oxides. Mate and cocoa exhibited the highest carbon and lignin content, and high heating value. The dried wastes had high heating value, from 17.1 MJ/kg to 20.8 MJ/kg. The results indicate the energy potential of wastes for use as fuel in power generation.

***Keywords*—**Agro-industrial waste, biomass, briquettes, combustion.

I. Introduction

THE current energy crisis has become a serious threat to the sustainability of the planet. Since the industrial revolution, fossil fuels have generated many environmental problems such as global warming and cities with heavy air pollution, due to a significant increase of carbon dioxide in the atmosphere. Furthermore, with the increase of the world population and growing demand for energy, the diversification of the energy sources is necessary to prevent power outages [1], [2]. Among alternative energy sources, biomasses play the most important role, accounting for about 80% of the energy generated by renewable energy carriers worldwide. The main difference between biomass and other renewable is the possibility of its utilization as a fuel. Biomass is also the only renewable energy source that can be stored and applied to produce heating, electricity and fuels. In addition, it is expected to contribute to the development of new markets, promote local economic structures and create new jobs in rural areas [3]-[7].

M. O. Palm, Department of Chemical Engineering, University of Joinville Region, Joinville/SC, Brazil, CEP 89219710 (phone: +55 47 34619209; e-mail: maira.o.palm@gmail.com).

C. Marangoni, Federal University of Santa Catarina, Blumenau/SC, Brazil, CEP 89065300 (phone: +55 48 37216308; e-mail: cintia.marangoni@ufsc.br).

O. Souza, Masters in Process Engineering, University of Joinville Region, Joinville/SC, Brazil, CEP 89219710 (phone: +55 47 34619056 e-mail: ozair.souza@univille.br).

N. Sellin, Masters in Process Engineering, University of Joinville Region, Joinville/SC, Brazil, CEP 89219710 (phone: +55 47 34619209, e-mail: nsellin@yahoo.com.br).

Brazil is generating about 330 millions of tons of biomass wastes that include agro-industrials and crop wastes. The agro-industrial wastes are generated after the processes of some yields, while crop wastes are the residues which remain in the field after harvesting. In general, agro-industrial wastes are composed of different constituent who can add value to the different wastes [8].

Lignocelluloses materials, consisting mainly of cellulose, hemicelluloses and lignin, are the most abundant polymers in nature and there are a large variety of lignocelluloses raw materials around the world [9]-[12]. Lignocelluloses waste can be recycled or reused as raw material in a different process. For instance, the wastes can be used in the production of heat energy, steam, electricity, or they may be recovered in solid form, such as briquettes or charcoal. Among the technologies developed and used for power generation from these wastes are the thermo chemical processes, such as pyrolysis, gasification and combustion [13]-[15].

Briquettes produced from these wastes, by a simple and inexpensive process, are in many cases an excellent source of cheap energy and environment-friendly, ideal for replacing fossil fuels currently used. The main advantages of using briquettes are reducing deforestation due to the replacement of the wood used, cheaper energy production, reducing the environmental impact caused by the large amount of wastes and facility of transportation and logistics of biomass by compression of the material [16]-[18].

In the production process of a vegetal extracts industry are used various raw materials of lignocelluloses origin and in large quantities, such as toasted oak, barley hulls, cocoa, Guarana, toasted mate, coffee, among others. After the extraction process by specific solvents, such as water and ethanol, a part of the generated wastes is generally stored and subjected to the composting and used as compost by the company itself in the cultivation of various crops, but another part is sent to industrial landfills. Aiming to expand the use and add value to this waste as well as reducing environmental impact, in this work was conducted the physical, chemical and thermal characterization of cocoa, oak, mate and Guarana wastes and evaluated its potential as a biomass fuel in the briquettes form for power generation.

II. Materials And Methods

Cocoa, oak, Guarana and mate wastes were collected in the industry after the extraction process of extracts. These residues were chosen because of their lignocelluloses origin and they are generated in large quantities. The solvent used in the extraction of cocoa, oak and Guarana extracts was ethanol and for mate was water. Fig. 1 shows pictures of the wastes in nature in particulate form.

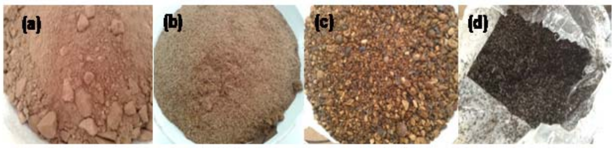

Fig. 1 Wastes samples *in nature* of cocoa (a), oak (b), Guarana (c) and mate (d)

A. Waste Characterization

1. Particle Size Analysis

The wastes were submitted for granulometric analysis using the Tyler series sieves with shaking time of 15 min and 80 Hz frequency. The particle sizes were determined from the procedures of ASTM E828-81.

2. Proximate Analysis

Proximate analysis was performed on the biomass samples for the determination of moisture (M), volatile matter (VM), ash and fixed carbon (FC) contents following the ASTM standardized procedures. The moisture content was determined by the mass loss in a stove at 105 °C using the procedures described in ASTM E871-82. The volatile matter was measured as mass loss after exposing at 950 °C for 7 min, based on the procedures of ASTM E872-82. The ash content was determined by the residue after burning in a muffle furnace at 575 °C, according to ASTM E155-01. The fixed carbon content was calculated by difference using the formula % FC = 100 - (% Ash + % VM) [19]. All analyses were performed in triplicate.

3. Ultimate Analysis

Ultimate analysis was performed to determine the elemental composition of biomass. The carbon (C), hydrogen (H) and nitrogen (N) contents were measured in the Perkin-Elmer CHN 2400 elemental analyzer. The method consists of burning the samples in oxidizing atmosphere, with fully developed combustion. The samples are reduced to a group of gases such as CO_2, H_2O and N_2, which are continually measured and based on this, the C, H and N element percentages are calculated. The sulfur (S) content was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in the Spectro Ciros CCD equipment. The analyses were carried out in triplicate.

4. Structural Analysis

Structural analysis was conducted for the determination of the lignocelluloses fractions (cellulose, hemicelluloses and lignin). The current analysis was carried out per Van Soest and Wine method [20]. The hemicelluloses content was determined from the difference between acid detergent fiber and neutral detergent fiber and by mass difference between the sample digested with detergent acid and the oxidation carried out with the buffered solution of acetic acid and potassium permanganate the lignin was determined. The cellulose content was determined by the difference in mass between the dry residue generated in the lignin analysis and the same residue was calcined in a muffle furnace at 500 °C for 2 h. The analyses were performed in triplicate.

5. High Heating Value

The higher heating value (HHV) was determined in a static and adiabatic bomb calorimeter, Parr model 1241, based on the procedures of ASTM D2015-00, recommended for coal and coke, although adapted for other solid fuels, such as vegetable biomass. For this analysis, the wastes were dried in an oven at 105 °C until constant weight. The analyses were carried out in duplicate.

6. Thermal Analysis

The thermal behavior was evaluated by TGA and DTA under oxidizing atmosphere (synthetic air), in a range from ambient temperature up to 900 ºC with heating rate of 10ºC/min in a simultaneous thermal analyzer, Netzsch model STA 449F3.

7. Bulk and Energy Density

The bulk density expressed by kg/m^3 of the wastes was determined from the procedures of ASTM D5057-10 and ASTM D2854-09 by the relation between mass and volume of the sample and the energy density was determined by multiplying the bulk density and the high heating value of briquettes.

III. Results and Discussion

The results of granulometric analysis show that 92.2% of the oak particles presented sizes less than 1 mm and 67.4% of mate particles presented sizes between 1.20 mm and 1.85 mm. Due to the cocoa waste being in powder form with some agglomerations, 47.3% of its particles had sizes smaller than 2 mm and 39.2% presented sizes between 4.83 mm and 9.5 mm. After the aromas extraction process, the Guarana waste still had pieces of shell and fruit seeds, thus presented 27.1% of the particles with sizes smaller 2 mm and 59.2% with sizes between 3.19 and 4.83 mm. In briquetting processes, biomasses with different particle sizes facilitate the compaction of the particles providing briquettes with better properties. The particle sizes ranging from smaller than 1 mm to 10 mm, which are defined depending on the type of material and configuration of briquetting machines [21], [22]. Biomass with smaller particle size results in denser briquettes and requiring lower compression pressures in briquetting machine, while biomasses with larger particle size are more difficult to agglomerate, requiring larger die in the extruder Briquetting machines.

In Table I are shown the results of proximate analysis (moisture, volatile matter, ash and fixed carbon contents), ultimate analysis (carbon, nitrogen, hydrogen and sulfur contents), and higher heating value, energy density and lignocelluloses fractions. As observed in Table I, the wastes presented high moisture content, requiring prior drying before Briquetting. The higher moisture content was found in mate waste because water was used as an extraction solvent while for the others wastes the solvent used was ethanol. The suitable moisture content for Briquetting processes generally ranges from 8 to 12% [23]. Excess moisture can cause an explosion in the Briquetting machine due the vapor formation. However, very dry biomasses hinder the process of particle agglomeration. High moisture content causes the formation of low quality briquettes, because in the combustion process, part of the energy is used to dehydrate the sample, thus reducing energy efficiency. Residues with high moisture content must be pre-dried, requiring higher energy consumption in the process and need for additional equipment such as dryers.

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS, HHV AND LIGNOCELLULOSES FRACTIONS OF AROMA INDUSTRY WASTES

	Cocoa	Oak	Guarana	Mate
Proximate analysis (%)				
Moisture	30.6 ± 0.01	33.9 ± 0.02	44.5 ± 0.01	66.3 ± 0.01
Volatile Matter*	60.2 ± 0.02	58.5 ± 0.02	28.4 ± 0.18	21.6 ± 0.09
Ash*	5.2 ± 0.01	0.3 ± 0.01	2.6 ± 0.01	3.1 ± 0.01
Fixed carbon	34.6	41.2	68.9	75.3
Ultimate analysis (%)*				
C	47.3 ± 0.05	46.5 ± 0.03	44.6 ± 0.21	52.8 ± 0.33
H	6.6 ± 0.11	6.4 ± 0.04	6.6 ± 0.06	6.9 ± 0.19
N	3.6 ± 0.01	0.1 ± 0.01	1.6 ± 0.03	2.4 ± 0.18
S	0.3 ± 0.04	0.1 ± 0.02	0.2 ± 0.03	0.1 ± 0.03
Higher heating value (MJ/.kg)*				
	20.1 ± 5.00	17.1 ± 5.00	17.1 ± 5.00	20.8 ± 5.00
Energy Density (MJ/m^3)*				
	15,580.8	6,164.4	10,233.8	5,909.3
Lignocellulosic fractions (%)				
Cellulose	24.2 ± 6.20	63.1 ± 2.84	29.9 ± 3.20	56.9 ± 0.43
Hemicellulose	8.2 ± 4.44	22.0 ± 2.23	13.1 ± 0.18	7.14 ± 0.87
Lignin	5.3 ± 1.24	4.2 ± 0.10	4.4 ± 1.15	14.0 ± 7.28

*Dry basis.

Cocoa and oak waste showed high volatile matter content, 60.2% and 58.5%, respectively, while low values were observed for Guarana and mate, 28.5% and 21.6%, respectively. However, these last two wastes had high fixed carbon content, of 75% and 69%, respectively, because they were torrified before the aroma extraction process and some of these materials were volatilized in the process. The volatile matter is related to the lignocellulosic fractions of the biomass and the fixed carbon represents the percentage of mass after the release of volatile compounds, excluding ash and moisture contents. As higher this content the greater the reactivity of biomass and the heat released in the combustion [16].

The ash contents of the wastes were low, with the highest value of 5.3% observed for cocoa and the lower value of 0.41% for oak. These low values are satisfactory for briquetting processes because this material has low heating value and reduces the energy efficiency in the combustion process [24]. Moreover, at high temperatures, they may melt, causing fouling and acting as resistance to heat transfer in thermal exchange equipment (boilers, for example) [15]. The values determined by the proximate analysis vary with the composition of the biomass. The values found for the cocoa and oak waste were very close to those presented in the literature for others biomass [6], [16], [19], [25].

As shown in Table I, the mate waste showed the highest carbon content, 52.8%, while cocoa, oak and Guarana showed respectively, 47.4%, 46.5%, and 44.6%. The carbon content for cocoa bean husk was 43.3% and for oak was 46.9% [19]. All wastes exhibited hydrogen content around 6.6%. Similar values of hydrogen were found for wood pellets of 6.13% [15] and for species of grasses cultivated for bioenergy production, about 5.5% to 6.2% [26]. Carbon and hydrogen are oxidized by exothermic reactions, generating energy in the form of heat and directly influencing the heating value of the fuel [25].

The wastes had low nitrogen and sulfur contents, with cocoa and mate presenting the highest nitrogen content of 3.59% and 2.37%, respectively. The highest sulfur content was 0.30% and 0.20% for cocoa and Guarana, respectively. Oak and mate exhibited sulfur content of 0.10%. A similar result was found for *P. Polyandra* Bench fruit plant [27]. The combustion of biomass with low sulfur and nitrogen contents will generate low percentages of sulfur and nitrous oxides [28].

High cellulose content was observed for oak and mate, by 63.1% and 56.9%, respectively. Regarding the lignin, cocoa and mate had the highest contents, of 5.3% and 14.0%, respectively. Cellulose and hemicelluloses have lower internal energy due to their higher level of oxidation, different from lignin that increases the heating value of the biomass [29]. The lignocelluloses biomass composition may vary depending on the plant species, age, growing conditions and others [30]. Woody biomass (forestry crops or fruit tree pruning) presents the structure physically larger, structurally stronger and denser than non-woody biomass (straw, grasses or stalks) because their physical properties and chemical compositions [31]. The lignocellulosic fractions may still vary depending on the analysis used for its determination. Furthermore, in lignocellulosic analysis, cocoa and Guarana showed, respectively, 24.2% and 29.9% of cellulose content and, 8.2% and 13.1% of hemicellulose content. Sorghum bagasse presents 45.2% of holocellulose (combination of cellulose and hemicellulose), 11.3% of lignin and 43.5% of extracts [32]. The main compounds present in the extracts of lignocellulosic materials are resin acids, terpenes, sterols, phenolic substances, sugars, etc. [33]. Cocoa, for example, has in its composition high cocoa butter content (fat composed of 98% of triglycerides), and even in the form of cocoa powder, it still has 10% to 12% cocoa butter in its composition [34]-[36].

The dried wastes showed high heating values, varying from 17.1 MJ/kg to 20.8 MJ/kg, very close to the values reported in the literature for lignocellulosic biomass from agro-industrial and crop wastes [9], [16], [25], [37]. The differences observed for the HHV of the wastes are related to the results of the elemental analysis, in which cocoa and mate had the highest carbon and hydrogen contents. These wastes exhibited the highest HHV, 20.8 MJ/kg and 20.1 MJ/kg, respectively, presenting greater potential for energy generation. Due to the high HHV, the wastes also showed high values of energy density. The cocoa and Guarana presented energy density of 15,580.8 MJ/m^3 e 10,233.8 MJ/m^3, respectively. The energy density of these wastes can be compared with banana pseudostem briquettes, of 14,751 MJ/m^3, and rice husk, of 16,290 MJ/m^3 [16]. In this way, the cocoa can be subjected to the combustion process without undergoing briquetting process. For oak and mate, after briquetting process, a significant increase in their apparent and energy densities is expected. The energy density of the material is an important parameter to check the feasibility of biomass for energy generation, because it influences economic factors, as the cost of transportation, as well as fuel quality, quantifying the energy generated by volume [29].

Fig. 2 shows the TGA and DTA curves under oxidizing atmosphere of the aroma industry wastes.

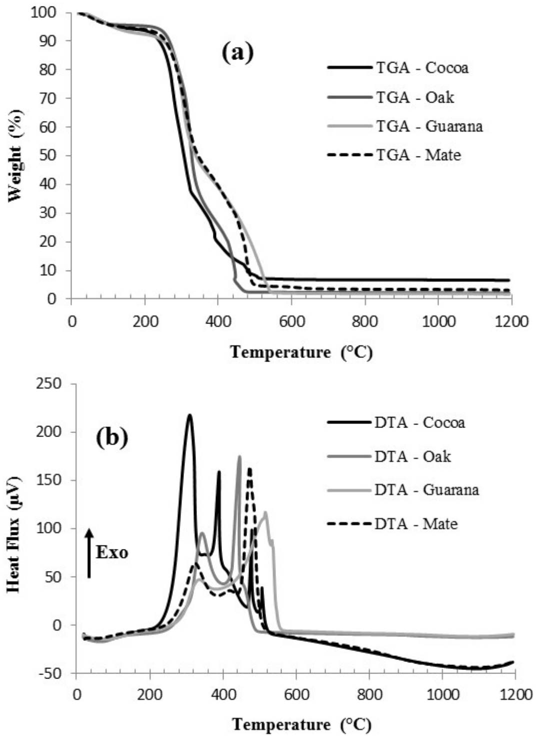

Fig. 2 (a) TGA and (b) DTA curves under oxidizing atmosphere of the wastes

Is observed in Fig. 2 (a) that the wastes samples showed two main events of thermal degradation; the first, from the room temperature up to until approximately 150 °C with an endothermic peak attributed primarily to the evaporation of water (moisture). In this region also happen the evaporating of ethanol, the solvent used in the extraction process of cocoa, oak and Guarana. The second, from approximately 150 saccharides up to 565 °C, with exothermic peaks corresponding to the energy released in the degradation of volatile matters (hemicellulose, cellulose and lignin) [38]. In this region occurs the largest mass loss percentage for all wastes. In studies with rice husk and wood chips under similar conditions of TGA, the authors found that over 60% of the original mass is degraded until approximately 500 °C [15].

The cocoa residue in approximately 320 °C had more than 60% of its mass degraded, with greater degradation of volatile matter at lower temperatures and thus lower thermal stability compared to others wastes which at the same temperature had a little more than 40% of mass loss. The oak showed the largest degradation peak up to 400 °C, which may be associated to the high volatile matter content and high hemicellulose and cellulose contents. The hemicellulose is composed of saccharides (xylose, mannose, glucose, galactose, etc.) and has a random structure, amorphous, rich in ramifications, being easily degraded at lower temperatures, from 220 °C to 315 °C. The cellulose has a long polymer chain of glucose, without branches, with ordered structure (crystalline), resistant and with high thermal stability, with degradation from 315 °C to 400 °C [25], [39].

The mate had its highest loss mass at higher temperature (456 °C) compared to other wastes and this may be occurred due to the high lignin content. Above 565 °C, variations in the TGA curves related to the degradation of residual lignin are not observed. This might have occurred because the materials were subjected to extraction of extracts upon heating processes, facilitating release of lignin structure and its degradation in the thermal analysis. Lignin is composed of aromatic rings, with multiple ramifications. Due to strong chemical bonds its degradation is slow and occurs in wide temperature range of 100 °C to 900 °C [6], [9], [27], [39]. There was low generation of residue (ash) at the end of the process for all wastes, corroborating the results of the proximate analysis.

In DTA curves, Fig. 2 (b), cocoa exhibited four exothermic peaks at maximum temperatures of 311 °C, 390 °C, 478 °C and 506 °C. The other wastes presented two peaks at higher temperature, the first peak between 320 °C and 340 °C, and the second one between 445 °C and 515 °C. Cocoa had the lowest thermal stability in relation to the others wastes and higher energy release at lower temperatures, which may be associated to the high content of extractives, which degrade at not so high temperatures. Guarana had the lowest energy release in ATD and presented the lowest heating value.

These results are close to those reported in studies of thermal degradation of vegetable biomass, where was verified that the lignocellulosic components have their fractions degraded in different regions, and the chemical composition influences the thermal behavior of the biomass [6], [25], [37], [40].

IV. Conclusion

The characterization and evaluation of physical, chemical and thermal properties of lignocellulosic wastes generated in the process of vegetal extracts industry were performed. The wastes had particles of suitable sizes for briquetting. Cocoa and oak wastes had higher volatile matter content, while mate and Guarana exhibited higher fixed carbon content. All wastes had low ash content. Due to the high moisture content, the wastes will need drying before briquetting process. The wastes exhibited high carbon and hydrogen content, increasing their energy potential as fuel, and had low sulfur and nitrogen content, ensuring low emissions of greenhouse gases such as SO_2, NO_x and N_2O during the combustion of briquettes. Mate and oak showed high hemicellulose and cellulose content, with degradation temperatures between 150 °C and 530 °C. Cocoa showed low hemicellulose and cellulose content, and high degradation rate and loss mass at lower temperatures than other wastes. Mate and cocoa had the highest lignin, carbon and hydrogen contents, corroborating with the high heating values presented. Guarana showed the lowest carbon and lignin contents and heating value among the four wastes. However, all wastes, including Guarana, showed high heating values (17.1 MJ/kg to 20.8 MJ/kg), and compared to others biomass. The wastes showed high energy densities with attractive values for energy generation, when compared with wastes already in the form of briquettes. Comparing the characteristics of the wastes evaluated with others described in the literature it showed potential for use as biomass fuel in the form of briquettes.

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