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Charcoal Briquette Production Using Orange Bagasse and Corn Starch

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Carbonization technique (muffle furnace at 450 °C) was applied on the orange bagasse (solid wastes) to produce charcoal briquettes, using corn starch as binder and a 1.0 ton-force manual hydraulic press. The tests applied on the orange charcoal powder and on the orange charcoal powder with corn starch (5, 10 and 15 % w/w) were the proximate analysis, the elemental analysis and the determination of the higher heating value HHV). On the other hand, some tests were carried out on the orange charcoal briquettes, which were the determination of density and the mechanical strength (compressive strength and friability). The results showed that the obtained orange charcoal (OC) has a significant high heating value of 29,000 J/g, and can be used in different processes. When mixed with the binder, its HHV has a small decrease, 27,611 J/g to OC with 5 % of corn starch, 26,857 J/g to OC with 10 % of corn starch and 26,476 J/g to OC with 15 % of corn starch, but still they are considered high values. The fixed carbon content of dehydrated orange bagasse increased from 11.444 % to 68.782 % when it was charred, but it was also observed that fixed carbon content of the charcoal had a maximum decrease of 67 % due to adding the binder (15 % w/w). The briquette that had the highest fixed carbon content was the one with 5% of binder, since this one has the highest amount of pure carbon. However, the briquette with the highest mechanical strength was the one with 15 % of corn starch in its composition. With respect to the carbon content in its composition, all the briquettes showed high content of it (70.67 %, 69.07 % and 70.90 %, respectively to 5, 10 and 15 % of corn starch). The briquette with 10 % of binder also presented a satisfactory mechanical strength, having a loss of 14,932 % in friability testing, ranking as slightly friable and resisted a pressure of 1.406 MPa in the compression test. Thus, the charcoal briquette with 10 % of corn starch is appropriate for use in domestic and commercial way.

1. Introduction

The search for new alternatives for power generation has been intensified in the scientific community. In Brazil, investments for energy have not adapted to the evolution of demand, therefore, research on different options for additional power generation has a singular importance. In this context, there is an increase in the interest of the use of biomass waste as an energy source, using gasification systems, combustion and pyrolysis, aiming at the replacement of fossil fuels by renewable energy sources. Biomass is any organic material of vegetable origin, which possesses energy available for burning. Brazil stands out as a country with great potential for the use of biomass in the thermochemical conversion process, especially wood and forest wastes, livestock and agricultural wastes. Among the agricultural wastes, the solid waste from processing orange juice (orange bagasse) can be highlighted. Brazil tops the rank among the most important countries in the production of citrus fruits. So, the search for the use of these wastes as by-products, becomes interesting.
An alternative would be the application of carbonization (slow pyrolysis) in the solid waste. As reported by Tienne et al. (2004), this technique would convert the orange bagasse into orange charcoal, expanding its uses and, at the same time, facilitating transportation, storage and handling. Besides having the additional advantage of

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reducing the exploitation of native forests. Charcoal particles are composed mainly of carbon, without any binding mechanism when compressed. Therefore, the greatest difficulty into the briquettes production is the search for a binder that promotes the necessary features that a charcoal briquettes should have. The most commonly used binders in the energy densification step is the corn starch, but other binders have been studied in order to improve the charcoal briquettes characteristics. However, the corn starch is found in abundance and cause the briquettes to have the necessary properties for its use. In this way, this work has as main objective the use of the corn starch as binder, and a different kind of raw material (orange bagasse) to make the charcoal briquette using a manual hydraulic press, with the objective to produce biofuels for combustion. The choice of corn starch was taken so the binder could be used as reference to others works in the literature.

2. Materials and methods

2.1 Biomass preparation

The orange bagasse (solid wastes) obtained from local restaurants, passed through a grinding process to separate the orange bagasse into pieces of 1.0 cm² (*ca*). Despite slow pyrolysis does not require small particles of biomass, the grinding step brings the homogeneity of the feedstock, aiming the achievement of the complete carbonization of all biomass at the end of the process. A pre-drying of the sample was performed to remove surface moisture from biomass, and consequently, increase the yield of the solid product and decreasing the carbonization time. This drying was carried out in an oven with forced air circulation at 105 °C until moisture content between 15 and 20 w/w was achieved. After drying, the dehydrated bagasse was stored in airtight bags.

2.2 Carbonization process

The pyrolysis was conducted in a fixed bed system which consists of a muffle furnace, with limited oxygen supply and gas output. The slow pyrolysis methodology, used by Alho, (2012) was applied. The previously dehydrated sample was placed inside the muffle. The heating rate of 10 °C/min was applied until it reaches the temperature of 450 °C, remaining for 1 hour. The solids yield was obtained by $Y_{solids}(\%) = \frac{m_{OC}}{m_{ini}} \times 100$, where Y_{solids} is the solids yield percentage obtained in the pyrolysis process, m_{ini} is the initial mass of dehydrated orange bagasse and m_{OC} is the mass of orange charcoal. According to Antal and Gronli (2003), this representation of the efficiency of the carbonization process is intrinsically vague because it does not reflect the fixed-carbon content of charcoal product, which varies widely. In this context, a more meaningful measure of the carbonization efficiency is given by the fixed carbon yield. This yield represents the efficiency realized by the pyrolytic conversion of the ash-free organic matter in the feedstock into a relatively pure, ash-free carbon and this yield is given by $Y_{fc}(\%) = Y_{solids} \times \left(\frac{\%FC}{100-\%Feed\_Ash}\right)$, where Y_{fc} is the fixed carbon yield, $\%FC$ and $\%Feed\_Ash$ are the fixed carbon and the feedstock ash content, both obtained by the proximate analysis.

2.3 Energy densification process

The energy densification process was conducted using a manual uniaxial hydraulic press and a cylindrical mold. The applied methodology for the mixture between the charcoal and binder followed the method proposed by Teixeira et al. (2011), with slight modifications. The briquettes were prepared by mixing the charcoal particles, the binder (5, 10 and 15%) and water (2:1, water: charcoal, w:w), and heating at 100 °C, to activate the binder, until gum point. This mixture was then pressed. An applied compression of 1.0 ton force was maintained during 1 min for each sample. After compression step, the briquettes were sent for the drying process. It was used an oven with forced air circulation at 80 °C until a final moisture content of 8 to 12 %. The binder used was corn starch. Corn starch was chosen since it is abundant and widely used as a binder in briquetting, due to its high adhesive power and power generation to make charcoal briquettes with high strength. This way it is possible to analyze if the charcoal obtained from orange bagasse has the necessary features to be used.

2.4 Proximate and ultimate analysis

The moisture content was determined by weight loss using the gravimetric method in an oven with forced air circulation at 105 °C until constant weight. The volatiles ($\%V$)and ash contents ($\%Ash$) were determined by the gravimetric method using a muffle furnace. After determination of the volatile material and ashes, the fixed carbon content $\%FC$ was obtained by difference, i.e. $\%FC = 100 - \%V - \%Ash$. All assays were performed in triplicate.

Ultimate analysis was performed in triplicate in the dehydrated biomass, in the charcoal particles and in the mixture of charcoal and binder. Ultimate analysis took place on an elemental analyzer of carbon, hydrogen and nitrogen. The oxygen fraction is determined by difference ($100 - \%C - \%N - \%H$).

2.5 Higher heating value (HHV)

The higher heating value (HHV) was determined using a device called bomb calorimeter. This technique measures the heat released, through the determination of the temperature difference before and after the complete combustion process of a given quantity of sample introduced into the container submerged in a water bath (Da Silva, 2012).

2.6 Density and mechanical strength

The density of the charcoal briquettes was measured using an analytical balance and a digital caliper 72 hours after compaction. The density results were determined by the ratio between the mass and the volume of each briquette.The mechanical strength of charcoal was determined by analysis of resistance to compression and friability analysis. The compressive strength was carried out on a universal testing machine. The adjustment and the initial speed were 0.3 cm.min^{-1}. In this test, the briquette was submitted to continuous and progressive pressure until its fracture. To determine the friability index, it was used the tumbler method. This method evaluates the difference between the initial and final mass of the briquette. The samples were placed on the tumbling drum and submitted to 25 rpm. After 20 minutes, the material was removed and rated according to its percentage of weight loss. All mechanical strength tests were performed in triplicate.

3. Results and discussion

3.1 Carbonization and energy densification process.

Before the carbonization process, it was determined the moisture content of the raw material, and the obtained value was 81.65 %, similar to that reported by Zanella et al. (2013). the carbonization process aims to obtain the solid product. The solids conversion yield obtained in the orange bagasse carbonization process into charcoal (34 assays) was 32.817 ± 1.229 %. This result was above of those found in literature (Tienne et al., 2004; Aguiar et al., 2008). Besides, the fixed carbon yield was 24.197 ± 0.531 %. This value drop was expected, since it disregards the amount of ash of the samples. After the carbonization process, as already said, the charcoal particles were ground into 2.0 to 4.0 mm and then mixed with water and corn starch. This mixture was pressed to form the orange charcoal briquettes, as shown in Figure 1.

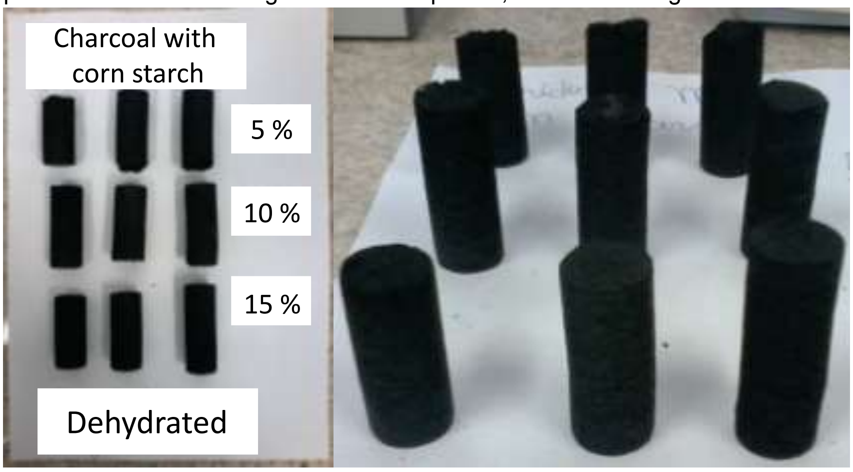

Figure 1: Orange charcoal briquettes with 5, 10 and 15 % of corn starch.

3.2 Proximate analysis

Table 1 brings the results of the proximate analysis of dehydrated orange bagasse, orange charcoal, corn starch, OC with 5 % of corn starch, OC with 10 % of corn starch and OC with 15 % of corn starch. The fixed carbon content was obtained by difference. It can be seen in Table 1 that the material which has the higher volatile content is corn starch. Its addition gradually increased the volatile content of the briquettes and so reduced the fixed carbon content. It can be also verified that the feedstock, the charcoal and the charcoal with binder showed approximately the same ash content. This happened due to the fact that the binder does not have ashes in its composition, only volatile. Therefore, its addition into the charcoal did not influence the ash content of the briquettes. Regarding the fixed carbon content, it is noticed that there is a remarkable increase between the fixed carbon content of coal (68.78 %) and the dehydrated orange bagasse (11.44 %). The fixed carbon content of the charcoal is in agreement with the literature. Tienne et al. (2004) obtained a 68.75 % of fixed carbon content in the orange peel carbonization at 450 °C. Miranda et al. (2009) applied the carbonization process to the dehydrated orange peel at 700 °C, and also obtained a fixed carbon content of 68.49 %. As reported by Santos (2008), for a charcoal to be used in the steel industry, it should have an ash content below 1 %. As in this work all the charcoal/binder samples have an ash content above this threshold, their application is intended for domestic and commercial use as biofuels for combustion.

Table 1: Proximate analysis of the samples (wt.%)

Sample	Total moisture	Volatile matter	Ash	Fixed carbon
Dehydrated orange bagasse	2.715 ± 0.151	81.840 ± 1.485	6.716 ± 1.059	11.444 ± 0.453
Orange charcoal (OC)	1.528 ± 0.112	23.078 ± 1.932	8.140 ± 0.806	68.782 ± 1.509
Corn starch	12.297 ± 0.845	95.113 ± 0.619	-	4.887 ± 0.619
OC w/ 5 % of corn starch	6.855 ± 0.158	48.499 ± 2.421	8.586 ± 0.250	42.915 ± 2.564
OC w/ 10 % of corn starch	2.563 ± 0.104	63.091 ± 2.017	7.973 ± 0.149	28.936 ± 2.164
OC w/ 15 % of corn starch	7.521 ± 0.230	69.256 ± 1.305	8.053 ± 0.830	22.691 ± 1.734

3.3 Higher heating value (HHV) and elemental analysis

The measured results of higher heating value (HHV) of the samples are shown in Table 2.

Table 2: Higher heating value of the samples

Sample	HHV (J/g)
Dehydrated orange bagasse	17,614 ± 70.20
Orange charcoal (OC)	29,000 ± 13.50
Corn starch	14,956 ± 18.00
OC w/ 5 % of corn starch	27,611 ± 30.50
OC w/ 10 % of corn starch	26,857 ± 24.50
OC w/ 15 % of corn starch	26,476 ± 181.50

From the values of the higher heating value, it is found that there is a significant increase when comparing the dehydrated orange bagasse with orange charcoal. This is due to the biomass carbonization process. The literature brings the HHV of the biomass and it is noted that the value found in this work for the dehydrated orange bagasse is in accordance therewith (Roy and Corscadden, 2012; Maia et al., 2014). According to Teixeira et al. (2011) the found HHV for the orange charcoal is close to the HHV for wood coal. The same author obtained a HHV of 28.326 J/g for charcoal obtained from sugarcane bagasse. Since the HHV of corn starch is the lowest among all samples, it was expected that the HHV decreased with the addition of binder in the charcoal. And this is observed by the values obtained with the addition of 5, 10 and 15 % of corn starch. According to Kurkova et al. (2003), a potential coal has a HHV between 24500-31800 J/g. Thus, all the charcoals obtained in this study are considered as a potential charcoal and can be destined to domestic and commercial use. In Table 3, it can be seen the results of the elemental analysis and the atomic ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C) of the dehydrated orange bagasse, orange charcoal (OC), corn starch, OC with 5 % of corn starch, OC with 10 % of corn starch and OC with 15 % of corn starch.

Table 3: Elemental analysis (wt.%) and atomic ratio of the samples

Sample	C	N	H	O*	Atomic Ratios	
					H/C	O/C
Orange bagasse	8.45 ± 0.20	0.20 ± 0.01	9.85 ± 0.15	81.51 ± 0.06	13.91 ± 0.55	7.24 ± 0.18
Dehydrated orange bagasse	44.33 ± 0.55	1.12 ± 0.01	6.09 ± 0.07	48.46 ± 0.63	1.64 ± 0.01	0.82 ± 0.02
Orange charcoal	74.37 ± 0.21	2.37 ± 0.05	5.37 ± 0.12	17.90 ± 0.29	0.86 ± 0.01	0.18 ± 0.01
OC w/ 5 % of corn starch	70.67 ± 0.46	2.27 ± 0.09	4.80 ± 0.08	22.27 ± 0.47	0.81 ± 0.01	0.19 ± 0.08
OC w/ 10 % of corn starch	69.07 ± 1.07	2.10 ± 0.08	4.70 ± 0.08	24.13 ± 1.18	0.81 ± 0.01	0.27 ± 0.02
OC w/ 15 % of corn starch	70.90 ± 0.82	2.30 ± 0.08	4.80 ± 0.08	22.00 ± 0.86	0.81 ± 0.01	0.27 ± 0.02

*Obtained by difference

The results for the elemental fractions of dehydrated orange bagasse are consistent with data reported in the literature for other dehydrated biomass (Žandeckis et al., 2014; Maia et al., 2014), but for charcoal fractions and charcoal with binder fractions, the results obtained in this study are higher than those reported in the literature (Oh et al., 2011). It is observed that there was no drop in the value of the elemental fractions with the addition of the binder. As expected in the pyrolytic process, the C content increased, while de H and the O contents decrease with increasing pyrolytic temperature. This effect is a typical response to the carbonization process, where the feedstock loses surface functional OH groups due to dehydration and also loses C bound to O and

C atoms at higher temperatures due to structural core degradation (Novak et al., 2009). This also means that the heating value of biomass is lower due to the lower energy contained in C-O and C-H bonds than those for C-C bonds (Miranda et al., 2012).

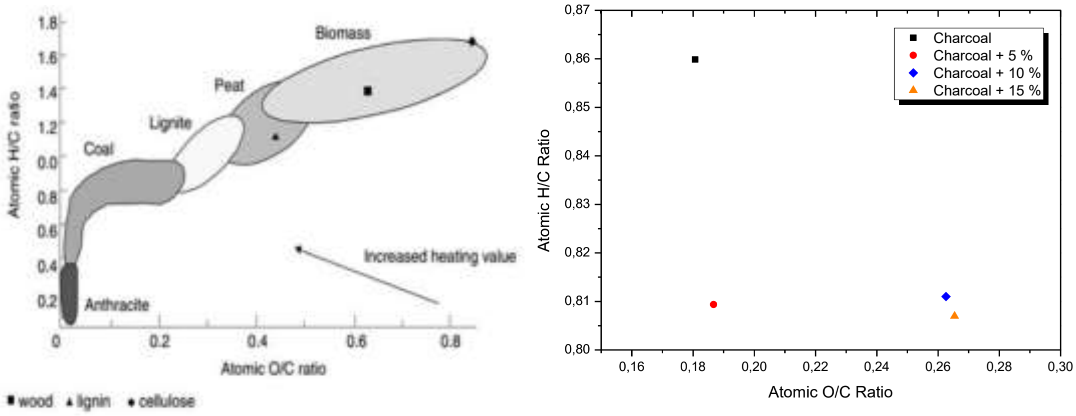

Figure 2: The Van Krevelen diagram for solid fuels and Atomic ratios of the samples

It can be noticed in Figure 2, that the values of the atomic ratios for the orange bagasse are not present on the Van Krevelen diagram, since the raw material has a low amount of carbon (Table 2). So, we can conclude that the raw material is not a good solid fuel. In this way, the drying/carbonization process is a necessary step. The effect of the drying/carbonization process can be notice on the atomic ratios of dehydrated orange bagasse and in the atomic ratios of orange charcoal. This occurs because with drying at 105 ° C, the feedstock is present in the diagram as biomass (H:C 1.637, O:C 0.816), and when it is charred at 450 ° C it lies in the diagram as coal (H:C 0.860, O:C 0.181) and has the higher heating value. All the mixture between charcoal and corn starch also lies in the diagram as coal. This mean that all this charcoal/corn starch mixture obtained in this work have a good potential as fuel.

3.5 Density and mechanical strength

Table 4 shows the density values of the charcoal briquettes and the results of stress and strain from their resistance to the compression test. The density results show that there are no difference in the density values of the briquettes made with 5, 10 and 15 % of corn starch. Density is an important characteristic in the charcoal quality. The higher its value, the higher the energy/volume ratio. In addition, the briquettes density has a dependence on its feedstock and on the applied force in the densification energy step (Demirbas and Sahin-Demirbas, 2004). In this way, we can see that the all the produced briquettes are homogeneous.

Table 4: Density and compression results of the briquettes

Briquettes	Density* (g/cm³)	Stress (MPa)	Friability
OC w/ 5 % of corn starch	0.629 ± 0.008^{A}	0.760 ± 0.020	35.381 ± 0.333
OC w/ 10 % of corn starch	0.594 ± 0.017^{A}	1.406 ± 0.184	14.246 ± 0.908
OC w/ 15 % of corn starch	0.610 ± 0.024^{A}	2.177 ± 0.149	5.838 ± 0.651

*Means follow by the same letter in the same column do not statistically differ (p > 0.05) according to Tukey's test.

Regarding to the stress applied in the compression test, the founded results were expected, *i.e.,* the briquette that most resisted to the application of compression was the one with more binder in its composition (15 %). This happened because a higher amount of corn starch provides a higher agglomeration between the charcoal particles and makes the briquette stronger than the ones made with a low amount of binder. It is possible to observe by the friability test results that the % of weight loss decreases as increases the mass of the binder. This result was expected since the binder addition provides greater adhesion among charcoal particles. So, with larger amount of corn starch, the adhesion was higher, and consequently, the weight loss was lower. According to the classification presented by Oliveira and Almeida (1982), the charcoal briquette with 5 % of corn starch is considered as extremely friable, due to it loss being above 30 % (35.381 %). The charcoal with 10 % of corn starch is regarded as slightly friable, it presents weight loss between 10 and 15 % (14.246 %), and coal with 15 % of binder is considered as not friable, since its weight loss is less than 10 % (5.838 %). However, the larger the amount of binder, the more expensive the briquette becomes. Among the presented results, the chosen amount of binder would be 10 %, because it is a reasonable amount to be mixed with the charcoal and the briquettes produced with this percentage has a satisfactory mechanical strength results.

4. Conclusions

In this study, the results showed that the orange bagasse is a potential biomass for the production of charcoal briquettes using corn starch as binder. This is due to the obtained charcoal briquettes presented satisfactory mechanical strength (compression and friability test) and good quality (proximate and ultimate analysis), with a high amount of carbon, allowing them to be used as domestic and commercial charcoal.

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