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Solid Fuel Produced from Mandarin Peels and Rice Husks

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Abstract

Biomasses like tangerine peels and rice husks are seen among the most abundant and accessible sources for conversion into products with a higher added value. One possibility is the production of solid fuels for the decentralization of energy production and utilization of agricultural residue. It is important to highlight that sustainable bioenergy must have high efficiency, therefore we have evaluated the higher and lower heating values of the specimens produced from rice shells husks, mandarin peels, cornstarch, glycerol, citric acid, and acetic acid. We have determined the total moisture content, ash content, and higher and lower heating value of the sixteen collected specimens. We have also determined the compressive strength, in which all samples presented a maximum resistance appropriate for the storage and handling of the developed solid fuels. The composites with a higher quantity of mandarin peels showed greater higher and lower heating values, of 19.18 MJ/kg and of 17.92 MJ/Kg, respectively. All developed samples have shown to be capable of replacing traditional heat sources like firewood (7.12-10.47 MJ/kg) with a better energy performance.

Keywords: Solid Fuel, Rice husks, Ponkan peels

1. Introduction

The use of agro-industrial residues for different ends is in line with the concept of sustainable development, which seeks food safety, environmental protection and energy efficiency (ONU, 2015; Thi et al., 2016; Matharu et al., 2016; Fernandez et al., 2017; Ong et al., 2018; Yates, 2017). The United Nations Sustainable Development Summit has adopted the document "Transforming our world: the 2030 Agenda for Sustainable Development", prioritizing the Objectives of Sustainable Development to protect the planet, end poverty, and guarantee prosperity for all. In this sense, we highlight objective number 12 which has the title "Ensure sustainable consumption and production patterns", has such goals as: efficient utilization of natural resources; reduction of food loss throughout the chain of production and supply, including post-harvest losses; keeping impacts to human health and the environment to a minimum; substantial reduction of residue generation by means of prevention, reduction, recycling and reuse; making sure people everywhere will hold relevant information and be aware of sustainable development and environmentally harmonic life styles; among others (ONU, 2015). The chain of food production and consumption is an important target in order to reach that goal, and it can be supported by agro-ecology (UNGA, 2015).

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Bioenergy systems are subject to legal, technical, environmental, social and economical settings. The implementation of bioenergy has been associated to risks and concerns, especially regarding plants with large-scale combustion (Schubert; Blasch, 2010). These concerns are related to biodiversity, deforestation, and the increased demand due to water and land scarcity (GBEP, 2011), causing an impact in the social acceptance of bioenergy (Dwivedi; Alavalapati, 2009; McCormick, 2010). However, on a regional level, bioenergy may encompass agricultural traditions and offer solutions to residue management. Moreover, agroecology lays the foundation for the development of sustainable agricultural styles departing from three dimensions: the ecological dimension approaches the recovery and maintenance of natural resources, including quality of the soil, biodiversity, water springs and other natural resources, placing a high value on energy and material recycling; the economic dimension seeks a growing independence from factors such as energy, inputs and services, and aims at making the relation between farming production and consumption of non-renewable resources compatible, while motivating practices like consumption of materials produced in the property; finally, the social dimension is concerned with the importance of general public access to the products yielded by the agricultural systems, so all segments of society may enjoy them in a more sustainable and renewable way (Lima, 2014; Zabaniotou, 2018).

It can be observed that in developing countries with low GDP, massive losses take place mainly during the initial and intermediate stages of the food supply chain (Lin et al., 2013). This organic material usually goes through conventional processes of residue handling like composting and burning, or are destined to irregular landfills, as is sometimes the case in Brazil, in spite of the legislation (Law 12305/10), which established the National Policy for Solid Residues. These leftovers are wrongly treated as residues, once they are in fact substrates with a diversity of functional chemical compounds, that can be used for the development of new products with market value (Garrido et al., 2014; Matharu et al., 2016; Yates, 2017). Thus, there is a need to prioritize the integrated use of resources of biological origin and to rethink practices in agriculture and the food industry, especially in what concerns the discarding of food and agricultural residues. The conventional processing of food residues does not explore the molecular complexity present in biomasses for useful products with added value, as for example, energy generation (Cortez et al., 2008; Lin et al., 2013; Escobar, 2015). Bioenergy, besides generating carbon sink, may play a fundamental role in energy security, in rural development, and may help increase family income. One of the ways food wastes can be explored is by reducing the volume for higher energy efficiency, once the more compact the material is, the greater is the energy stored by area (Nones et al., 2017; Zabaniotou, 2018).

Ideally, the resources used should have as closed material and energy cycles as possible in the agricultural systems, making longer use of them and extracting all the energy from the raw material. A production that makes use of inputs generated in its own property not only offers healthier products, but also prevents environmental pollution, preserves natural resources, and reduces the level of dependence of inputs derived from oil (Lima, 2014; Blades et al., 2017; Egea et al, 2018). On the regional level, bioenergy will be able to strengthen family agriculture, producing income, and reducing expenses and environmental impacts, especially by attaching men to rural areas (Zabaniotou, 2018).

Decentralization for small-scale energy needs is one of many options that could be adopted to produce energy in a reliable, economical, and environmentally sustainable way. A productive economic variety would follow, as families would become involved and artisanal agrarian family industries would be created. Food by-products and agricultural residues represent an extraordinary source of materials considered to be crucial to some Brazilian industries, and an alternative towards reducing losses and contributing to the development of the agro-industry in the country (Singh, 2017). Egea et al. (2018) explain that a bio-economical model must satisfy the demand and the social-economical expectations of the region, taking regional differences into consideration. Therefore, there is no single bio-economical model that can cater for all needs of the different regions of the country, once they must take territory, climate, diversity and availability of biomass, flora, and the local agricultural systems into consideration (Szarka et al., 2017).

Family agriculture in Brazil is characterized by the fact that its production is destined to local consumption and, as in many human activities results in waste/residues at the end of the process. In small amounts, the residue can be returned to its natural environment which will then, gradually recover, however, in most cases the volume exceeds the capacity of environmental recovery (Paula et

al., 2011; Sellin et al., 2013; SEBRAE, 2012). For this reason, a productive management of residues – that will decrease and reuse them - is necessary. One process that could be highlighted is that of briquettes manufacture, which consists of increasing the density of residual biomass by applying pressure and high temperatures, making the material compact and less humid, thus increasing the energy capacity of these fuels to a level higher than that found in the raw material (Paula et al., 2011; Sellin et al., 2013; Nones et al., 2017). When this fuel is produced in the property, it can be used to generate energy to small equipment, like boilers, wood ovens, stoves and fireplaces. It can also be used by households as alternative kitchen fuel, or in heating systems, reducing the rate of deforestation for common charcoal or firewood (Lubwama; Yiga, 2018). In the service sector it can be used for heating in a variety of establishments like hotels, gyms or restaurants, for example (Jacinto et al., 2016).

The appropriate management of the residues from local seasonal harvests, like rice husks, mandarin peel, or sugarcane straw is essential for the implementation of new sustainable uses and promotion of sustainable development of family agriculture. In the international market, according to data from the United States Department of Agriculture (USDA), world production of rice will be at 483.66 million tons in the 2017/18 crop (USDA, 2017). In the Mercosul, the countries should produce a total of 15.4 million tons of husked rice, and Brazil will be responsible for 76.14% of the production of the bloc (FAS/USDA, 2018). Also according to USDA, Brazil is the lead producer of citrus fruits, with special attention to the orange production of 17,300 (1,000 Metric Tons) in 2017/2018 (USDA, 2018), harvested mostly in the states of São Paulo and Minas Gerais, with a prediction for a final stockpile in 2017/2018 of an estimated 207 thousand tons (CEPEA, 2017). The sustainable paths of bioenergy must be selected on a high-efficiency basis, in this context, a study was conducted about the Higher Heating Value and Lower Heating Value of specimens obtained from mandarin peels and rice husks for use as solid fuel.

2. Method

Biomass of rice husk (*Oryza sativa*), mandarin peel (Ponkan - *Citrus reticulata*), cornstarch, glycerol, acetic acid, citric acid and distilled water were used for the production of solid fuel. Rice husks and mandarin peel were ground with a blender, then sieved using a 2 mm sieve (Solotest); only particle sizes less than 2 mm were used. Cornstarch powder was obtained from Fungini®, glycerol from Vetec®, and acetic acid from Vetec®. The commercial reagents were used as received and in accordance with the safety recommendations of the manufacturers.

For the preparation of the specimens, the cornstarch was manually mixed in 100 ml of distilled water. The mixture was then heated on a hot plate for about 10 min at a temperature of 250 °C. After this process, the mixture showed a gel-like aspect, and ground rice husk and mandarin peel were added. Specimen composites containing glycerol and acetic acid were mixed with cornstarch gel, homogenized, and then incorporated into the husks. The mixture was placed in PCV molds 10 cm high and 4.5 cm in diameter, and compressed by pressure of 100 N for about 1 min. The samples were oven dried (DeLEO®) for 48 h at 105 °C. After this period, the samples were manually demolded. The specimens were made in triplicate, and the mixture components were weighed accurately in a digital scale (Shimadizu®). To moisture content in the specimens was weighed using a precision scale (Shimadizu®) previously weighed/measured for qualification, the samples were then placed in an oven at a temperature of 105 ± 2 °C. After that, they were taken from the oven and placed into a desiccator with anhydrous calcium sulfate to cool and be weighed. The heating and cooling operations were repeated until constant weight, according to the ABNT NBR 8112/86 parameter and recommendations by Dias (2013) were reached.

The ash content was also calculated in the samples. First the material was placed in a moisture-free porcelain capsule to burn, then it was transferred to a pre-dried and weighed crucible, and then placed into a furnace (700 +/- 10 °C) for 3 hours. After this process, the material was cooled in a desiccator containing anhydrous calcium chloride until a constant mass was reached (ABNT NBR 8112/86; Dias, 2013). To measure the volume of solid fuels the diameter of the specimen was considered to be 4.25 cm and its height approximately 7.6 cm, the volume was calculated according to the method described by Dias (2013). The apparent density was estimated as the mass per unit volume of the specimens.

The method described by Dias¹³ was used to calculate the higher and lower heating values, which were compared with those of the Food and Agriculture Organization. The higher heating value (HHV) was measured in MJ/kg, using the ash content (A) and the moisture content (M) of the fuel according to the equation 1: $HHV = 20.0 \times (1 - A - M)$. To calculate the lower heating value (LHV) in MJ/kg, the ash content (A) and the moisture content (M) were taken into account, according to the equation 2: $LHV = 18.7 \times (1 - A) - 21.2 \times M$.

The mechanical tests were carried out by compressing 30 kN load cell in a universal testing equipment (EMIC DL-30000). In these tests, three cylindrical-shaped specimens (10 cm high, 4.5 cm in diameter) were subjected to pressure incrementation until plastic deformation occurred, at room temperature.

3. Results and discussion

The solid fuels were mainly obtained from rice husks and mandarin peels biomass the material was ground and easily thickened. The different composites presented cellulose and hemicellulose agglutination and produced specimens with an appropriate compressive strength for energy efficiency (Quirino et al., 2005; Luz et al., 2006; Chou et al., 2009; Paula et al., 2011; Vieira, 2014; Costa et al., 2017). In Fig. 1 the specimens from Series 3-04 can be observed.



Fig. 1. Solid fuels made from rice husk biomass (30 g), mandarin peel (30 g), cornstarch (15 g), glycerol (10 ml) and acetic acid (5 ml).

Table 1 shows the values determined for moisture content, ash content, lower and higher heating value in the 16 prepared compositions. Series 1 did not contain mandarin peel in its composition, while series 2, 3, and 4 showed 10 g, 30 g, and 50 g of mandarin peels, respectively. Of the four prepared series, series 4 had the lowest moisture content and the largest quantity of mandarin peels (Table 1). In all series, the specimens with no glycerol and acetic acid addition showed the lowest moisture content values. Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), the respective anion acetate (CH_3CO_2^-), and glycerol (triol) may be solvated by the water through hydrogen bonds, and keep a greater quantity of liquid in the sample. Gonçalves et al. (2009) suggest a moisture level of 15-20% for burning, considering that higher water values reduce the combustion heat, the temperature of the combustion chamber and the temperature of the exhaust gases. That is, all composites prepared are below these values, being that series 4 composites yielded the best results. The mean of the moisture content of the samples in this study was between 0.74% and 13.10%, which is lower than the moisture in firewood (25-30%), therefore, the requirements were met for the samples to be feasible heat sources (Gonçalves et al., 2006).

The lowest ash content of the four series was found in series 4 (which contained the largest quantity of mandarin peel). In complete combustion we found 18-25% of rice husk mass turned into ash, while in mandarin peels ash value is no higher than 2% (Foletto; Hoffmann, 2005; Gondim, et al., 2005; Dias, 2012). Cornstarch [$(\text{C}_6\text{H}_{10}\text{O}_5)_n$], glycerol ($\text{C}_3\text{H}_8\text{O}_3$) and acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) should not be responsible for ash contents, once their components are all oxygenated hydrocarbons that, during the process of complete combustion, generate CO_2 and H_2O . Thus, as rice husks are replaced with mandarin peels we can observe the reduction of the ash content in the specimens. All samples displayed lower ash content than that of 42.16% found by Morais et al. (2006) in rice husk coal briquettes and those found in our previous studies using rice husk biomass (Costa et al., 2017). Thus, the ash content found in the samples can be justified especially by the inorganic content of the inputs rice husks and Mandarin

peels. The results are also in accordance with Dias (2012) who asserts that most biomass residues have low ash content, with the exception of rice husks, which may contain up to 25% of ash. For this reason, so that a material can be used as solid fuel to generate heat, it is expected to yield the smallest possible amount of solid residues. This way, the problems created by ashes (like equipment corrosion) can be avoided. Moreover, all resulting ash must be given appropriate destination.

Table 1. Moisture content, ash content, higher heating value and lower heating value in sixteen composite samples.

Specimens		Cornstarch (15 g) in 100 ml of distilled water					Moisture content [%]	Ash content [%]	HHV [MJ/Kg]	LHV [MJ/Kg]
		Rice husk [g]	Mandarin peel [g]	Glycerol [ml]	Acetic acid [ml]	Citric acid [ml]				
Series 1	01	50	-	-	-	10	7.73 (0.05)	7.06 (1.07)	17.04 (0.22)	15.74 (0.21)
	02	50	-	-	05	10	8.40 (1.40)	8.19 (0.30)	16.68 (0.23)	15.39 (0.25)
	03	50	-	10	-	10	8.58 (0.57)	7.62 (0.22)	16.72 (0.10)	15.46 (0.10)
	04	50	-	10	05	10	13.10 (0.93)	9.21 (0.24)	15.47 (0.15)	14.12 (0.17)
Series 2	01	50	10	-	-	-	7.65 (0.11)	9.6 (0.22)	16.55 (0.04)	15.28 (0.04)
	02	50	10	-	05	-	7.90 (0.89)	9.04 (0.05)	16.61 (0.01)	15.33 (0.01)
	03	50	10	10	-	-	9.29 (0.19)	7.18 (0.06)	16.70 (0.01)	15.39 (0.01)
	04	50	10	10	05	-	9.88 (0.97)	7.21 (0.08)	16.58 (0.02)	15.26 (0.02)
Series 3	01	30	30	-	-	-	7.65 (0.09)	6.27 (0.25)	17.22 (0.05)	15.90 (0.05)
	02	30	30	-	05	-	7.90 (0.87)	6.12 (0.29)	17.20 (0.06)	15.88 (0.06)
	03	30	30	10	-	-	9.29 (0.067)	5.82 (0.14)	16.98 (0.03)	15.64 (0.03)
	04	30	30	10	05	-	9.88 (0.18)	5.10 (0.03)	17.00 (0.01)	15.65 (0.01)
Series 4	01	10	50	-	-	-	2.26 (0.06)	4.19 (0.25)	18.71 (0.05)	17.44 (0.05)
	02	10	50	-	05	-	4.31 (0.92)	4.00 (0.11)	18.34 (0.02)	17.04 (0.02)
	03	10	50	10	-	-	1.74 (0.75)	3.34 (0.11)	19.18 (0.01)	17.92 (0.01)
	04	10	50	10	05	-	1.57 (0.76)	3.41 (0.05)	19.00 (0.01)	17.73 (0.01)

() standard deviation

Higher heating value (HHV), is that in which combustion happens in constant volume, where the water formed during burning condenses and heat is recovered. The HHV of the specimens (Table 1) ranged from 19.18 MJ/kg to 15.47 MJ/kg and are represented in Fig. 1 (left). Among the four prepared series, the best results were found for the samples in series 4, which vary from 19.18 MJ/kg to 18.34 MJ/kg. According to Dias (2012), the briquettes with rice husk residues usually present higher heating value at 15.90 MJ/Kg, but the developed materials showed higher HHV numbers.

The HHV results found in the samples were higher than those in the reference values from FAO (Food and Agriculture Organization) of 17-18 MJ/kg (Eriksson et al., 1990) and were also above the values of 13,47-11,61 MJ/kg found in a previous study on rice husk biomass (Costa et al., 2017). Fig. 1 (right) shows the three series that contain mandarin peels. Considering the total mass of biomass (rice husks and mandarin peels) 60 g, replacing the rice husks with mandarin peels generated an increase in HHV.

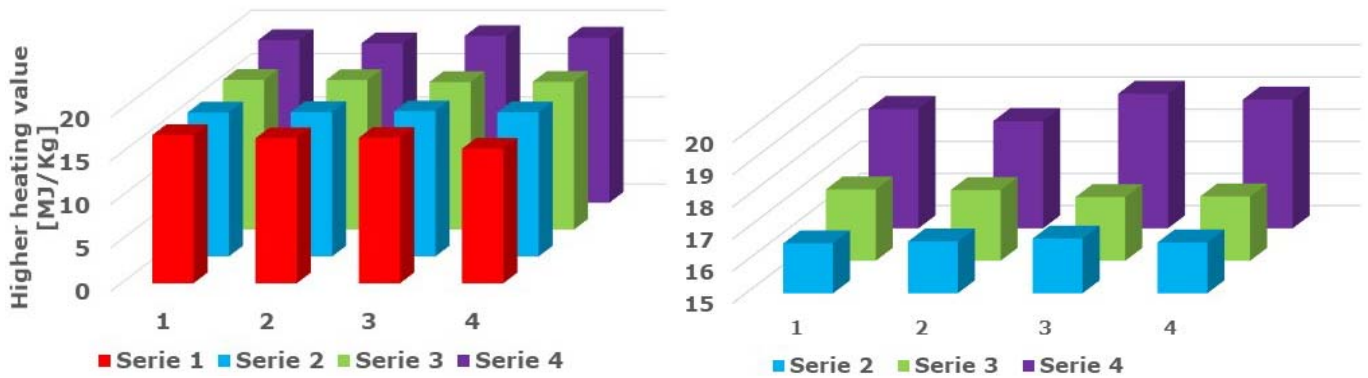


Fig. 2. HHV (UHV) of all produced specimens with variation in components (rice husks, mandarin peels, cornstarch, citric acid, glycerol, and acetic acid) (left) and specimens with mandarin peels (right).

In Fig. 2 (right), considering specimens 1 of the three series, the composite with 50 g of rice husks and 10 g of mandarin peels had a HHV of 15.28 MJ/kg, the one with 30 g of rice husks and 30 g of mandarin peels displayed a HHV of 15.88 MJ/Kg, and for the one with 10 g of rice husks and 50 g of mandarin peels the HHV was of 17.44 MJ/Kg. This behavior can also be observed in the remaining samples of the three series. Of the three series containing mandarin peels, series 4, with a larger amount of peels presented better results. In series 4 an increase in HHV could be observed when glycerol was added to the formula, in the third and fourth composites of the series; HHV of 19.18 MJ/Kg and 19.00 MJ/Kg, respectively. Glycerol is a component of the alcohol group (triol), with a flash point at 176 °C (FISPQ, 2014), that is, glycerol combustion generates enough heat to set the other components on fire, thus contributing to the HHV. In specimens with no glycerol the value found was of 17.44 MJ/Kg.

Lower Heating Value (LHV) is the free energy by unit of mass of a fuel, after the losses to water evaporation are subtracted (Jara, 1997). For this reason it is fundamental to analyze the LHV of a fuel, once it allows the actual quantification of the energy in the material. The LHV of the specimens are shown in Table 1. The values ranged from 17.92-14.122 MJ/Kg. These values were higher than those of firewood (7.12-10.47 MJ/kg), those found by Vieira (2014), and the ones identified in the rice husk briquettes previously developed (10.27-12.07 MJ/kg) (Costa et al., 2017). The LHV of the samples were also superior to those pointed by FAO, which predicts a spectrum from 15.4-16.5 MJ/kg (Eriksson et al., 1990). The best results were the ones found in the specimens in series 4, of 17.92-14.04 MJ/kg.

Fig. 3 shows the compressive strength of the prepared specimens, the ones with mandarin peels are on the right-hand side. The compressive strength of the developed solid fuels is important once these must be able to tolerate enough load to resist handling, transportation, and storage with no loss of mass or deformation.

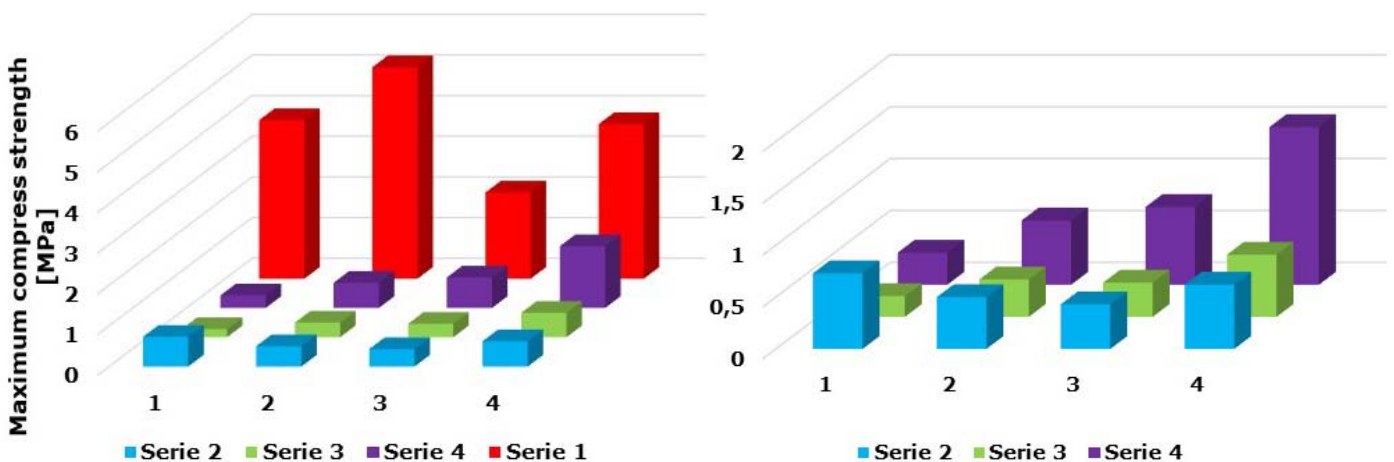


Fig. 3. Compressive strength of all specimens in the study with varying components (rice husks, mandarin peels, cornstarch, citric acid, glycerol, and acetic acid) (left) and specimens with mandarin peels (right).

In Fig. 3 (left) the specimens that presented greater compressive strength were the ones from series 1, with rice husks, citric acid, cornstarch, glycerol, and acetic acid. That may be due to the intermolecular bonding of these inputs. The carboxylic acid groups of the citric acid ($\text{CO}_2\text{HCH}_2\text{C}(\text{CO}_2\text{H})(\text{OH})\text{CH}_2\text{CO}_2\text{H}$) are likely to have formed esters with the OH groups in the cellulose, the hemicellulose, and the glycerol promoting the formation of copolymers, resulting in the compressive strength of series 1. Glycerol and citric acid were added to facilitate bonding of cellulose with hemicellulose, and acetic acid was added to catalyze these reactions, which favor agglutination of the components (Costa et al., 2017). In series 1 the addition of glycerol reduces the compressive strength of the specimen (3), and does not favor the formation of copolymers like cellulose and hemicellulose. Series 2, 3, and 4 showed lower values than those of series 1 for compressive strength. In Fig. 3 (right) it can be observed that, in general, addition of glycerol and acetic acid contribute to the increase in compressive strength of the samples. It can also be suggested that hydrogen bonds can occur among molecules of the inputs. Intermolecular and intramolecular bonds are responsible for the compressive strength observed in these specimens.

Overall, nitric acid brought improvements concerning the compressive strength of the specimens and did not exhibit noteworthy reduction of the higher and lower heating values of the samples.

4. Final Remarks

The specimens prepared with rice husk and mandarin peel biomass have shown to be appropriate for using as solid fuel in what concerns higher and lower heating values. The incorporation of biomass furthers the creation of new products from agricultural wastes generating thus, food by-products. Prepared solid fuels increase the possibilities of use of the local biomass and may be consumed in the property where they were produced. Therefore, it consists of decentralized energy generation, and national production. The use of biomass can be environmentally advantageous considering that the released CO_2 is absorbed by the plants during photosynthesis, keeping the quantity of the gas constant in the atmosphere. Such benefits make biomass a strategic option for the country. In general terms, biomass used as discussed here would perfectly fit the concept of sustainable development, as it would allow the creation of jobs in the region, make economic activities more dynamic, reduce costs related to distribution and transmission of energy, and, if used sustainably, would not damage the environment.

For future studies we suggest investigating the constitution of the ashes and gases generated in the combustion process.

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