MANDARIN PEELS AND RICE HUSKS AS SUBSTRATES FOR SOLID BIOFUEL

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Biomass, such as mandarin peels and rice husks, are among the most abundant and accessible sources for the conversion of crops into solid biofuel. It is important to highlight that sustainable bioenergy must have high efficiency; therefore, the heating values of biofuel samples produced from rice husks, mandarin peels, corn starch, glycerol, citric acid and acetic acid have been evaluated in the present study. The total moisture content, ash content and heating values of the sixteen biofuels produced were determined. The compressive strength was also determined and it was found that all the samples presented maximum resistance, appropriate for the storage and handling of the developed solid biofuel. Replacing rice husks with mandarin peels resulted in a reduction of the silica mass in the ash content. In addition, in four specimens, the amounts of nutrients (N, P, K, Ca and Mg) and heavy metals (Cu, Zn, Fe, Mn, Cd, Pb, Cr and Al) found in the ash were measured. It was found that the amount of nutrients increased proportionally with the quantity of mandarin peels in the solid biofuel. The solid biofuel with a higher quantity of mandarin peels showed greater high and low heating values, which were 19.18 $MJ.kg^{-}1$ and 17.92 $MJ.kg^{-1}$, respectively. All the developed biofuels were shown to be capable of replacing traditional heat sources, such as firewood (7.12-10.47 $MJ.kg^{-1}$).

Keywords: rice husks, mandarin peels, solid biofuel, HHV and LHV, nutrients and heavy metals

INTRODUCTION

The use of agro-industrial residues for different products is in line with the concept of sustainable development, which seeks food safety, environmental protection and energy efficiency.[1] The chain of food production and consumption should also tend towards reaching this goal,[2] and it can be supported by agro-ecology.[3-5]

On the international market, according to data from the United States Department of Agriculture (USDA), the world production of rice reached 483.66 million tons in the 2017/2018 crop. Countries in the Southern Common Market produced a total of 15.4 million tons of husked rice, and Brazil was responsible for 76.14% of that production. Also, according to the USDA, Brazil is the leading producer of citrus fruits, with a notable orange production of 17,300 (1,000 metric tons) in 2017/2018, with 207 thousand tons contributed to the final stockpile in 2017/2018.[6] For this reason, the appropriate management of residues from local seasonal harvests, such as rice husks, mandarin peels, or sugarcane straw, is essential for the implementation of new sustainable uses and the promotion of the sustainable development of agriculture.[5-7,8]

It can be observed that in developing countries with a low gross domestic product, massive losses occur mainly during the initial and intermediate stages of the food supply chain.[9] Organic residues usually go through conventional processes of waste management, such as composting and burning, or are destined for irregular landfills, as is sometimes the case in Brazil, despite the legislation that established the National Policy for Solid Residues.[10] These by-products are wrongly treated as residues; 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.[4,5,7,9,11]

One of the ways in which food waste can be avoided is to use food by-products for bioenergy production.[12-14] As an example, pine pellets,[15] olive stones,[16] avocado stones,[17] almond shells,[18] mango stones,[17] and herbaceous biomasses blended with woody biomasses[4] are all used to prepare solid biofuels.[19]

However, no existing studies are known to the authors on the use of biofuels prepared from mandarin peels and rice husks to improve their potential as solid biofuels. Glycerol, acetic acid, and citric acid were also used in the production of biofuels because they are co-products (biodiesel, citrus peels) or wastes of production processes (pickle and grape processing), with low added value or in need of treatment. However, these inputs may contribute to the formation of intermolecular covalent bonds by modifying the mechanical properties of biofuels.

When such fuel is produced on farms, it can be used to generate energy to power small equipment, such as boilers, wood ovens, stoves and fireplaces. It can also be used by households as alternative kitchen fuel or in heating systems, which reduces the rate of deforestation for common charcoal or firewood.[20]

Decentralization for small-scale energy needs is one of the many options that could be adopted to produce energy in a reliable, economical, and environmentally sustainable way. Food by-products and agricultural residues represent an extraordinary source of materials that are considered to be crucial for some industries as an alternative energy that will reduce losses and contribute to the development of the agro-industry in the country.[21] Egea *et al*.[22] explain that a bio-economical model must satisfy the social-economical demand and expectations of the region, taking regional differences into consideration.[23]

The sustainable paths of bioenergy must be selected on a high-efficiency basis; in this context, the objectives of this study were, first, to assess the properties of mandarin peel with rice husks (compressive strength, Fourier transform infrared analysis, moisture content, ash content, high heating value and low heating value) as a solid biofuel and, second, to determine the silica mass, the amount of nutrients (N, P, K, Ca and Mg) and of heavy metals (Cu, Zn, Fe, Mn, Cd, Pb, Cr and Al) found in the ashes, which can be considered a contribution to the soil quality, to describe the ability of this biomass residue to serve as an energy resource for residential and industrial heating facilities.

EXPERIMENTAL

Materials and methods

Rice husks (*Oryza sativa*), mandarin peels (Ponkan – *Citrus reticulata*), corn starch, glycerol, acetic acid, citric acid and distilled water were used for the production of solid biofuel. These chosen rice and mandarin varieties are cultivated in all Brazilian states. The inputs (glycerol, acetic acid, citric acid and distilled water) were added to evaluate their influence on the mechanical resistance of solid biofuels.

Corn starch powder was obtained from Fungini® (São Paulo, Brazil), while citric acid (97%), glycerol (98% purity), and acetic acid (glacial) were obtained from Vetec® (São Paulo, Brazil). The commercial reagents were used as received and in accordance with the safety recommendations of the manufacturers. Rice husks and dried mandarin peels were ground manually with a mortar and pestle, and then sieved using a 2 mm sieve (Solotest); only particle sizes less than 2 mm were used.

Preparation of biofuels

Initially, corn starch was mixed in 100 mL of distilled water and heated to 90 °C for 10 min. Then, the specific input was added for each formulation (Table 1), and, finally, mandarin peels and rice husks were added. The mixture was placed into PCV moulds 10 cm high and 5 cm in diameter, and compressed at a pressure of 100 N for approximately 1 min. The samples were oven dried (DeLEO®) for 48 h at 105 °C. After this period, the samples were manually demoulded. Biofuels were triplicated.

Moisture and ash content

Moisture and ash content were determined according to the standards set by the International Organization for Standardization.[25,26]

High and low heating values

High and low heating values were compared to those established by the Food and Agriculture Organization. The higher heating value (HHV) was determined in $MJ.kg^{-1}$, using the ash content (A) and the moisture content (M) of the biofuel according to Equation 1: $HHV = 20.0 \times (1 - A - M)$.

To calculate the lower heating value (LHV) in $MJ.kg^{-1}$, the ash content (A) and the moisture content (M) were used, according to Equation 2: $LHV = 18.7 \times (1 - A) - 21.2 \times M$.[24]

Mechanical resistance to compressive strength

The mechanical tests were carried out by compressing a 30 kN load cell of EMIC DL-30000 Universal Testing Equipment. In these tests, three cylindrically shaped samples (10 cm high, 4.5 cm in diameter) were subjected to pressure incrementation until plastic deformation occurred at room temperature.[27]

Infrared analysis

Fourier transform infrared (FTIR) spectra were collected in the 4000 to 650 cm^{-1} range, using a Perkin-Elmer FTIR spectrometer (model 781). The samples were ground to a fine powder, mixed with KBr and then pressed in a Specac press, with a total load of 9 t, to obtain a disc (sample scan time, 16 s; background scan time, 16 s; and resolution, 4.0 cm^{-1}).

Silica analysis

The silica content of the samples was determined from 1 g of ash dissolved in 50 mL of distilled water, added to 1 mL of HCl and stirred for 1 h at 90 °C. After cooling, the mixture was vacuum filtered. Then, 50 mL of a 1.5 $mol.L^{-1}$ NaOH solution was added to the mixture while continuously stirring for 1 h at 90 °C. Once again, the mixture was vacuum filtered. Once the resulting filtered mixture with Na_2SiO_3 was still basic, a solution of 0.1 $mol.L^{-1}$ HCl was slowly added until the mixture reached a neutral pH. To remove sodium chloride, the gel was repeatedly washed with distilled water, and the resulting gel was dried in a drying oven at 50 °C and then weighed.[28,29]

Nutrients and heavy metals

The determination of the N, P, K, Ca, Mg, Cu, Zn, Fe, Mn, Cd, Pb, Cr and Al contents in the samples was performed by nitroperchloric digestion (AOAC, 2005), and subsequent quantification was performed by flame atomic absorption spectroscopy (FAAS) with a GBC 932 AA instrument.

Determination of the relative density of black smoke

The samples were placed in a porcelain container in which they were burned. The resulting smoke was assessed by using the Ringelmann scale.[30] The experiment was conducted for approximately 5 min in an exhaust hood; smoke images were captured and compared to the scale using VirtualRingelmann® software.

RESULTS AND DISCUSSION

The solid biofuels were obtained mainly from rice husks (*Oryza sativa*), mandarin peels (Ponkan – *Citrus reticulata*) and corn starch. The different solid biofuels prepared presented cellulose and hemicellulose agglutination, and produced biofuels with an appropriate compressive strength for energy efficiency.[24] In Figure 1, the solid biofuel made from rice husk biomass (30 g), mandarin peels (30 g), corn starch (15 g), glycerol (10 mL) and acetic acid (5 mL) is shown.

Table 1 shows the values that were determined for the moisture content, ash content, low and high heating values and compressive strength of the 16 prepared formulations. Biofuels were prepared with rice husk biomass and citric acid, combinations of rice husk and mandarin peels, and variations of glycerol and acetic acid (Table 1).

Specimen 13 had the lowest moisture content; its composition was 10 g of rice husks, 50 g of mandarin peels and 15 g of corn starch. Generally, the biofuels without the addition of glycerol and acetic acid showed the lowest moisture content values. Acetic acid (CH_3CO_2H), the respective anion acetate ($CH_3CO_2^-$), and glycerol (a triol) may be solvated in water through hydrogen bonds, which would retain a greater quantity of water in the sample. Gonçalves *et al*. suggested an optimum 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. All of the prepared solid biofuels were below these values, and samples 13, 14, 15 and 16, with 50 g of mandarin peels, yielded the best results.

Figure 1: Solid biofuel made from rice husk biomass (30 g), mandarin peels (30 g), corn starch (15 g), glycerol (10 mL) and acetic acid (5 mL)

Table 1
Moisture content, ash content, heating values and compressive strength of sixteen solid biofuel samples

Specimens	Corn starch (15 g) in 100 mL of distilled water					Moisture content (%)	Ash content (%)	HHV (MJ/kg)	LHV (MJ/kg)	Compressive strength (MPa)
	Rice husk (g)	Mandarin peel (g)	Glycerol (mL)	Acetic acid (mL)	Citric acid (mL)					
1	50	-	-	-	10	7.73±0.05	7.06±1.07	17.04±0.22	15.74±0.21	3.90±0.01
2	50	-	-	05	10	8.40±1.40	8.19±0.30	16.68±0.23	15.39±0.25	5.20±0.02
3	50	-	10	-	10	8.58±0.57	7.62±0.22	16.72±0.10	15.46±0.10	2.12±0.02
4	50	-	10	05	10	13.10±0.93	9.21±0.24	15.47±0.15	14.12±0.17	3.80±0.01
5	50	10	-	-	-	7.65±0.11	9.6±0.22	16.55±0.04	15.28±0.04	0.73±0.02
6	50	10	-	05	-	7.90±0.89	9.04±0.05	16.61±0.01	15.33±0.01	0.5±0.03
7	50	10	10	-	-	9.29±0.19	7.18±0.06	16.70±0.01	15.39±0.01	0.43±0.05
8	50	10	10	05	-	9.88±0.97	7.21±0.08	16.58±0.02	15.26±0.02	0.62±0.03
9	30	30	-	-	-	7.65±0.09	6.27±0.25	17.22±0.05	15.90±0.05	0.20±0.02
10	30	30	-	05	-	7.90±0.87	6.12±0.29	17.20±0.06	15.88±0.06	0.36±0.02
11	30	30	10	-	-	9.29± 0.07	5.82±0.14	16.98±0.03	15.64±0.03	0.33±0.01
12	30	30	10	05	-	9.88±0.18	5.10±0.03	17.00±0.01	15.65±0.01	0.60±0.01
13	10	50	-	-	-	1.57 ± 0.06	4.19±0.25	18.71±0.05	17.44±0.05	0.31±0.01
14	10	50	-	05	-	4.31 ± 0.92	4.00±0.11	18.34±0.02	17.04±0.02	0.62±0.02
15	10	50	10	-	-	1.74 ± 0.75	3.34±0.11	19.18±0.01	17.92±0.01	0.75±0.04
16	10	50	10	05	-	2.26 ± 0.76	3.41±0.05	19.00±0.01	17.73±0.01	1.52 ± 0.03

±standard deviation

The mean moisture content of the samples in this study was lower than the moisture content of firewood (25-30%); therefore, the samples met the requirements for feasible heat sources.[31]

The ash content after complete combustion was found in the range of 3.34-9.60%, with the lowest ash content found for specimen 15, which contained 10 g of rice husks, 50 g of mandarin peels, 10 mL of glycerol and 15 g of corn starch.[32,33] Corn starch [$(C_6H_{10}O_5)_n$], glycerol ($C_3H_8O_3$) and acetic acid ($C_2H_4O_2$) are not present in the ash contents, since their components are all oxygenated hydrocarbons that generate CO_2 and H_2O during the process of complete combustion.[34,35] Thus, the amount of ash increases as the rice husk content increased in the samples. All samples displayed lower ash content than that of 42.16% found by Morais *et al*. in rice husk coal briquettes and those found in previous studies using rice husk biomass.[24] Thus, the ash content found in the samples can be justified, especially by the inorganic content of the inputs of rice husks and mandarin peels. The results are also in accordance with those of Dias,[33] who asserts that most biomass residues have a low ash content, with the exception of rice husks, which may contain up to 25% ash. For this reason, for a material to be successfully used as a solid biofuel to generate heat, it is expected to yield the smallest possible amount of solid residues. Small ash yields mitigate the problems created by ash (such as equipment corrosion). Moreover, all the resulting ash must be properly disposed of.[34]

A higher heating value (HHV) is when combustion occurs at a constant volume, where the water that formed during burning condenses and the heat is recovered. The HHV of the samples (Table 1) ranged from 19.18 $MJ.kg^{-1}$ to 15.47 $MJ.kg^{-1}$. In samples 15 and 16 (Table 1), an increase in HHV could be observed when glycerol was added to the formula, with HHVs of 19.18 $MJ.kg^{-1}$ and 19.00 $MJ.kg^{-1}$, respectively. Glycerol is a component of the alcohol group (triol), with a flash point at 176 °C;[36] that is, glycerol combustion generates enough heat to set the other components on fire, thus contributing to the HHV. In samples with no added glycerol, the values were lower. The best HHV was found for specimen 15, which was 19.18 $MJ.kg^{-1}$. According to Dias,[33] briquettes made from rice husk residues usually present an HHV of 15.90 $MJ.kg^{-1}$, but the developed materials showed higher HHVs. The HHV results that were found in the samples were also higher than the 17-18 $MJ.kg^{-1}$ reference values set by the Food and Agriculture Organization (FAO) and were above the values of 11.6-13.5 $MJ.kg^{-1}$ found in a previous study on rice husk biomass.[24,37] The values that were obtained were similar to those described for pine,[19] olive stone,[16] avocado stone,[17] almond shell[18] and mango stone[38] solid biofuels, which had HHVs of 19.82 $MJ.kg^{-1}$, 17.88 $MJ.kg^{-1}$, 19.15 $MJ.kg^{-1}$, 18.20 $MJ.kg^{-1}$ and 18.05 $MJ.kg^{-1}$, respectively.

The lower heating value (LHV) is the free energy by unit of mass of a fuel after the losses to water evaporation are subtracted.[39] For this reason, it is fundamental to analyse the LHV of a fuel, as it allows for the actual quantification of energy in the material. The LHV of the biofuels are shown in Table 1, and the values ranged from 14.1-17.9 $MJ.kg^{-1}$. These values were higher than those of firewood (7.1-10.5 $MJ.kg^{-1}$) found by Vieira[40] and those identified in the previously developed rice husk briquettes (10.3-12.1 $MJ.kg^{-1}$).[24] The LHV of the samples were also superior to those reported by the FAO, which predicts the range of 15.4-16.5 $MJ.kg^{-1}$.[37] The best result was found for specimen 15, which was 17.92 $MJ.kg^{-1}$. Generally, the values obtained were similar to or greater than those described for pine,[15] olive stone,[16] avocado stone,[17] almond shell,[18] and mango stone,[17] solid biofuels, which had LHVs of 18.50 $MJ.kg^{-1}$, 16.50 $MJ.kg^{-1}$, 17.89 $MJ.kg^{-1}$, 17.92 $MJ.kg^{-1}$ and 17.27 $MJ.kg^{-1}$, respectively.

In Figure 2, a trendline of moisture content, ash content and HHV for solid biofuels can be observed. It may be remarked that with the reduction of the amount of rice husks, there is a tendency for a reduction in moisture and ash content and a slight increase in HHV of the solid biofuels. Among the biofuels containing mandarin peels (samples 5-16, Fig. 2), those with a larger amount of peels presented improved results for HHV and LHV.

In general, citrus biomass is rich in limonene,[41,42] which is a non-aromatic cyclic hydrocarbon with a flash point of 48 °C.[43] Unlike the occasions when this biomass is used for biogas and bioethanol production, where limonene is usually the main obstacle,[44-46] in solid biofuels, limonene seems to contribute to an increase in the calorific value. Thus, mandarin peel briquettes may be considered an alternative to traditional fuels, such as firewood and common charcoal, and may also help prevent the negative effects of petroleum products. Mandarin peels can be used as an adequate substrate for combustion

processes, thereby preventing energy losses.[45]
The compressive strength experienced by industrial fuel briquettes (0.375 MPa) could be far more severe than those experienced by domestic fuel briquettes (0.006 MPa).[25-47] In Table 1, for the 16 prepared biofuels, four (9, 10, 11 and 13) did not achieve the mechanical resistance that was considered for industrial fuel briquettes, but when the value for briquettes of domestic fuels was considered, all of the biofuels reached the reference value of 0.006 MPa. Specimen 2 (Table 1) presented greater compressive strength (5.20 MPa) than that of the other samples, similar to that observed by Costa *et al.* (2017). Glycerol and citric acid were added to facilitate the bonding of cellulose with hemicellulose, and acetic acid was added to catalyse these reactions, which favour agglutination of the components.[24,35]

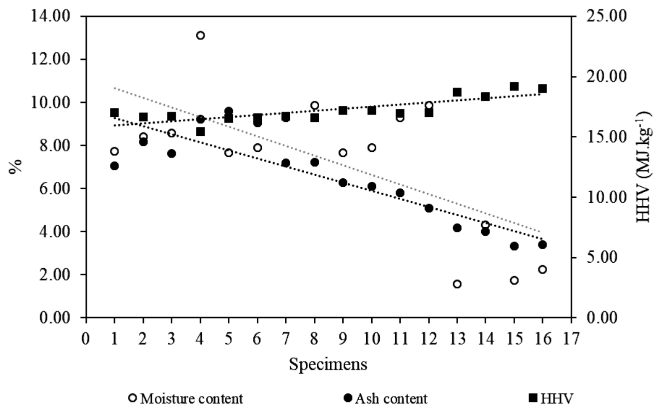


Figure 2: Trendline of moisture content, ash content and HHV for solid biofuels

The carboxylic acid groups of citric acid ($CO_2HCH_2C(CO_2H)(OH)CH_2CO_2H$) could have formed these linkages with the OH groups in the cellulose, hemicellulose, and glycerol to promote the formation of copolymers, which results in a higher compressive strength for some biofuels. It is also suggested that hydrogen bonds can occur among molecules of the inputs. Overall, citric acid improved the compressive strength of the samples.[35] For the analyses of FTIR, nutrients and heavy metals, samples 1, 5, 9 and 13 were selected, as these present the influences of the replacement of rice husks by mandarin peels.

In every IR spectrum (Fig. 3), a broad band in the axial stretching region occurs at approximately 3429 cm^{-1}. This band indicates the presence of the hydroxyl groups existing in cellulose, hemicellulose, and citric acid and the hydrogen bonds (polymer association) of these components. The range between approximately 2929 cm^{-1} and 2886 cm^{-1} is attributed to aliphatic C–H groups, and the carbonyl stretching band was observed at 1736 cm^{-1} (C=O), which were noted in all the spectra. The peaks at wavenumbers of 1630 and 1480 cm^{-1} correspond to aromatic vibrations, and the band at 1024 cm^{-1} was attributed to the tension vibration of C–O. Thus, for samples 1, 5, 9 and 13, which did not have added acetic acid and/or glycerol, the compressive strength was attributed to the intermolecular forces between the input materials.[48]

The use of biomass as an energy source to help mitigate climate change and to increase energy security must have a closed carbon cycle. Carbonaceous residues of bioenergy production with a potential for soil carbon sequestration and residue management have been broadly employed as soil conditioners, as they hold a significant amount of plant nutrients (macro and micronutrients).[15,49] Biomasses usually consist of cellulose, hemicellulose and lignin in different proportions.[50] They also contain a considerable amount of minerals, such as silica (especially in rice husks) and other macro nutrients that are found in varying quantities in vegetables.[51,52] It was observed that these carbon residues displayed the potential to improve the basic physiology of the soil, as well as its chemical and biological properties.[49,53]

In the solid biofuel, 1.01 g (σ = 0.04), 1.22 g (σ = 0.16), 0.93 g (σ = 0.02) and 0.24 g (σ = 0.47) of silica were measured in samples 1, 5, 9 and 13, respectively.[34] The presence of mandarin peels in specimen 5 as a substitute for citric acid in specimen 1 provided an increase in silica content.

Replacing rice husks with mandarin peels (samples 5, 9 and 13) resulted in a reduction in silica mass in the ash content.

In addition, the full use of the residue and its contribution to improving the chemical properties of the soil depend mainly on the levels of nutrients that are found in the ashes of the biomass. However, attention must be paid to handling the ashes due to the presence of elements that topically trigger environmental concern, but are commonly found in biomass. Figure 4 shows the level of nutrients (A), microelements and heavy metals (B) found in samples 1, 5, 9 and 13.

Figure 4A shows the obtained concentrations of phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) in the form of oxides, confirming that samples 1, 5, 9 and 13 are alkaline.[34] Although these nutrients are present in all the samples, it was observed that as the amount of mandarin peels in the solid biofuels increased, the quantity of nutrients also increased.

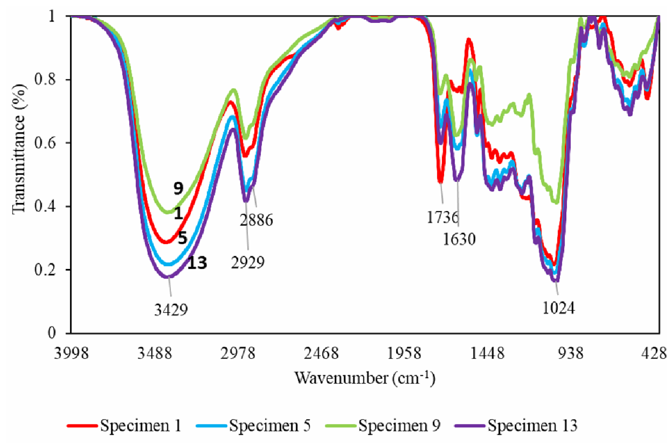
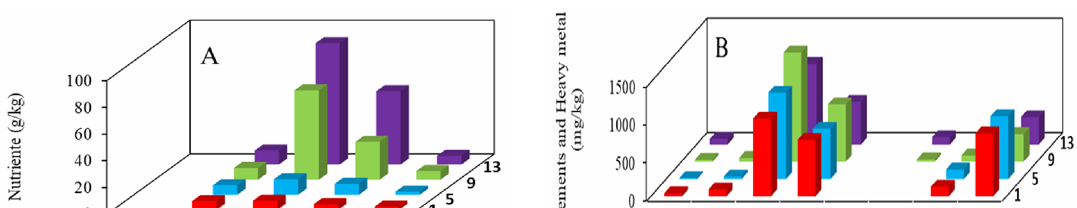


Figure 3: FTIR spectra of solid biofuel samples 1, 5, 9 and 13



	N	P	K	Ca	Mg
Specimen 1	--	6.63	6.85	4.30	2.43
Specimen 5	--	7.18	11.58	8.18	2.33
Specimen 9	--	8.72	66.75	28.30	6.45
Specimen 13	--	10.38	90.60	54.75	6.60

	Cu	Zn	Fe	Mn	Cd	Pb	Cr	Al
Specimen 1	40.00	92.00	1020.50	741.50			126.50	825.50
Specimen 5	14.00	34.50	1135.00	662.00			126.50	825.50
Specimen 9	26.00	51.00	1436.00	755.50		31.50	82.50	364.00
Specimen 13	74.50	172.50	1060.00	560.50		96.00	51.00	360.00

Figure 4: (A) Levels of nutrients: nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg); and (B) elements and heavy metals: copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), cadmium (Cd), lead (Pb), chromium (Cr) and aluminium (Al), in samples 1, 5, 9 and 13

Figure 4B shows the obtained values of the elements and heavy metals: copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), cadmium (Cd), lead (Pb), chromium (Cr) and aluminium (Al) for samples 1, 5, 9 and 13. Biofuels with increasing mandarin peel and decreasing rice husk contents showed variations in the quantities of copper (14.00-74.50 mg/kg), zinc (34.5-74.50 mg/kg), iron (1020.50-1436.00 mg/kg) and manganese (560.50-755.50 mg/kg), a reduction in the quantities of aluminium (360.00-825.50 mg/kg) and chromium (51.00-126.50 mg/kg), and an increase in the lead content (31.50-96.00); additionally, no cadmium was detected.

The relative density of black smoke (Ringelmann's scale) was determined, by examining the colour of the smoke released during the combustion process. The smoke emanating during burning was not black (shade 1-2). Shade 1 is slightly grey and is usually categorized by air pollution boards as acceptable, and it corresponds to an opacity of 20%.[30] Shades

2, 3, 4 and 5 correspond to opacities of 40%, 60%, 80% and 100% (completely black), respectively, and are usually considered to be black smoke by air pollution boards of most countries.

CONCLUSION

In this study, solid biofuels composed of rice husks, mandarin peels and corn starch were prepared with and without the addition of citric acid, glycerol and acetic acid. The experimental results show that the interaction between vegetal fibres can be improved by chemical treatments (citric acid, glycerol, and/or acetic acid). Therefore, chemical treatment increased the compressive strength of the solid biofuel; the optimal results were obtained with the addition of citric acid.

All the prepared solid biofuels had overall moisture content and ash content that were less than those of wood. This study showed that mandarin peels accounted for lower ash content in the biofuels than rice husks. As the amount of mandarin peels increased in the composition of the solid biofuel, decreasing values of silica and increasing values of nutrients (P, K, Ca, and Mg) were found in the ashes. It is recommended that the soil be monitored as ashes are added, so that it does not reach toxic levels of micro- or macronutrients; that is, soil protection must be conducted in a preventive way. The biofuel samples with an increasing mandarin peel content showed variations in the quantities of copper, zinc, iron and manganese, a reduction in the quantities of aluminium and chromium, an increase of lead and no detection of cadmium.

The higher heating value that was obtained (19.2 $MJ.kg^{-1}$) is greater than that of other biomass sources that were evaluated by previous studies and is in line with those of other sources of biomass that are currently used in home and industrial heating applications.

The results show that it is possible to obtain solid biofuel with a higher HHV and LHV than those of firewood, and a valuable chemical feedstock from mandarin wastes. As a suggestion for future work, analysis of the gases resulting from the combustion of biofuels is recommended.

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