CELLULOSE CHEMISTRY AND TECHNOLOGY

SOLID BIOFUEL FROM GLYCEROL AND AGRICULTURAL WASTE AS A SOURCE OF ENERGY

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Rice husk is among the most abundant, low-cost renewable sources available for conversion into value-added products. The objective of this study was to evaluate the properties of specimens made from rice husk, cornstarch, glycerol, and acetic acid. For the preparation of the specimens, cornstarch was manually mixed in distilled water and heated up. Then, rice hulls (2 mm) were added to the main mixture. Specimen composites containing glycerol and acetic acid were mixed with cornstarch gel, homogenized, and then incorporated into rice husk. Four different composites were prepared, molded into cylinders and taken to the oven for drying. Overall moisture content, ash content, and upper and lower heating values were determined for all the specimens. The composites were characterized by Fourier transform infrared spectroscopy (FTIR), mechanical resistance to compressive strength, and smoke monitoring. Rice husk and cornstarch composites had the lowest overall moisture content (15.62%), whereas rice husk, cornstarch, and glycerol composites showed the lowest ash content (11.71%). The prepared solid fuel that reached the highest heating value was the one containing rice husk, cornstarch and glycerol, reaching an upper heating value of 13.47 MJ/kg and a lower heating value of 12.07 MJ/kg. The most resistant specimens (1.23 MPa) were those composed of rice husk, cornstarch, glycerol, and acetic acid. The developed solid fuels could replace satisfactorily traditional calorific sources, and were similar or better than conventional firewood and charcoal briquettes.

Keywords: biofuel, cornstarch, solid fuel, rice husk, glycerol

INTRODUCTION

Today's society is enjoying the comfort offered by non-renewable raw materials, mainly in the form of fuels and products. However, the negative environmental impacts are increasingly serious and cannot be ignored. Examples are climate changes caused by global warming and conventional oil reserves depletion, combined with an intense socioeconomic development, requiring constant growth in demand for energy sources.[1-3]

However, we are encouraged to use renewable raw materials, which can replace, at least partially, fossil fuels, such as oil, coal, and natural gas. The reuse of waste materials has been promoted as well. This is a widely discussed topic among academics and in the society, as it involves technical, economic, and environmental aspects.[2] Furthermore, energy production from materials that would otherwise be discarded is one of the key factors for economic and social development.[3]

Brazil has been a world leader in agro-energy in the last decades. The domestic energy supply in Brazil was 624,3 TWh in 2015. Renewable energy sources accounted for 39.4% of this amount, of which 11.5% came from hydro-produced electricity, 8.1% from firewood and charcoal, 15.7% from sugarcane derivatives, and 4.1% from other renewable sources (Brazil, 2015).[4]

From the point of view of energy production, the Brazilian Electricity Regulatory Agency considers that biomass includes all renewable resources derived from organic matter of plants and animals that can be used for energy production.[5] When the bonds between carbon, hydrogen, and oxygen atoms are broken by combustion, digestion or decomposition, the chemical energy stored in these substances is released. The use of biomass as raw material for thermal conversion depends on the chemical and physical properties of molecules.[1,3,6]

Brazil is one of the largest agricultural producers in the world, due to the availability of cultivation area, diversity of cultures, geographical location, ideal climatic conditions, as well as its rich biodiversity and advanced technology. Therefore, the country has a great potential to provide raw materials (wastes) for the production of renewable fuels.[7]

In southern Brazil, rice-based raw materials are important for biofuel production. The national production of rice, according to the Brazilian Institute of Geography and Statistics (IBGE) in 2015 was of about 12 million tons.[8] The South region accounted for 60% of the national production, whereas the state of Santa Catarina was the second largest domestic producer.[9]

Glycerol can be a blend of both animal and vegetable oils to form triacylglycerol molecules. During the biodiesel transesterification process, glycerol is generated as a by-product. The use of glycerol is well-established,[10] but its price per liter has dropped over the years due to growing supply.[11]

One of the high priority alternatives to minimize negative environmental impacts consists in biofuels, because they help reduce the overall CO_2 emission rate. In addition to global issues, biofuels have superior environmental benefits over fossil fuels. Biofuel burning does not cause emission of sulfur oxides (SO_2 and SO_3), toxic air pollutants responsible for acid rain, because it does not contain sulfur in its composition. However, the combustion of biomass containing nitrogen leads to the formation of nitrogen oxide, *e.g.*, NO_2. This oxide is formed even because of the mixture of air gases that support combustion.[2,10]

The interest in the preparation of specimens composed of rice hulls, cornstarch, and glycerol lies in the possibility of forming solid composites that are suitable to be used as a solid biofuel.

In this study, we have developed a method to form a solid biofuel for the use of lignocellulose materials for power generation, incorporating rice husk, cornstarch, glycerol, and acetic acid. Burning tests were carried out, and the upper and lower heating values were calculated.

EXPERIMENTAL

Material preparation

Biomass of rice husk, cornstarch, glycerol, and acetic acid was used for the production of solid fuel. Rice hulls were ground by using a blender (Britain Diamond Filter 400 W) for 3 min, and then sieved by using a 2 mm sieve (Solotest). Only particle sizes less than 2 mm were used. Cornstarch powder was obtained from Fungini®, whereas glycerol from Vetec®, and acetic acid from Biotec®. The commercial reagents were used as received and in accordance with the safety recommendations of the manufacturers. Water was distilled by using a Pilsen type distiller (SPlabor®).

Preparation of specimens

For the preparation of the specimens, 10 g of cornstarch was weighed and manually mixed in 100 ml of distilled water. The mixture was then heated on a hot plate (Fisaton®) for about 10 min at a temperature of 250 °C. After this process, the mixture showed a gel-like aspect, and 50 g of ground rice hulls with particle sizes less than 2 mm was added. Specimen composites containing 10 ml of glycerol and 10 ml of acetic acid were mixed with cornstarch gel, homogenized and then incorporated into rice husk. The mixture was placed in PCV molds 10 cm high and 4.5 cm in diameter, cut in half lengthwise, and compressed by manual pressure for about 1 minute. The samples were oven dried (DeLEO®) for 48 h at 105 ± 2 °C. After this period, the samples were manually demolded. The specimens were made in triplicate, and the mixture components were weighed accurately on a digital scale (Shimadizu®).

Moisture content

The specimens were weighed by using a precision scale (Shimadizu®) previously weighed/measured on for qualification, and placed in an oven at a temperature of 105 ± 2 °C. After removing them from the oven, they were placed into a desiccator with anhydrous calcium sulfate to cool and then weigh. The heating and cooling operations were repeated until constant weight was reached, according to the ABNT NBR 8112/86[12] parameter and recommendations by Dias.[13]

Ash content

The sample was placed in a moisture-free porcelain capsule to burn, 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.[12,13]

Volume of solid fuels

Considering that the diameter of the specimen was 4.25 cm and the height of approximately 7.6 cm, the volume was calculated according to the method described by Dias.[13]

Apparent density

The apparent density was estimated as the mass per unit volume of the specimens.[13]

Upper and lower heating values

The method described by Dias[13] was used to calculate the upper and lower heating values, which were compared with those of the Food and Agriculture Organization. The upper heating value (UHV) was measured in MJ/kg, using the ash content (A) and the moisture content (M) of the fuel according to Equation 1:

$$UHV = 20.0 \times (1 - A - M) \qquad (1)$$

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 Equation 2:

$$LHV = 18.7 \times (1 - A) - 21.2 \times M \qquad (2)$$

Mechanical resistance to compressive strength

Cylindrically shaped specimens (10 cm high, 4.5 cm in diameter) were used to conduct compression testing. The assay was performed by using a CBR press, Fortest model, with a capacity of up to 5,000 Kgf. The specimens were subjected to load increments until plastic deformation of the material occurred at room temperature.

Smoke monitoring

The specimens were placed inside a porcelain container where they were burned. Assessment of the smoke was performed by using the Ringelmann scale. The experiment was conducted for about 10 min in an exhaust hood; smoke images were captured and compared to the scale, using the SMOKESHOT software.

Infrared analysis

FTIR spectra were collected in the 4000 to 650 cm-^{1} range using a Perkin-Elmer (model 781).

RESULTS AND DISCUSSION

Preparation of specimens

The specimens were prepared in four different compositions. In three of them, glycerol and/or acetic acid was added, as shown in Table 1. Biomass briquettes composed of rice husk, cornstarch, glycerol, and acetic acid are shown in Figure 1.

Ground rice hulls provided the best contact area between the components, wherein particle sizes less than 2 mm were used. Grain size associated with temperature and time of agitation provided the interaction between the components. The temperature and time used for preparing the biomass briquettes led the binding power of cellulose and hemicellulose present in rice hulls and cornstarch, thus producing specimens capable of converting mechanical energy into electrical energy.[6,14-16]

Glycerol and acetic acid were added to promote bonding between cellulose and hemicellulose.

Table 1
Composition of the specimens

Specimen	Ground rice hulls (50 g) and cornstarch (10 g) in 100 ml of water	
	Glycerol (ml)	Acetic acid (ml)
1	--	--
2	--	10
3	10	--
4	10	10

Figure 1: Rice-husk fuel pellets

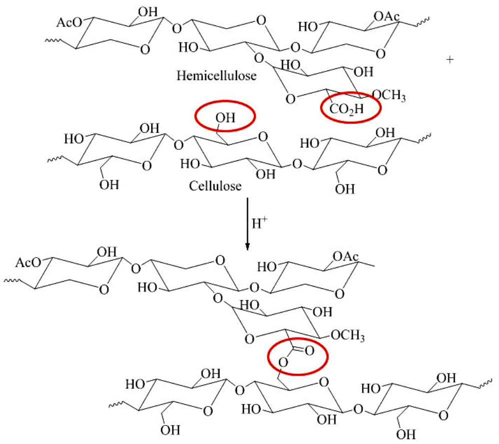

Figure 2: Esterification reaction between acid-catalyzed cellulose and hemicellulose

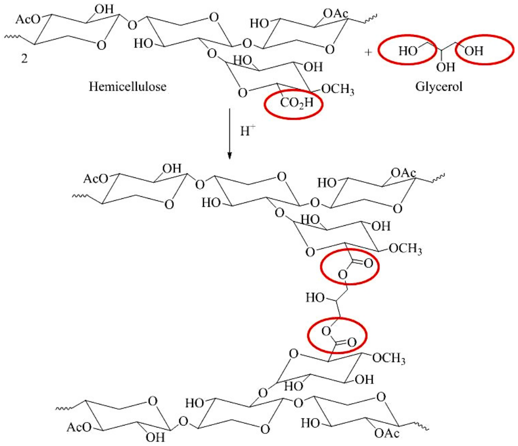

Figure 3: Esterification reaction between hemicellulose and glycerol catalyzed by acid

Figure 2 shows one of the binding possibilities between molecules of cellulose and hemicellulose, favoring ester formation and bonding between the components. A chemical process similar to that illustrated in Figure 2 may occur when glycerol is added. Figure 3 shows the formation of ester bonds between hemicellulose and glycerol, also catalyzed by acetic acid.

Infrared (IR) analysis

Figure 4 presents infrared spectra of rice hulls and of the four composites prepared from solid fuels.

In every IR spectrum (Fig. 4), a strong band in the axial stretching region occurs around 3425 cm^{-1}. This band indicates the presence of the OH group existing in cellulose, hemicellulose, and glycerol. Ranges around 2929 cm^{-1} and 2892 cm^{-1} also appear in all spectra of Figure 4. These are due to the presence of C-C and C-H stretching, respectively. The carbonyl stretching region ranges from 1850-1650 cm^{-1}; here a stretching region of 1638 cm^{-1} was observed, with minor variations in all samples. In IR spectra 4 and 5, a stretch is also visible near 1730 cm^{-1}, which can be attributed to the new ester bond, according to the reactions shown in Figures 2 and 3.

Moisture content, ash content, upper and lower heating values

The specimen compositions, overall moisture content, ash content, upper and lower heating values are shown in Table 2. In this study, the mean overall moisture content ranged from 15.62% to 24.08%, as shown in Table 2. The moisture content can be explained as the constituents of rice husk, cornstarch and glycerol can form bonds between hydrogen and water, thus keeping water in their composition.

The overall moisture content of specimen 1 was 15.62% (Table 2). The sample was composed of rice husk and cornstarch, and had the lowest overall moisture content among the analyzed specimens. The composites to which acetic acid was added showed the highest moisture content (Table 2). Acetic acid (CH_3CO_2H) and the acetate anion ($CH_3CO_2^-$) may be solvated by water molecules, retaining a higher amount of water in the sample.

Gonçalves, Sartori, Leão[17] suggested a 15-20% moisture content for the combustion, given that excess amounts of water can reduce the combustion heat and the temperature of the combustion chamber and exhaust gases. This means that two of the four composites were prepared according to what was stated in the literature, *i.e.*, rice husk and cornstarch composites, and rice husk, cornstarch and glycerol. Rice husk and cornstarch composites had the lowest overall moisture content, which was 15.62%.

The mean overall moisture content ranged from 15.62% to 24.08%, being lower than wood moisture content (25-30%), which makes it feasible to be used as a source of heat.[17]
Cornstarch, glycerol, and acetic acid were the raw materials used as additional energy sources to rice husk. The molecular formula for cornstarch is $(C_6H_{10}O_5)n$, for glycerol is $C_3H_8O_3$, and for acetic acid is $C_2H_4O_2$.

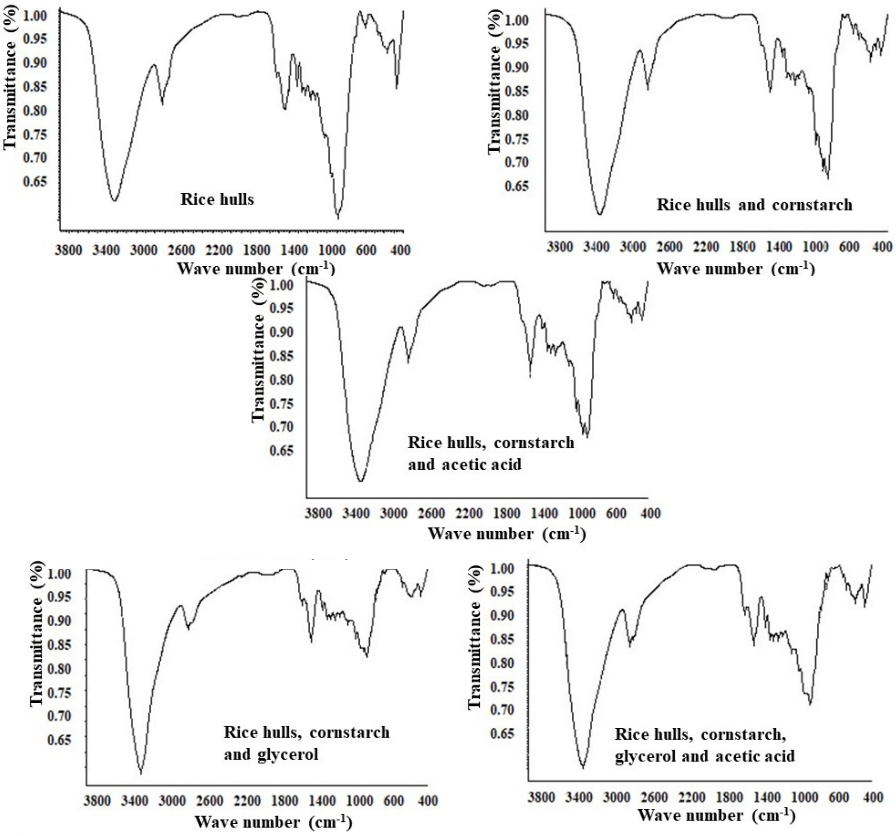

Figure 4: IR spectra of rice hulls and four composites of solid fuel

Table 2
Overall moisture, ash content, upper heating value (UHV) and lower heating value (LHV) in four specimen composites

Specimen	Ground rice hulls (50 g) and cornstarch (10 g) in 100 ml of water		Moiture content (%)	Ash content (%)	UHV (MJ/Kg)	LHV (MJ/Kg)
	Glycerol (ml)	Acetic acid (ml)				
1	--	--	15.62 (1.07)	24.81 (2.23)	11.91 (0.65)	10.75 (0.64)
2	--	10	23.58 (2.52)	18.41 (0.02)	11.61 (0.53)	10.27 (0.67)
3	10	--	20.94 (2.79)	11.71 (2.79)	13.47 (0.91)	12.07 (0.91)
4	10	10	24.08 (3.26)	16.85 (1.06)	11.81 (0.79)	10.44 (0.82)

(…) standard deviation

They will not be responsible for high ash levels, given that their chemical components are all oxygenated hydrocarbons, generating CO_2 and H_2O during the combustion process.

With regard to the ash content shown in Table 2, the lowest percentage of ash was found in specimen 3, composed of rice husk, cornstarch, and glycerol (11.71%). Meanwhile, the rice husk, cornstarch, and glycerol composites showed 18.41% of ash content. Glycerol composites had the lowest ash content levels. In this study, the ash content levels of all specimens were lower than those found by Morais *et al.*[18] in rice husk charcoal briquettes (42.16%). The experiments revealed that the materials containing glycerol had the lowest ash content levels, being 11.71% in specimen 3 and 16.85% in specimen 4. Ash content levels found in the different specimens shown in Table 2 are explained by inorganic compounds present in rice hulls, primarily due to the silica content of the raw material. The findings from this study are comparable to those of Dias,[13] who stated that most biomass wastes have low ash content, except for rice husk, which can contain up to 25% ash.

The ash content corresponds to the percentage of inert materials in the generation of heat present in the sample. Therefore, the aim is to obtain the smallest amount of solid residues after burning, indicating a high heat generating potential. The resulting ash should be properly placed in disposal sites to avoid equipment corrosion and other issues.

The upper and lower heating values were calculated, providing an indicative of the fuel quality. The prepared solid fuel that reached the highest heating value was the one containing rice husk, cornstarch, and glycerol, which reached an upper heating value of 13.47 MJ/kg and a lower heating value of 12.07 MJ/kg. The upper heating value (UHV) is the one in which combustion takes place at constant volume, wherein the water formed during combustion condenses and heat is recovered. The UHVs of each specimen are described in Table 2. The UHV values ranged from 11.61 MJ/kg to 13.47 MJ/kg. Specimens containing glycerol had the highest UHV, being 13.47 MJ/kg in specimen 3 and 11.80 MJ/kg in specimen 4.

Glycerol is a constituent of the alcohol group (triol), a liquid fuel that helps to complete combustion of the specimen. Its boiling point is 290 °C and vapor pressure is less than 1 mmHg at 20 °C, factors that determine an increase in the boiling temperature, reaching the flash point at 176 °C.[19] These characteristics mean that glycerol does not evaporate, but suffers a combustion reaction, so as to avoid compromising efficiency of the material during the burning process. Glycerol starts the combustion process, generating enough heat to ignite the other components (acetic acid, cornstarch, and rice husk).

The specimens without the addition of acetic acid had higher upper heating values compared with those to which acetic acid was added. Comparisons between specimen 1 (11.91 MJ/kg UHV) and specimen 2 (11.61 MJ/kg UHV), and between specimen 3 (13.47 MJ/kg UHV) and specimen 4 (11.81 MJ/kg UHV) revealed that specimen composites containing acetic acid had higher upper heating values than their counterparts. The boiling point of acetic acid is about 118 °C and has a vapor pressure of 11.4 mmHg at 20 °C, and a flash point at 43 °C.[20] The physical properties of the material favor evaporation, which means that combustion does not recover the heat.

According to Dias,[13] rice husk briquettes generally have an upper heating value around 15.90 MJ/kg. In this study, the specimen composites showed lower values than that, reaching 13.47 MJ/kg at maximum. They were also lower than the reference values of the Food and Agriculture Organization (FAO), which range from 17 to 18 MJ/kg.[21] This study suggests that these heating values occur due to high humidity in the specimens. Moisture content of solid fuels must be reduced to improve the outcomes.

Lower heating value is the free energy per unit mass of fuel, minus heat loss through water evaporation.[22] Therefore, it is essential to determine the LHV of a fuel as a way to quantify the effective energy of the material.

LHVs of the specimen composites are shown in Table 2. They ranged from 10.27 to 12.07 MJ/kg. The specimen composed of rice husk, cornstarch, and glycerol showed the best lower heating value, which was 12.07 MJ/kg (Table 2).

The specimens without the addition of acetic acid had higher LHV levels compared to those in which acetic acid was added. This can be observed when comparing specimen 1 (10.75 MJ/kg LHV) with specimen 2 (10.27 MJ/kg LHV), and comparing specimen 3 (12.07 MJ/kg LHV) with specimen 4 (10.44 MJ/kg LHV). The effect of acetic acid upon the lower heating value is similar to what occurred in the upper heating value.

In this study, lower calorific values ranged from 10.27 to 12.07 MJ/kg, which were higher in comparison with those of wood, which ranged from 7.12 to 10.47 MJ/kg. LHV values found in this study were higher than those found by Vieira,[6] but lower than those suggested by FAO,[21] which predicts a range between 15.4-16.5 MJ/kg.

Ringelmann scale

In this study, we used SMOKESHOT software, released by Actsistemas, to measure the emission rate of black smoke through computer technology. The method consists of using the Ringelmann scale, adopted as a worldwide measurement system of black smoke emission from diesel engines and industrial chimneys.[23] This technology was used to examine the color of smoke released during the combustion process under analysis. Figure 5 shows the captured images of the smoke emitted by the specimens during burning, which were correlated with the Ringelmann scale. As can be seen in Figure 5, the smoke emanated during burning was not black.

Determining composite burning characteristics is critical, given that fuels taken to complete combustion should form carbon dioxide (CO_2) and water (H_2O). However, black smoke is not desirable during the burning process. Black smoke is primarily derived from incomplete combustion, when carbon (C) is produced in the form of soot as a combustion product.[24]

In Figure 6, the highest peaks are shown in a grey scale (149-170) along the abscissa axis. As they are light gray, they are at level 2. These results support what was displayed in Figure 6, *i.e.*, the smoke from burning was not black, and all specimens scored 2 on the Ringelmann scale, which equals approximately 40% of the smoke density.

The use of rice husk for power generation reduces improper disposal, thus avoiding environment degradation and waste accumulation in the agroecosystem. With regard to the combustion of solid fuels, the choice of cornstarch as a binder is environmentally suitable, because it belongs to the group of binders that does not produce significant soot when burned.[25]

Mechanical resistance testing

Figure 7 shows the compressive strength-deformation profile for the following specimen composites: rice husk and cornstarch; rice husk, cornstarch and acetic acid; rice husk, cornstarch and glycerol; rice husk, cornstarch, glycerol and acetic acid. It can be observed that maximum compressive strength depends on the composition of the samples. The most resistant specimens were those composed of rice husk, cornstarch, glycerol and acetic acid (1.23 MPa).

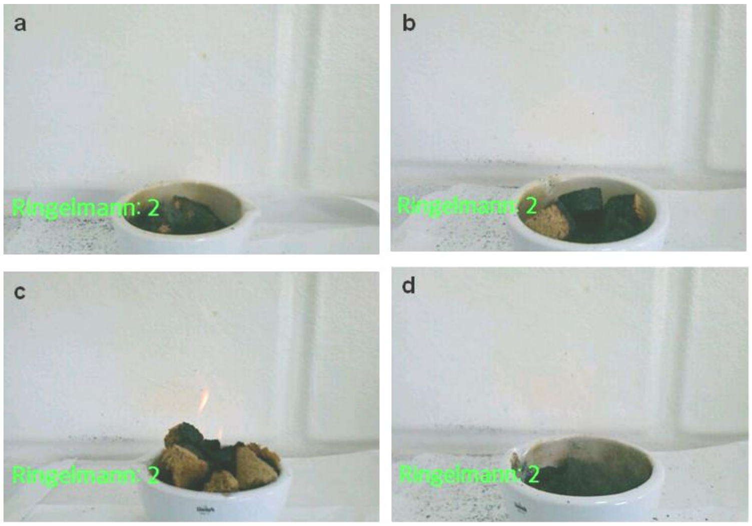

Figure 5: Photographs of the smoke from burning specimens; (a) cornstarch and rice husk; (b) rice husk, cornstarch and acetic acid; (c) rice husk, cornstarch and glycerol; (d) rice hulls, cornstarch, glycerol and acetic acid

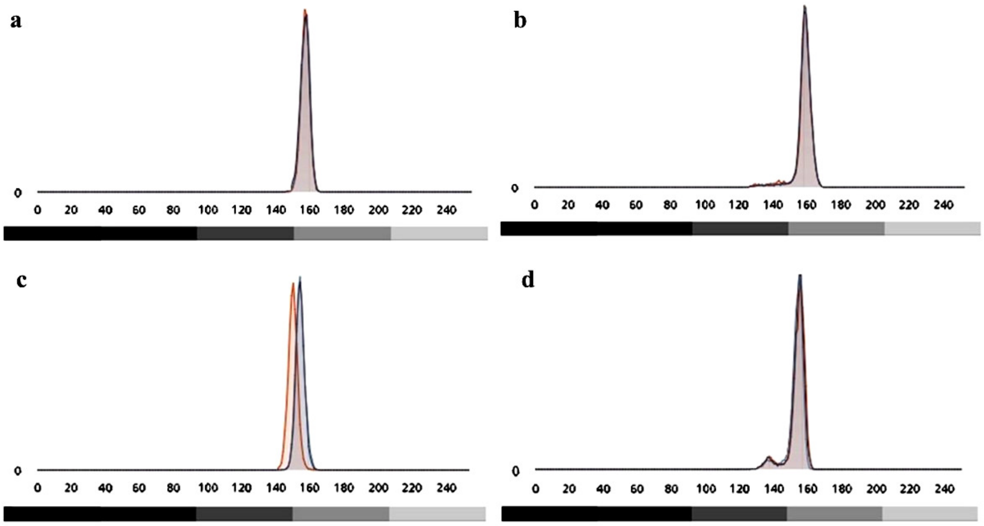

Figure 6: Ringelmann scale of the smoke from specimen composites: (a) rice husk and cornstarch; (b) rice husk, cornstarch and acetic acid; (c) rice husk, cornstarch and glycerol; (d) rice husk, cornstarch, glycerol and acetic acid

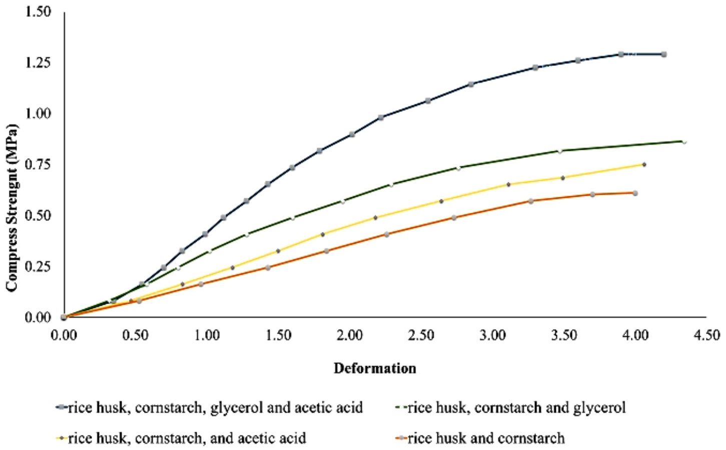

Figure 7: Compressive strength deformation profile for the specimen composites

The most resistant specimens were those composed of rice husk, cornstarch, glycerol, and acetic acid, which can be due to the binding of these materials. Mechanical resistance to compressive strength can be explained by the type of chemical bonding that occurs between constituents, namely the binding power of cellulose and hemicellulose, which leads to copolymer formation, as suggested in Figures 2 and 3.[15]

The specimen composed of rice husk, cornstarch, glycerol, and acetic acid showed an increase in maximum compressive stress. One could suggest that acetic acid acts as a catalyst between cellulose molecules and hemicellulose, and between hemicellulose and glycerol, leading to the formation of strong bonds between molecules, such as carbon-oxygen bonds (Figs. 2 and 3). It may also be suggested that glycerol, cellulose, and hemicellulose form hydrogen bonds between molecules. The intermolecular and intramolecular bonds are responsible for increasing maximum compressive strength observed in these specimens.

Mechanical resistance of the developed solid fuels is important because they must withstand a sufficient load to be handled, transported, and stored without suffering wear and loss of mass, *i.e.*, without material deformation.[26]

CONCLUSION

In this study, we prepared solid fuel specimens composed of rice husk and cornstarch, with and without the addition of glycerol and/or acetic acid. The experimental results show that the interaction between vegetal fibers can be improved by chemical treatments.

All specimen composites had the overall moisture content less than that of wood (25.0-30.0%). The specimen composed of rice husk and cornstarch had the lowest moisture content (15.62%).

Specimens containing glycerol had the lowest ash content (11.71%), and showed the best upper and lower heating values. Samples containing acetic acid had high ash content and low upper and lower heating values, and thus were considered inadequate for the production of biofuel. Finally, this study concluded that rice husk accounted for the ash content in the samples, and that the glycerol and acetic acid components affected significantly UHVs and LHVs.

Chemical change increased the compressive strength of the fiber-polymer composite and consequently reduced the material deformation.

The color of the smoke from burning materials was not black in all composites, which indicates complete combustion of the specimens according to the Ringelmann scale.

The results from this study have indicated the technical viability of biofuel production from rice husk, cornstarch, and glycerol. Because rice hulls and cornstarch residues are energy sources of vegetable origin, these lignocellulose residues and the glycerol by-product are useful for the production of biodiesel. The primary environmental benefit from this study was to provide a sustainable and cost-effective raw material to replace non-renewable fossil fuels.

The specimens have shown to be suitable to replace conventional heat sources, even compared with traditional firewood and charcoal briquettes. Further research on total energy balance should be conducted to examine the production of these solid fuels.

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