Effect of the Incorporation of Biomass Wastes on the Properties of Fired Clay Bricks

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Abstract: In this work, the feasibility of reusing two biomass wastes: sunflower shells and rice husks is analyzed through their incorporation in clay mixtures for the production of porous ceramic materials. For this purpose, the raw materials were first characterized by different techniques. The ceramic pieces were obtained by means of uniaxial pressure at 25 MPa of commercial clay-biomass waste mixtures, the latter added in 10% by volume. After a drying period, they were thermally treated at 1000°C following firing curves similar to those used by the ceramic industry. The products obtained were characterized by various techniques: porosity, permanent volumetric variation, weight loss on ignition, mechanical properties, among others. The ceramic products obtained present homogeneous tonality, well-defined edges and angles, without shelling of the structure. The results of the porosity test show that the waste aggregates increase this property in the ceramic materials studied.

Keywords: biomass waste, porous ceramics, sunflower shells, rice husks

Introduction

The production sectors related to food industries and the exploitation of natural resources (such as agricultural, forestry and fishing), have realized the need to increase the productive efficiency of their processes. This is possible by generating goods and products, directly related to production chains and growing demands by the population, which have increased at high rates in previous decades.

The traditional production cycles grew into modern by focusing on new techniques and equipment that have increased productivity, with the consequent increase in raw materials consumption, waste generation, extensive use of arable land and, as a consequence, environmental impacts associated with these activities.

These transformations in the markets for agricultural and forestry products have led to an increase in the rate of production, which results in an increase in the waste generation. These wastes are almost exclusively composed of residual biomass, similar to the products that give rise to them, and they are not usually used because they are not products by themselves. The wastes generated by these activities therefore have a high potential for exploitation, considering that they are continuously and widely produced in all environments and therefore the accessibility to these resources is not affected by specific conditions of the territory. From this point of view, they are an important source of resources, considering also that they come from a biogeochemical cycle and therefore a renewable source that will last in the time that, if it is used in a sustainable way, allows an inexhaustible supply that depends on the sun as the main precursor.

Agricultural wastes have been used for animal feed, fertilizer, and fuel for energy production. Several authors have studied the incorporation of biomass residues in clay bricks to obtain porous materials (Muñoz et al., 2016). The studied residual materials include corn cobs (Njeumen Nkayem et al., 2016), spent shea waste (Adazabra et al., 2017), olive stone flour, wheat straw residues (Aouba et al., 2016), saw dust, tobacco residues, grass (Demir, 2008), bagasse from the brewing industry, coffee ground residue (Eliche-Quesada, 2011), grapes and cherries seeds, sawdust (Barbieri et al., 2013). In general, the firing temperatures are included in the range 900°C to 1200°C, and the most common properties evaluated are linear shrinkage, water absorption, porosity, apparent density and flexural strength. In most cases the amount of biomass waste added is less than 10% in weight.

In this work, the feasibility of incorporating sunflower shells and rice husks in clay mixtures for the production of porous ceramic materials is studied.

Materials and methods

Sunflower shells (SS) were supplied from a producer of vegetable oil. In this industry, firstly, sunflower seeds are grinded and unshelled. Then, the obtained material with a small volume of shells, necessary to achieve an adequate protein content, are derived to the production of oil by pressing. This process produces the oil but also a residue that still contains high percentages of oil. This residue is directed to a process of solvent extraction, which removes the remaining oil and creates a by-product that is intended to feed animals. This process generates a great volume of biomass residue, consisting mainly of sunflower shells.

Rice husks (RH) were provided by a rice cooperative. The rice production process begins with a preliminary cleaning where different machines are used to extract stalks, dust, stones and other impurities of different sizes. The rice grains are then transported to the dryers where they are dried by natural or forced convection. Before entering the husking process, the rice undergoes a new cleaning process using a suction and plow cleaner in order to eliminate impurities and increase the capacity and efficiency of subsequent operations. During the husking process, the grain loses its surface coating. At this point in the process, husked or "brown" rice and one of the main by-products of the industry, rice husk, are obtained.

The commercial clay used in this work comes from a national ceramic industry.

The raw materials were characterized by scanning electron microscopy (SEM) with X-ray electron dispersive analysis (EDS), X-ray diffraction (XRD), differential and thermogravimetric thermal analysis (DTA-TGA).

In addition, the weight loss on ignition (LOI) of these powder materials was determined. SEM analyses were performed with FEI Inspect S50, with an X-ray detector (EDAX-Phoenix). The X-ray diffraction patterns of the powders were obtained with PANalytical X'Pert PRO equipment, with CuKα radiation (λ = 1.5406 nm). The operating conditions were 40 kV, 40 mA. The DTA-TGA essays were conducted on a Shimadzu DTA-50 analyzer TGA-50 with YC-50 WSI. The LOI essays of the powder raw materials were made in an oven for three hours at 550°C.

The particle size of the raw materials (clay and biomass residues) used in this work is less than 1 mm.

The ceramic pieces were obtained by means of uniaxial pressure at 25 MPa of commercial clay-biomass waste mixtures, the latter added in 10% by volume, with addition of 8% in weight of water, into molds of 70 mm x 40 mm, resulting bricks with 15 mm in height, approximately. The decision of using 10% residue in the samples was made taking into account preliminary results.

After a drying period, the samples were thermally treated at 1000°C, at a rate of 2°C/min, following heating curves similar to those used in the ceramic industry.

The compact bodies were characterized with different techniques: apparent porosity, permanent volumetric variation (PVV), weight loss on ignition (LOI) and mechanical properties, among others.

Apparent porosity were determined in accordance with ASTM C20-00, by boiling water.

PVV and LOI were obtained by measuring the dimensions (length, width, thickness) and the weight of each sample before and after the thermal treatment at 1000°C.

The modulus of rupture was acquired following ASTM C133-97, on an Instron Model 1125 machine, with a maximum capacity of 10000 kg. The speed of the test was 0.5 mm/min.

From now onwards the samples will be referred to as follows:

CCB: brick made with commercial clay.

SSB: brick made with commercial clay and 10% in volume of sunflower shells.

RHB: brick made with commercial clay and 10% in volume of rice husk.

Results and discussion

Table 1 shows the semi-quantitative chemical analysis by EDS of the biomass wastes and clay used, expressed as weight percentage of their elements. From the analysis of these values, it is possible to see that in addition of C and O, the rice husk contains high percentages of Si and Fe, while the sunflower shell show K and Ca as the main elements.

Table 1: EDS analysis of the raw materials, in weight percentage of the elements

	C	**O**	**Na**	**Mg**	**Al**	**Si**	**K**	**Ca**	**Fe**
Sunflower shells	40.6	41.5	--	2.0	--	0.7	7.9	5.9	1.4
Rice husks	29.7	38.5	--	--	--	22.3	1.9	2.0	5.6
Commercial clay	24.9	33.6	1.1	1.3	7.5	21.7	2.5	0.5	6.9

Biomass wastes present a loss on ignition of 96.4% for sunflower shells and 72.8% for rice husks.
In Figure 1 the SEM images, with a magnification of 500x, of rice husk (a) and sunflower shell (b) are presented.

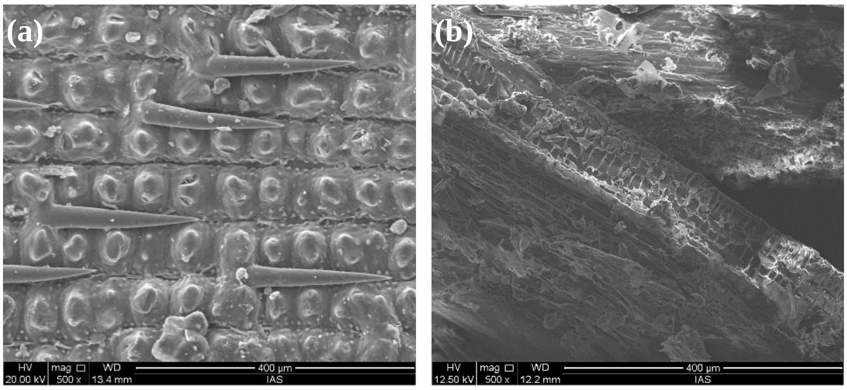

Figure 1: Scanning electron microscopy images of (a) rice husk, (b) sunflower shell.

As it can be seen in Figure 1(a) the microstructure of rice husks is globular showing a cell pattern which is well organized and has a corrugate structure. Regular spherical grains of almost equal sizes appear in parallel rows. In addition, some elongated structures, shaped like small hair are well visible. Other authors (De Souza do Prado et al., 2015; Battegazzore et al., 2014) also observed this morphology. The micrograph 1(b) reveals the fibrous structure of the sunflower shell, with areas of cellular texture made from the tightly packed hollow cells of various sizes.
XRD pattern of the commercial clay used in this work is presented in Figure 2. It is observed that the main crystalline phases present are quartz, hematite, potassium feldspar, aluminium oxide and iron.
The XRD patterns of the biomass wastes exhibit the distinct peaks corresponding to crystal structure of cellulose, with 2θ around 16°, 22°, 35° and 42°, and in the case of rice husk, quartz peaks are also observed.

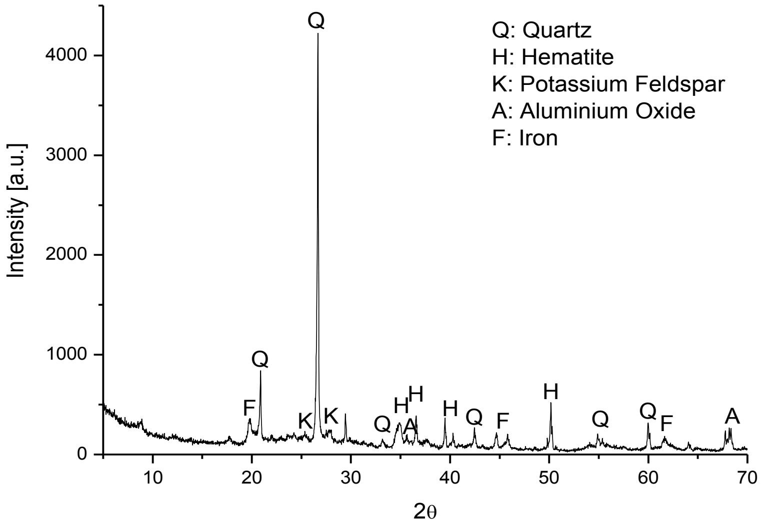

Figure 2: XRD pattern of commercial clay.

The DTA-TGA profile corresponding to rice husk is shown in Figure 3. Several exothermic peaks in the DTA curve that have been assigned to the combustion-decomposition of the biopolymers present in the biomass are observed. The rice husk sample presents a first pronounced peak at 326°C with loss of weight, followed by other small peaks at 332°C, 343°C and 356°C and finally another pronounced broad peak at 441°C, with continuous weight loss. This behavior corresponds to the presence of hemicellulose, cellulose and lignin. Since lignin, cellulose and hemicellulose are intimately related in the whole structure, the thermal decomposition of each one cannot be analyzed individually. However, it should be expected that lignin decomposition occurs at the highest temperature, while the hemicellulose degradation takes place at the lowest one. Taking this fact into account, it should be considered that the first peaks are associated with hemicellulose and cellulose decomposition and the last one with the lignin degradation.

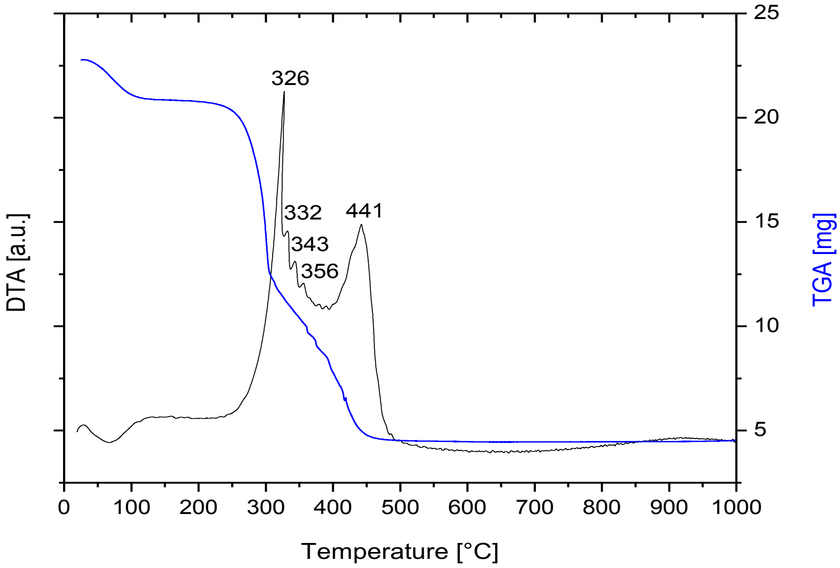

Figure 3: DTA-TGA of rice husk.

In DTA-TGA curves of sunflower shells, three exothermic peaks at temperatures of 301°C, 401°C and 441°C, are observed. These peaks are assigned to hemicellulose, cellulose and lignin, respectively.

The DTA-TGA analyses show that the incorporated organic materials burned in a wide temperature range, between 300°C and 450°C. This is important to ensure that the sintering process takes place without crack formation in the brick.

Figure 4 shows the macroscopic appearance of the obtained bricks with commercial clay, and with the addition of 10% in volume of rice husks and sunflower shells. It can be seen that these products have well defined edges and corners without shelling of the structure. It is clearly observable that the products with biomass residue additions are more porous than that obtained with clay only, due to the combustion of the organic phase during the firing process.

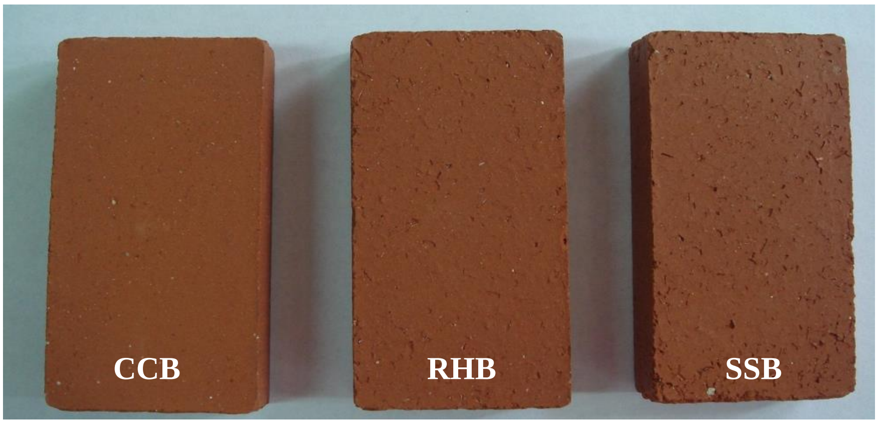

Figure 4: Macroscopic appearance of the obtained bricks.

Figure 5 shows the optical images of the samples. It is possible to observe in Figure 5(b) and 5(c) the presence of pores in the bricks with added biomass residue. The elongated shape of the produced pores is similar to that of biomass residue particles added and the pore size is less than 1 mm since that was the particle size of the raw materials used in this work, as it was mentioned in the materials and methods item.

Figure 5: Optical microphotographs of the samples (a) CCB, (b) RHB, (c) SSB. Magnification: 50X.

Table 2 shows the results of permanent volumetric variation, apparent porosity and flexural strength. The values of PVV for the samples with biomass wastes are 10-12% greater than the sample without them and are similar for both residual materials.

Table 2: Bricks characterization

	CCB	RHB	SSB
PVV [%]	-8.4	-9.4	-9.2
AP [%]	22.2	25.6	25.9
MOR [MPa]	8.5	7.1	7.1

An increase of 15% in apparent porosity for the samples with biomass wastes is observed. The fact that the porosity is greater in these samples with added wastes, and the formed pores have similar shapes and sizes of the aggregated biomass particles would indicate that the sintering process begins before or simultaneously with the combustion of these biomasses.

Flexural strength decreases with the addition of rice husks and sunflower shells. This behavior is related with the increase in the porosity that affects the cohesion and hence reduces the material resistance to failure.

The characteristics of the ceramic pieces obtained are within the values established by the market, although the value of flexural strength is at the limit of the range required for tile-like products.

Conclusions

In this work, the feasibility of reusing two biomass wastes: sunflower shells and rice husks is analyzed by their incorporation in clay mixtures for the production of porous ceramic materials.

The products obtained with 10% in volume of added residue have good physical and mechanical properties, with acceptable values of apparent porosity, modulus of rupture and permanent volume variation. The addition of sunflower shells and rice husks increases the porosity of the bricks.

In addition, the reusing of these agricultural wastes as an additive in construction materials provides an attractive and sustainable way of managing this type of residues.

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