

CHARACTERIZATION OF CLAY MATERIAL AND RICE HUSK FROM NORTHEAST COLOMBIA

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ABSTRACT

This research was to study materials from the region to use them industrially applying the circular economy concept. Clay Material and Rice Husk were evaluated in the manufacture of ceramic products. X-ray Diffraction and X-ray Fluorescence techniques were used to determine the raw materials' chemical and mineralogical composition. Thermal analysis techniques (TG and DTG) were used to complement the study. The XRD results showed an abundance of quartz. The results of the thermal analysis establish significant losses due to calcination. The thermal conductivity was also measured in ceramic specimens made from two types of pastes, one with 100% Clay Material and the other with a 5% substitution for Rice Husk. The results showed a decrease in thermal conductivity in the test tubes with the addition of Rice Husk. Consequently, the Rice Husk as a substitute for the Clay Material allows for ceramic production with thermal efficiency.

Keywords: Rice Husk, Clay Material, Ceramic, Thermal Conductivity, Characterization.

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INTRODUCTION

Rice is one of the most consumed foods globally because it is an essential part of the diet in most developing countries. To satisfy the high food demand rice production has increased significantly in recent years. For example, in 2017, there was an increase of 4.5 million tons compared to 2016.¹ Because of the high production volumes, the generation of waste from the process is directly proportional. Among the most common wastes is Rice Husk, a vegetable tissue made of cellulose and silica, which protects the grain from the outside environment. Since it is not edible, it is usually discarded during the processing (milling) of rice.^{2,3} Latin America and the Caribbean have one of the best prospects for rice production growth due to their favorable climate.⁴ Colombia is no stranger to it; the agro-industry collected 3 292 983 tons of rice and a planting area of 545,525 hectares in 2017.⁵ The Norte de Santander department follows the same trend, showing a sustained increase in production in recent years.⁶ In 2017, the region accounted for a little more than 180 thousand tons of mechanized rice. However, policies for adequate waste disposal are almost non-existent. Many of them are thrown into landfills, resulting in contamination of soils and bodies of water, which in turn affects human health.⁷ The circular economy seeks to maximize the use of waste generated by human activity through "reduce, recycle and reuse" and reduce its impact on the environment. Many agricultural and industrial wastes are being used in the construction sector to mitigate non-renewable materials.^{8,9} In the Norte de Santander department, the ceramic industry is one of the most robust lines of its economy, among other things, thanks to the quality of the clay material found in local geological formations and used as the primary raw material for manufacturing of ceramic products.¹⁰ The purpose of the present study was to characterize the Clay and Rice Husk produced in that region to develop a comparative analysis of their properties. Finally, tests were carried out on ceramic test pieces to recognize changes that the technological nutrient confers on the product from a thermal approach.

EXPERIMENTAL

Clay Material (CM) was collected in the "la Alejandra" village, El Zulia municipality, Norte de Santander (Colombia). The Clay is a typical red color in the Guayabo geological group.¹¹ The agroindustrial residue was Rice Husk (RH) that arises from the rice processing processes.

The X-ray diffraction technique characterized the Clay Material and the Rice Husk in a BRUKER D8 ADVANCE model D8 ADVANCE equipment with DaVinci Geometry (CuK α 1 radiation), step-by-step scanning at 0.02035 ° (2 θ), and time 3 s sampling time. Diffraction patterns (ICDD) PDF-2 were used to identify crystal structures. The amorphous phase was distinguished in diffractograms that did not match the recognized patterns by quantitative analysis using the Rietveld technique in conjunction with PANalytical's X'pert HighScore Plus software.

The elemental composition by oxides was determined using a sequential X-ray fluorescence spectrometer model S8 TIGER-BRUKER. The results were normalized to 100% with values of losses on calcination at the gradient of 3.08 °C / min until reaching a maximum of 950°C, maintaining the latter temperature for two hours.

The raw materials' thermal characterization was carried out using 20 mg of each material loaded in crucibles with an SDT-600 equipment from TA Instrument, under conditions of a pressure atmosphere, heating rate of 20 °C / min, and airflow. 100 ml/min.

Thermal conductivity measurements were made in two types of flat ceramic specimens obtained by an extrusion process, one with 100% clay and 5% Rice Husk replacing the Clay Material. Each sample was measured five times at times of 5 minutes with the Decagon Devices KD2-Pro kit.

RESULTS AND DISCUSSION

The microstructural (quantitative) characterization of the raw materials using XRD is presented in Table-1. Similarly, Table-2 shows the results of the chemical composition of CM and RH established by FRX. From the information presented in Table-1, it is evident in the case of the Clay Material composed predominantly of kaolinite and muscovite quartz. The chemical composition formulas of these minerals (SiO₂, Al₂Si₂O₅(OH)₄ y KAl₂(AlSi₃O₁₀)(OH)₂) show correlation with the composition results of Table 2, where the silica and the alumina are the predominant compounds.

Within the minority crystalline phases (Table-1), the presence of hematite stands out as a possible source of the reddish pigmentation of the Clay Material, as well as small amounts of microcline-type potassium feldspar and anatase. Another interesting aspect of the microstructural composition is an amorphous phase in a representative proportion (about 25%). The iron levels in Fe₂O₃ shown in Table-2 are much higher than those presented for the hematite identified by XRD. The iron should be present in other phases, perhaps in isomorphic replacement of the aluminum element in the phyllosilicates or forming the identified amorphous phase.^{12,13} The presence of potassium can be linked to the presence of muscovite and potassium feldspar (KAlSi₃O₈). Table-2 highlights the low fact of sodium within the group of alkaline elements. The presence of titanium is most likely due to the anatase (TiO₂) identified in Table-1. The other components in minority composition could be present in many phases, perhaps in traces of carbonates, exchange cations in Muscovite, even forming the amorphous phase identified by DRX.

Table-1: Microstructural Composition of Raw Materials (DRX-Rietveld)

Phase	% Weight *	
	Clay Material (CM)	Rice Husk (RH)
Quartz	47.4	0.2
Kaolinite	14.4	---
Muscovite	10.7	---
Hematite	1.1	---
Microcline	0.9	---
Anatase	0.4	---
Amorphous	25.1	99.8

*Decimals do not represent the accuracy of the result; their presence is justified due to Rietveld refinement's characteristics.

In Rice Husk, the results shown in Table-1 indicate the almost total predominance of the amorphous compound. Quartz was identified with a very low measured signal intensity, which in quantitative terms was not exceeded 1% by mass. When reviewing the chemical information in Table-2, it is evident that this material has a significant proportion of silica (15.5%), which is possible in an amorphous state according to the DRX results.

Finally, the calcination losses presented in Table-2 show significantly different values for each material. For RH, this high value is possibly associated with organic matter oxidation.

Table-2: Chemical Composition of CM and RH

Oxide	% Weight	
	Clay Material (CM)	Rice Husk (RH)
SiO ₂	65.66	15.56
Al ₂ O ₃	17.71	0.20
Fe ₂ O ₃	5.74	0.06
K ₂ O	1.60	0.28
TiO ₂	0.91	---
MgO	0.71	0.09
P ₂ O ₅	0.62	0.15
CaO	0.34	0.09
Na ₂ O	0.14	---
SO ₃	0.00	0.03
PPC	6.28	83.50

Thermal Behavior of Raw Materials

To better understand the mass losses seen in Table-2, the Clay Material (CM) and the Rice Husk (RH) were analyzed using TG/DSC. The profiles obtained are described in Figures 1 and 2.

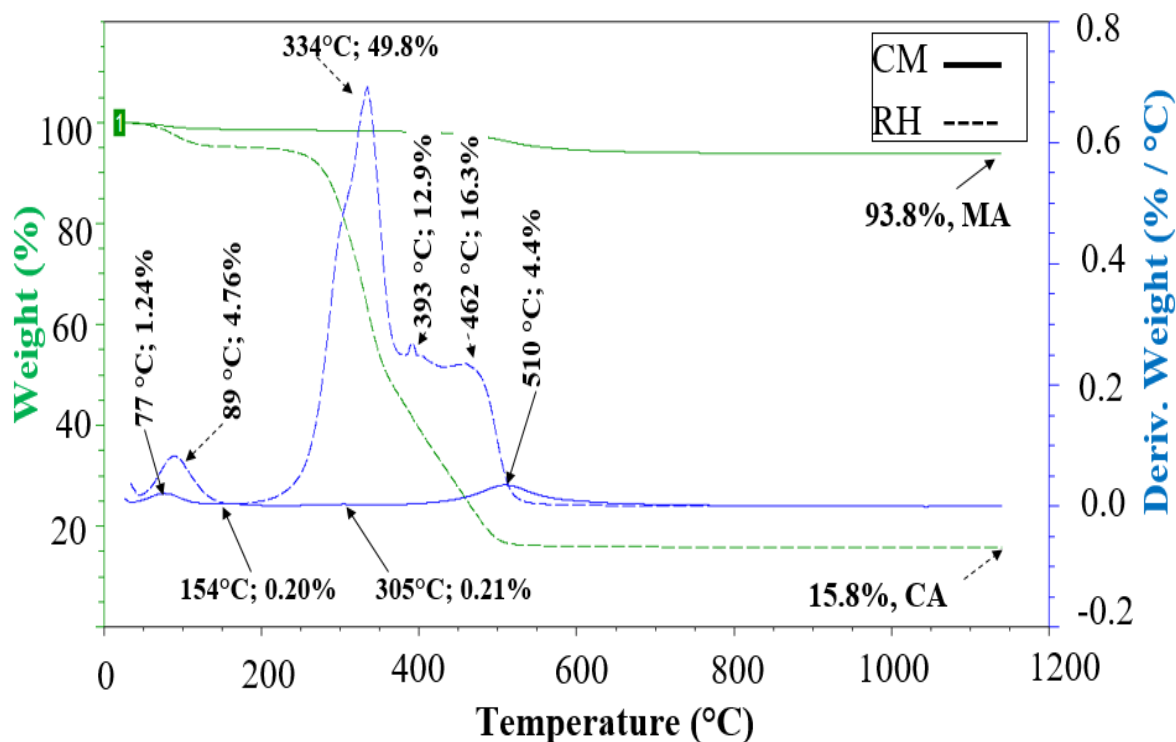


Fig.-1: TG and DTG Curves for RH and CM

The TG and DTG curves in Fig.-1 show different mass-loss events for CM and RH. In the reference material, four activities were recorded in which there were mass losses reached 77 °C, 154 °C, 305 °C, and 510 °C. Loss of free water present in the material in the form of moisture is common in the first temperature; the second event is possibly associated with water present in montmorillonite traces, as previously reported in other works.¹⁴ The event at 305 °C could be related to the decomposition of iron hydroxides present in the Clay Material, which, like montmorillonite, were not identifiable by XRD low proportion. The last event at 510 °C would be associated with kaolinite dihydroxylation.¹⁵ All of the above events are endothermic following the profile of the second derivative of heat flow presented in Fig.-2. According to this last figure, an endothermic event at 580 °C was evidenced, possibly associated with the change suffered

by quartz α to the β form. Small exothermic events were evidenced for CM above 980 °C, possibly due to recrystallization processes, especially to mullite formation.¹⁵

With the mass loss profile of the RH material (see Fig.-1), four mass loss events are also evident, whose maximum activity temperatures were 89 °C, 334 °C, 393 °C, and 462 °C. Like the Clay Material, the first of them could be the evaporation of water present in the material. The other events could be associated with the oxidation of hemicellulose, cellulose, and lignin, as reported in previous works on the characterization of this material.¹⁶ The heat flow profile and the second heat flow derivative show that the first mass loss event is endothermic, consistent with the type of energy required to evaporate the water present in RH. Between 300 °C and 500 °C, there are exothermic events associated with the combustion of the aforementioned organic matter. This contribution of heat is an aspect that could be favorable within the ceramic process when using Rice Husk as a substitute material. Two heat flux events occur above 600 °C. An exothermic event at 1047 °C could be related to the recrystallization process of amorphous silicon phases by XRD (see Table-1). Following the above, the present study analyzed this behavior when RH is incorporated in industrial applications, in this case, ceramic tiles, since these products undergo processes that involve a wide range of temperatures.

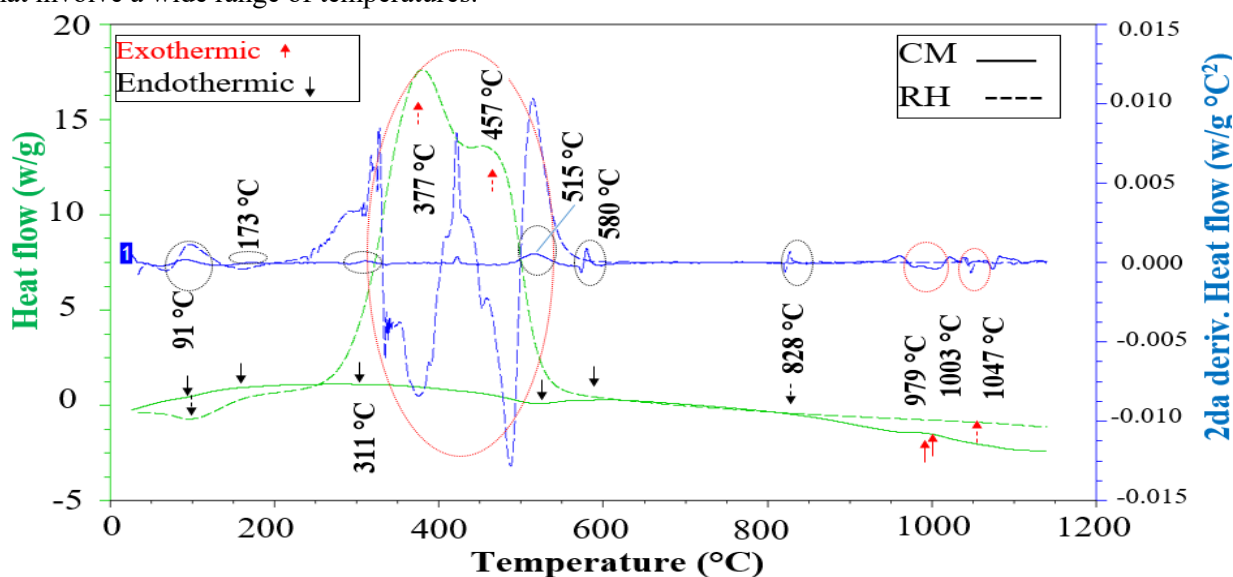


Fig.-2: Heat Flow Profile and Second Heat Flow Derivative

Thermal Conductivity

The thermal conductivity (TC) values were compared in ceramic specimens prepared with 5% Rice Husk for others made with the traditional material (CM) depending on the cooking temperature. The results obtained are presented in Table-3.

From Table-3, it is possible to observe how the thermal conductivity of the ceramic varies depending on the firing temperature and the presence of Rice Husk (RH). The TC values increase in the two materials. However, the increase is less marked in the material with 5% RH. This result infers that small substitutions of CM for RH improves the thermal insulation of an enclosure (walls) built with this type of ceramic. From the information recorded in Table 3, it can be established that at the firing temperature of 1150 °C, the differences in thermal conductivity between CM and 5% RH reach 44.3%. More detailed analyzes should be carried out to corroborate. Whether this significant decrease in thermal conductivity could bring energy and environmental savings once the ceramic is installed in civil works and operating in heated conditions. From Table-3, it is possible to observe thermal conductivity of the changes in the thermal conductivity for the specimens with 5% Rice Husk could be associated with increases in porosity due to the combustion of the organic phase present in Rice Husk and changes in the crystalline and amorphous phases formed at high temperature, could be responsible for this behavior.^{17,18} Regarding this last possibility, it has been evidenced in the literature that some crystalline and amorphous phases can increase or decrease the material's thermal conductivity, for example, the presence of mullite, quartz, feldspar phases rich in calcium.¹⁹

Table-3: Variation of Thermal Conductivity in Ceramics with MA and 5% CA with increasing Temperature

Temperature (°C)	Thermal Conductivity (W/m K)	
	CM	5% de RH
900	0.336	0.277
1000	0.407	0.375
1100	0.691	0.462
1150	0.777	0.433

CONCLUSION

The two studied materials present considerable differences in their microstructure. In the Clay Material, the elements that compose it are much more ordered and are united by recognizable structures in crystalline phases, different from the Rice Husk, and could be observed in the proportion of the latter's amorphous phase, equal to 99.8%. The preceding helps to understand the results of FRX, in which CM is mainly made of silica and alumina, while RH with calcination losses of 84%. This characteristic shows its organic character as a heat source during the cooking process, as revealed by the TG/DTG thermal analyzes. The curves of both materials make it clear that the Rice Husk creates more exothermic events than Clay Material when subjected to high temperatures.

The Rice Husk as an additive within the ceramic paste, the thermal conductivity in ceramic products for construction is significantly reduced. It may be related to the release of energy and favors the appearance of bubbles within the ceramic paste trapped during firing and when sintering the surface of the product, generating air capsules that mitigate point-to-point heat transfer within the solid, serving as insulation. This feature is particularly interesting for the building sector when you want to use versatile materials that improve interior comfort. It also avoids the use of artificial cooling systems caused by thermal incidence in buildings, contributing to reducing the carbon footprint.

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