Ceramics from clays and by-product from biodiesel production: processing, properties and microstructural characterization

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Abstract

The development of the modern world and the industrial process are based on the use of fossil fuels, coal and oil. These fuels are relatively easy to obtain, inexpensive to produce and easy to transport, have shifted to other energy sources.

Bio-fuels are currently the only available alternative to start replacing oil in transport, reducing environmental impacts, increasing security of supply and contributing to the development of local economies. The use of biodiesel can reduce greenhouse gases (CO_2 eq) from 57% to 88% for every kilometer driven compared to fossil diesel.

But how could it be otherwise, the production of these new fuels generates a series of waste or by-products which cannot be re-integrated into the same manufacturing process. For these cases the ceramic bricks are an interesting option to set in their structure a wide range of materials and composites, sometimes serving only as a reservoir for the inert residue, and other, having a positive effect on the ceramic material or process. The physic-chemical treatments for the production of biodiesel produce the so-called glycerine.

In the present communication, the incorporation of this waste in raw clays has been studied. Using conventional moulding and sintering processing methods to prepare clay-glycerine composites, the influence of the amount of waste added to clay has been evaluated.

The results were interesting to assess the properties of these composites, to improve the technological properties of the ceramic products and, hence, to establish the potential applications.

Keywords: Biodiesel waste, glycerine, lightweight bricks, environmental management.

1. Introduction

During the last few decades fossil in general and oil prices in particular led to the search for renewable energy sources alternatives and environmentally cleaner and also be technologically viable and competitively priced [1]. Biodiesel which has experienced a boom in the last decade stands out among more developed energy sources.

Biodiesel is generated by a chemical transesterification reaction that transforms the triglycerides contained in the oil from cultivation in fatty acid methyl esters (FAME) in which an alcohol and an alkaline catalyst (NaOH or KOH) are used as a by-product generated by chemical reaction of glycerol (propane-1,2,3-triol). On a molar basis, one mole of glycerol is produced for every three moles of FAME, and volumetrically, approximately 10% of the raw materials are transformed into glycerol [2]. Glycerol is a compound colorless, odorless, viscous and very low toxicity.

Biodiesel production in the European Union has grown exponentially in recent years [3-5]. The increase in the price of conventional fuels, increased political level of global awareness of climate change and improving energy stability [1] are among the reasons that have led to an increase in demand for biofuels. One of the consequences is the generation of waste and by-products which include gluten flour, gluten, pulp, waste and crude glycerol [1].

For the generation of biodiesel used crops are oil seeds such as soybeans, sunflower or palm. The vegetable oils content in plants have approximately 10% by weight of glycerine in its composition. In the valorization of the glycerine, the problem is that has impurities that make this product a low value. It comprises approximately between 80-84% of glycerol, 8-12% water, 2-6% ash and salts, 1-4% of fatty acids free and around 1% of rubber, but this composition mainly depends on the raw material used and the method of production of biodiesel used.

One of the by-products generated during the production of biodiesel is glycerine as a by-product of the transesterification of oils, and that for the most part it consists of glycerol, which has been used so far for commercial recovery in pharmacy (production of propyleneglycol,propionicacid andisopropanol)[2**]**, cosmetic products, as fertilizers[6], supplements inanimal nutrition [7], beverages and evenwasreused forenergy recovery. Its usein the pharmaceutical industryare necessaryanadequacyprevious stagesincludingrefinedby filtration, fractional distillationand chemical treatment. Crudeglycerolmay contain significantand varying amountsofmethanol, water, a mixture ofcatalyst andother organic materialsthatare appointedMONG(Matter OrganicNon-Glycerol) [8].

One of the possible valuations of glycerol, which is the main component of glycerine, might be its addition to biofuels. Glycerol has a moderate calorific value (~ 16 MJ/Kg) still has not been used as fuel on an industrial scale [1, 9] due to a series of practical impediments such as a high ignition temperature (about 370 °C) and the burning causes acrolein which is highly viscous and toxic. Some authors [10] have worked in experiments to achieve small amounts of glycerol can be added to gasoline in small proportions. Furthermore, have also reported works for the use of glycerol as raw material for a large amount of chemicals and fuels include hydrogen [7, 11-14].

Another option that is targeted is the reuse of the crude glycerol for processes combined heat and electricity by combustion near the centers of production of biodiesel [2]. However, some of the main problems of the combustion of the glycerol is that its composition can change drastically depending on the source and origin of commodity raw materials used to produce biodiesel.

As the production of biodiesel continues to grow globally the amount of glycerine that is accumulating begins to be important enough. For this reason, the use of this product for other sectors is being considered, mainly those that are able to absorb large quantities of them. One of the stated sectors could be the ceramic industry sector since this industry is capable of supporting different waste materials during the process without having to implement changes in it, as shown in previous work [15, 16-18,19,20]. This is because the raw materials used by the ceramic industry are clays having a similar chemical composition to that of many industrial waste [20] that makes them ideal candidates for support within its structure large amount of waste to produce ceramic firing process will be trapped in the glassy structure being thus rendered inert and encapsulated [19-21].

The ceramic industry is going through a critical moment, because of the rising costs of energy and raw materials and competition from other markets such as Asia, it is essential to undertake innovative actions [15]. Thus, there have been some efforts to evaluate the fluxing action on ceramics of glycerine ash produced during the manufacture of biodiesel [15].

Glycerine is a compound of organic origin, when it is incorporated to the clay combusted during firing process generating porosity in the clay microstructure. Glycerine changes microstructure and expected increasing its thermal insulation properties. In addition, the organic nature of the glycerine means an energy saving in the firing process.

The objective of this work is the characterization of the by-product glycerine, and its use as raw material in the manufacture of clay bricks. Also the effect of the amount of glycerine added (0-20 wt %) is evaluated through the study of the physical, mechanical and thermal properties of bricks with waste compared to bricks control (containing only clay).

2. Experimental

2.1. Materials

The clay was supplied by a clay pit located in Bailen, Jaen (Spain). It was obtained by mixing three types of raw clays in equal parts: red, white and black clay. The waste glycerine came from Linares Biodiesel Technologies S.A., located in Linares, Jaen (Spain).

2.2. Processing method

To obtain a uniform particle size, the clay were crushed and ground to yield a powder with a particle size suitable to pass through a 100 μm sieve. To determine the effect of the pore formation for organic waste materials in the clay matrix, different amounts of glycerine (5, 7.5, 10, 12.5, 15, 17.5 and 20 wt %) were added to the clay. To enable comparative results, fifteen samples per series were prepared for the tests. Waste-free mixtures of clay were also made as a reference. Homogenized mixtures in a blender was molded under 54.5 MPa of pressure, using a uniaxial laboratory press type Mega KCK-30 A. Solid bricks with 30×12 mm cross sections and a length of 60 mm were obtained. The shaped samples were dried for 24 h at 110 ºC. The dried samples were then fired in a laboratory furnace at a rate of 8 ºC/min up to 950 °C for 1 h. Samples were then cooled to room temperature by natural convection inside the furnace. The fired samples were designated as C for the brick without waste and GLA_x for the mixtures, where x denotes the content (wt %) of glycerine in the matrix clay.

2.3. Characterization of brick raw materials

The mineralogical composition was studied by X-ray diffraction (XRD). The original samples were gently ground in an agate mortar and random and oriented preparations were used for XRD. Oriented preparations were also saturated using ethylene glycol vapours to investigate the presence of smectites. The X-ray diffractometer X'PERT PRO from PANalytical was used at 36 kV and 26 mA with Ni-filtered CuK (alpha) α radiation and graphite monochromator. The 2θ range was from 3 to 70°, step size at 0.03° (2theta), scan speed at 0.05/240 (2theta/s) and counting time at 240 s. The divergence slit was 1/2 (°theta) and antiscatter slit was 1/4 (°2 theta) with detector X'Celerator. The chemical composition was determined by X-ray fluorescence (XRF) analysis using the Philips Magix Pro XRF model PW-2440. The thermal behaviour was determined by thermogravimetric and differential thermal analysis (TGA–DTA) with a Mettler Toledo 851e device in oxygen. The determination of the organic content was performed according to ASTM D-2974, Standard Test Method for Moisture, Ash, Organic Matter of Peat and Other Organic Soils [22]. The ignition temperature was 440 °C. The total content of carbon, hydrogen, nitrogen, and sulphur was determined by combustion of samples in O_2 atmosphere using the CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112. The higher heating value (HHV) was determined using a Parr 1341 Plain Oxigen Bomb Calorimeter.

2.4. Characterization of the bricks

To verify whether the resulting fired brick samples fulfilled the building standards, tests for linear shrinkage, mass loss on ignition, bulk density, water absorption capacity, water suction, open porosity and compressive strength were performed.

Linear shrinkage (%) was obtained by measuring the length of the samples before and after the firing using a calliper with a precision of ±0,01 mm according to ASTM standard C326 [23].

The mass loss on ignition (%) was determined as the mass loss between drying at 110 °C and firing at 950 °C.

Water absorption capacity (wt %) was determined according to the standard procedure [24] using dried samples (110 °C for 24 h) and weighed repeatedly until the mass difference was <1%.

Open porosity (in vol %) was calculated from the values determined of bulk density and water absorption capacity.

Water suction of a brick is the volume of water absorbed during a short partial immersion. The water suction (kg/m^2 min) was determined through capillary action according to the standard procedure [25].

The compressive strength of bricks is the bulk unit charge against breakage under axial compressive strength. For this trial, six fired samples were studied. Tests on compressive strength were carried out according to standard [26] on a Suzpecar CME 200 SDC laboratory press. The area of both bearing surfaces was measured and the average taken. All samples were tested by applying the load centred on the upper face of the brick with a speed <20 MPa/s until fracture. The compressive strength of each sample was obtained by dividing the maximum load by the average surface of both bearing surfaces, expressed in MPa with 0.1 MPa accuracy.

Freeze-unfreeze resistance was determined using the [27] and subjecting three samples of each series to 25 cycles of freezing-thawing for 24 h (18 of freezing and 6 of thawing) in a freezer. Prior to this test, the samples had been submerged in water until saturated.

Thermal conductivity was measured using a C-Therm TCi analyzer with a universal sensor. This equipment uses the modified transient plane source technique, applying a momentary, constant heat source produced by a one-sided, interfacial heat reflectance sensor to the sample.

Adsorption-desorption isotherms of N_2 at 77 K after outgassing for 2 h at 150 °C, the specific surface area (BET), micropore area, BJH cumulative volume of pores, BJH average pore diameter and pore size distribution were obtained in a Micromeritics equipment (TriStar II 3020 model), following the BJH method [28].

The microstructure of the pieces formed was observed by means of a scanning electron microscope (SEM), using the high-resolution transmission electron microscope JEOL SM 840. Samples were placed on an aluminium grate and coated with gold using the ion sputtering device JEOL JFC 1100.

3. Result and discussion

3.1. Analysis of materials

The chemical composition of the raw clay used in the study is summarized in Table 1. The composition of the clay was similar to that of typical clays used in industrial brick manufacturing with Si, Al, Ca, Fe and K as the main components [19]. Clay had high amounts of SiO_2 and Al_2O_3 of 55.82% and 12.13% respectively. The appreciable percentage of CaO was 9.21%, and it is related to the abundance of carbonates justifying the loss of ignition observed.

Table 1. Chemical composition of the clay obtained by XRF.

Oxide content (%)	Clay
SiO_2	55.82
Al_2O_3	12.13
Fe_2O_3	4.83
MnO	0.03
MgO	1.49
CaO	9.21
Na_2O	0.49
K_2O	2.78
TiO_2	0.83
P_2O_5	0.12
Zr (ppm)	279.3
LOI	11.50

The XRD pattern of the clay sample in oriented preparation (Fig. 1) exhibited the presence of clay minerals such as kaolinite and illite, with montmorillonite (d_{001}-value at 1.497nm). Quartz, calcite and feldspars (microcline and albite) were also identified as well as iron oxide. The random XRD pattern demonstrated that quartz is the main component and illite and kaolinite are the predominant clay minerals, with minor calcite and feldspars. The XRD pattern of this sample in oriented preparation after saturation with ethylene glycol vapours evidenced that the montmorillonite d_{001}-value changed from 1.497 nm to 1.715 nm.

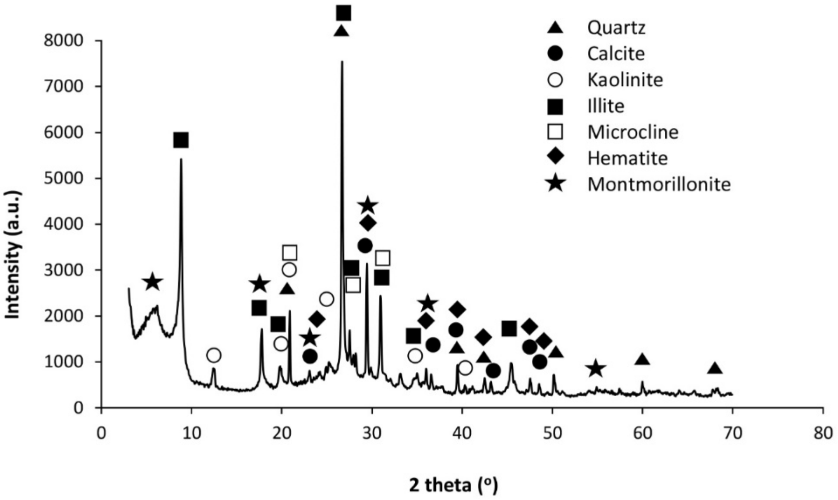


Fig. 1. XRD pattern of clay used as raw material in the preparation of bricks.

Glycerine presented a LOI of 99.0 wt %, due to its higher content of organic matter determined according with to the ASTM D-2974 standard [22], 92.90%, as well as by the large amount of carbon determined by CNHS analysis (Table 2) [16].

Table 2. Organic matter content, CNHS analysis and Higher Heating Value (HHV) of raw materials.

Sample	Organic matter content[*] (%)	%C	%H	%N	%S	HHV (kcal/kg)
Clay	3.62	2.41 ± 0.07	0.44 ± 0.01	0.05 ± 0.0	0.06 ± 0.01	-
Glycerine	92.92	46.90 ± 0.07	10.24 ± 0.07	0.23 ± 0.07	0.00	5535

[*] Determined according to ASTM D-2974

Brick manufacturing includes usually some materials with variable organic matter content like olive pomace or coke [16]. For example, in the case of coke, with an average higher heating value of 7680 kcal/kg, the addition of 1 wt % to the body represents 76.8 kcal/kg clay, equivalent to 10.7-32% of the heating requirements depending on the building product [29]. The HHV of the glycerine was 5535 kcal/kg, the higher heating values added 55.35 kcal/kg clay, that is 7.7–23%, of the heating requirements, which can be saved when glycerine was used as additive for brick manufacturing. Therefore the use of wastes to replace part of the fuel normally used in brick manufacturing implies an environmental benefit because it does not contain undesirable elements such as sulfur, chlorine, fluorine and aromatic organic compounds present in different proportions in the conventional fuels [16]. The residues meet the NPR-

CENT/TS 15359 EN standard [30] and can be used in incineration, obtaining a reduction of the atmospheric emissions.

The thermal behaviour of the clay and the glycerine is shown in Fig.2. The reactions taking place during firing processes using DTA-TGA curves were studied. The weight loss associated with pure clay, 9.0%, is due to the loss of organic material during the sintering process, the elimination of non-surface water by processes of dihydroxylation and the decomposition of the carbonates [20]. Before 600 °C, the loss is gradual due to release of physically absorbed water, combustion reaction of organic matter and dihydroxylation reactions of clay minerals. The decomposition of the carbonates with high CO_2 occurred from 600 ºC to 800 ºC. DTA curve showed that dehydration, release of OH (dehydroxylation reactions) and decarbonation reactions are endothermic process, peaks centered at 66 °C, 557 °C and 750 °C, respectively, while the decomposition of organic matter is an exothermic process, peaks centered at about 330 °C and 420 °C. After about 900 °C different exothermic effects appeared due to the crystallization of high temperature phases [16].

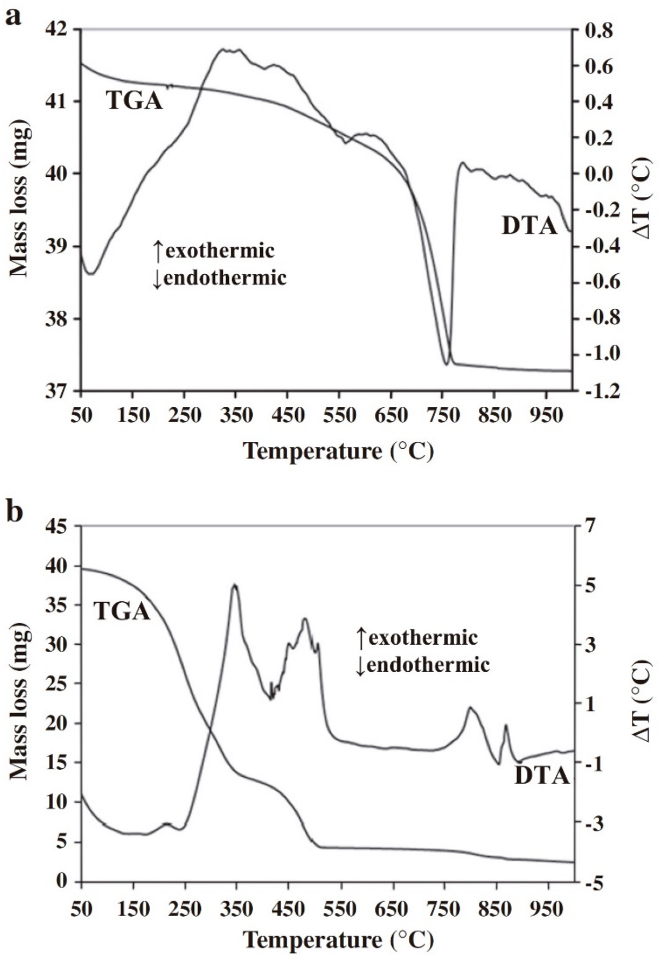


Fig. 2. DTA-TGA analysis of (a) raw clay and (b) glycerine.

TGA–DTA curves of glycerine (Fig. 2-b) showed that after the moisture is volatilized, the organic matter content started to leave the material and burns very rapidly as the two strong exothermic peaks centered at

340 °C and 470 °C. At 540 ºC the combustion of around the 90% of the glycerine is completed. Total mass loss of about 93.7% was observed at 1000 °C for glycerine [16]. The glycerine decomposition was not complete until 900 °C as indicated by the two endothermic peaks between 750 and 900 °C in DTA curve. Glycerine burns well, but it must be fired at high temperatures so it does not produce the corrosive gas acrolein, which is formed mainly between 200 °C and 300 °C [1,31].

3.2. Technological properties of waste-clay mixtures

Experimental tests have been carried out with mixtures of glycerine in different proportions (0-20 wt %) and clay in order to study their technological properties.

No defects as cracks, bloating or eflorescence were observed after firing. There was no black core observed on the fracture section of the residue containing fired samples.

The quality of brick can be further assured according to the degree of firing shrinkage. Linear shrinkage of control brick, without residue was 0.3%, exhibiting a contraction behavior (Table 3). The sintering mechanisms encourage greater proximity among the particles and this caused shrinkage when the samples were sintered at 950 °C. The addition of glycerine changed the linear shrinkage from contraction to expansion, which is a typical behavior of porous bricks, due to the high level content of organic matter in the samples. The glycerine waste has a content of organic matter very high of 92.2%. The proportions of glycerine only had a weak effect on the linear shrinkage for a firing temperature of 950 ºC. All the samples clay-glycerine expanded approximately 0.5~0.8%, most likely due to the decomposition of the gaseous components. These values are considered to be within the safety limits for industrial production of clay bricks.

Loss of ignition (LoI) of the brick mixtures, after firing process at 950 ºC is shown in Table 3. The loss on ignition of the clay samples was 14.15%.The control brick samples showed the lowest loss in ignition and it is related to the dehydroxilation reactions, loss of humidity and carbonates decomposition in clay minerals and the combustion of organic matter present in clay. The addition of glycerine increased the loss on ignition to values varying from 16.15% to 29.54%. As indicated in the thermal analysis results of the glycerine waste, glycerine is an organic waste and the mass loss was attributed to the combustion of organic matter. Therefore, with increasing the proportion of glycerine, the loss on ignition of fired bricks is expected to increase.

Table 3. Technological properties of construction bricks made from clay and clay-glycerine mixtures.

Sample	Waste content (wt %)	Linear shrinkage (%)	Loss on ignition (%)	Suction water (kg/m^{2}min)
C	0	0.33 ± 0.07	14.15 ± 0.15	2.87 ± 0.82
GLA_5	5	-0.80 ± 0.08	16.15 ± 0.24	2.10 ± 0.19
GLA_7.5	7.5	-0.78 ± 0.09	17.50 ± 0.95	2.09 ± 0.07
GLA_10	10	-0.74 ± 0.09	18.99 ± 1.16	2.11 ± 0.10
GLA_12.5	12.5	-0.54 ± 0.05	24.52 ± 0.34	2.82 ± 0.05
GLA_15	15	-0.67 ± 0.08	23.85 ± 0.50	3.45 ± 0.08
GLA_17.5	17.5	-0.57 ± 0.08	21.02 ± 0.78	3.73 ± 0.08
GLA_20	20	-0.50 ± 0.13	29.54 ± 3.42	4.34 ± 0.56

Fig. 3 shows the X-ray powder diffraction (XRD) diagrams (random oriented samples) for crystalline phase analysis corresponding to clay sample C fired at 950 ºC during 1 hour and samples with addition of glycerine in several percentages (5, 10, 15 and 20 wt %), fired at 950 ºC during 1 hour (GLA_5, GLA_10, GLA_15 and GLA_20). The XRD are investigated from 2º to 70 º (2θ). The crystalline phases identified by XRD in all these samples are α-quartz, feldspars (alkaline and alkaline-earth aluminium silicates: albite, anorthite and microcline) and hematite (α-Fe_2O_3). Illite (potassium aluminium silicate) is also identified as clay mineral, although it must be as minor dehydroxilated phase according to the firing temperature (950 ºC). Possibly, dehydroxilated illite would disappear if firing time is higher than 1 hour or firing temperature is higher than 950 ºC.

A semiquantitative estimation from XRD analysis of C sample indicates 70 wt % of α-quartz, 20 wt % feldspars, 5 wt % hematite and 5 wt % dehydroxilated illite. Similar percentages can be calculated if the XRD results of the mixtures are considered taking into account the error in these determinations (±5 wt %). It is concluded that there is not significative variation in the phases originated by firing of the clay mixtures as compared to the original fired sample. The same can be deduced if the semiquantitative XRD results of the mixtures are compared.

It should be noted that quartz is identified as α-quartz because the sample is fired at 950 ºC and subsequently cooled before the application of XRD technique. In fact, the phase transition α→β occurs at 573 ºC when the samples are heated with a noticeable change in dilatation-contraction. It must be taking into account this effect when pressed or extruded samples are cooled, for instance in the processing of firing brick clays, to avoid any defects.

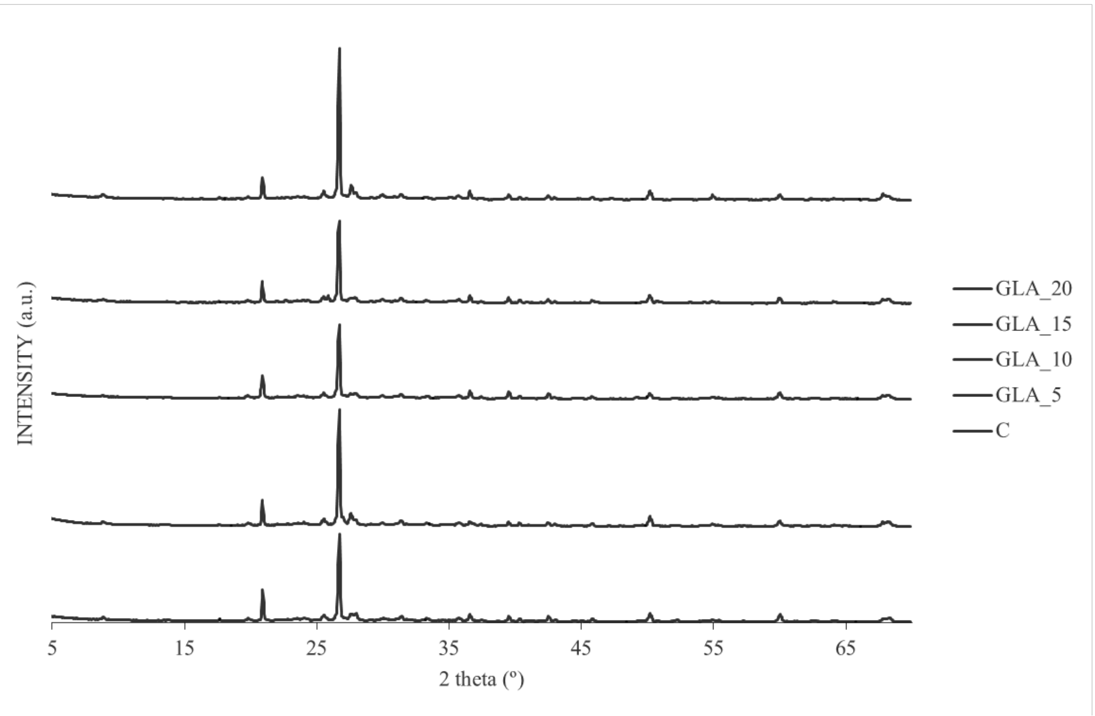


Fig. 3. XRD patterns of fired clay bricks and fired glycerine-clay bricks.

The addition of glycerine reduced the bulk densities of the fired bricks (Fig. 4), which exhibited values ranging from 1767 to 1492 kg/m^3 lower than the values for control bricks of 1804 kg/m^3. The addition of small quantities of glycerine, up to 10 wt % results in a reduction of bulk density between a 2.1 and a 3.2% achieving the minimum reduction with the addition of 7.5 wt % and the maximum reduction with the addition of 5 wt % of waste. However the addition of larger amounts of residue 12.5-20 wt % of glycerine produced a linear reduction in bulk density decreasing between 7.4 and the 17.2% this property with respect to control brick containing only clay. The reduction in bulk density is due to the combustion of the high organic content (92.2%) contained in the residue causing porosity in the clay body. However the bricks present values more high bulk density than expected, probably due to the high viscosity of liquid glycerine residue which could act as lubricant during the clay body forming, permiting a more efficient packing [32].

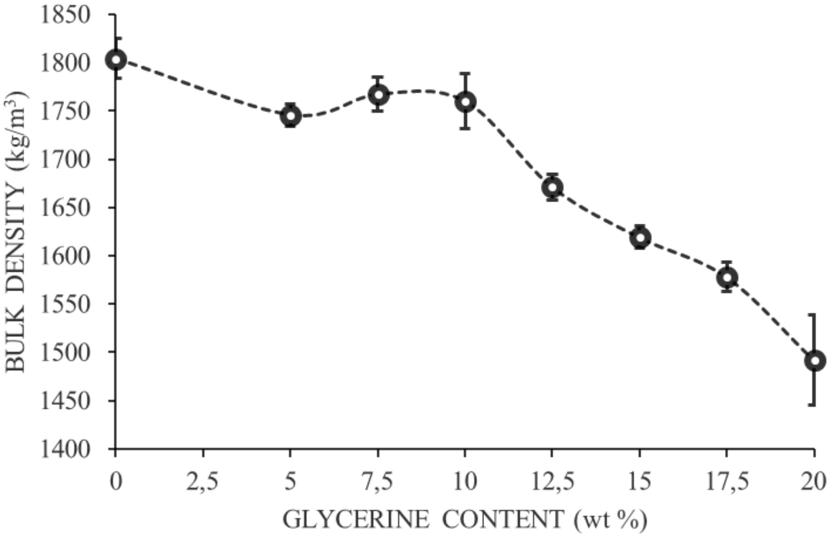


Fig. 4. Bulk density of the fired bricks as function of glycerine addition.

Water absorption is a key factor affecting the durability of brick. The less water infiltrates into brick, the more durability of the brick and resistance to the natural environment are expected. The water absorption is an indirect indicator of open porosity. Water absorption varied depending on the amount of added residue. The water absorption of the control bricks was 16.4%, the addition of small amounts of glycerine, up to 12.5 wt % resulted in a decrease of the open porosity, obtaining values between 12.5 and 15.1%(Fig. 5). However, major additions of residue caused an increase in the water absorption getting greater value open porosity, 19.1% when 20 wt % of glycerine was incorporated. Glycerine waste placed in clay matrix, incorporated organic matter that combusted during the firing process resulting in open and closed pores. Therefore, a glycerine contents up to 12.5 wt %,produced a greater proportion of spherical closed pores, as seen in the SEM images (Fig. 8). In samples with 15 wt % of glycerine waste, open porosity is barely increased, showing water absorption values similar to those of pure clay. At higher percentages of glycerine, 17.5 and 20 wt % the open porosity increased up to a maximum value of 19.1%. In any case, the maximum water absorption value is limited by standards. Depending on both, main purpose of brick and the environment, values must be below 17 % in case of bricks exposed to severe weathering and 22% when bricks are under moderate weathering [33].

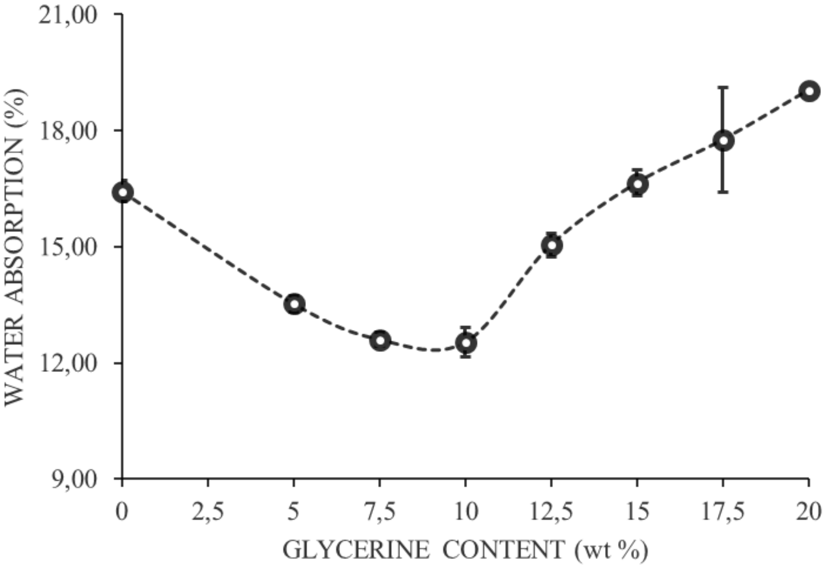
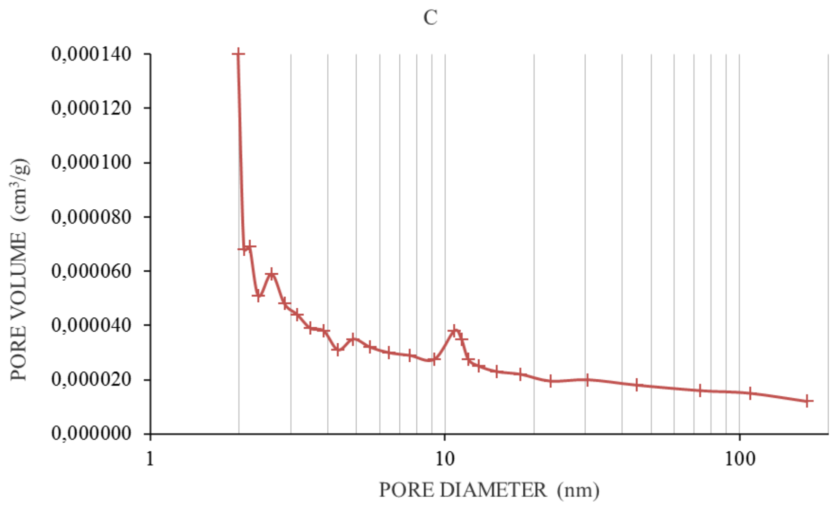


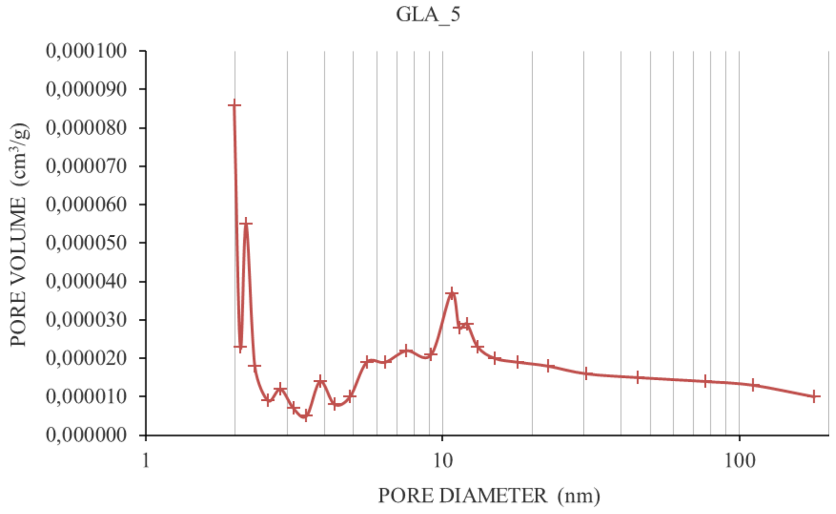
Fig. 5. Effect of glycerine concentration on water absorption.

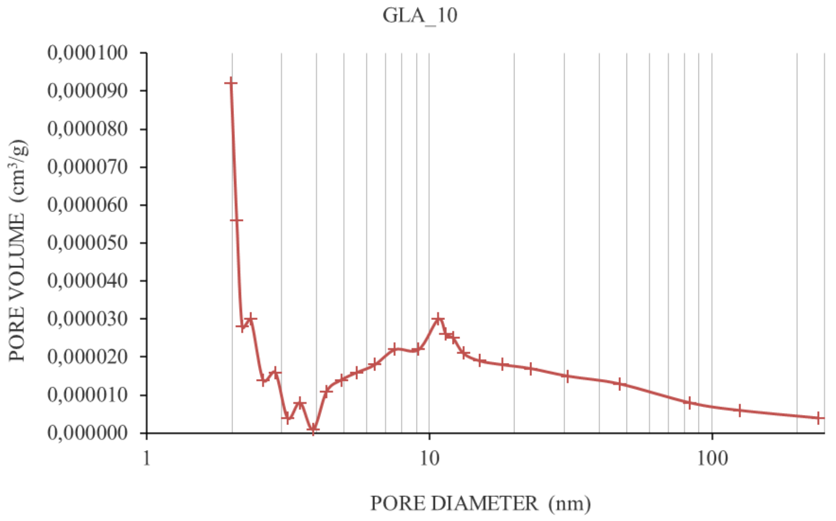
Water suction affects the quality and durability of the final materials. Lower values of water suction contributes to having good durability, and, consequently, higher resistance to the natural environment factors. The results of water suction, depending on the percentage of glycerine added, are shown in Table 3. Water suction of clay showed the value of 2.87 kg/m^2 min and varies with the added percentage of glycerine. A maximum suction value (4.34 kg/m^{2}min) was obtained in samples with the highest residue content (20 wt %). Adding increasing glycerine amounts up to 10 wt % decreases the water suction to 2.1 kg/m^{2}min, reaching water suction values lower than that of clay. The addition of 12.5 wt % of glycerine produced a water suction similar to clay and higher glycerine content (15-20 wt %) produced an increase in water suction. Therefore, it is necessary to incorporate large amounts of glycerine to produce an increase in the interconnected surface porosity possibly due to a growth of pores, both in size and in number, due to the organic waste content. In accordance with standard UNE bricks must be less than 4.5 kg/m^2 min water suction, and therefore all the bricks comply with regulations.

According to the Fig. 6, the average pore size is hardly affected by adding different percentages of glycerin to clay and only small variations are observed. Pure clay has a mesoporous structure with a pore size distribution between 2 and 50 nm. Additions of 5 and 10% glycerin modified slightly the average diameter of the mesoporosity and a peak at 2 nm in average diameter appears. Changes are even observed in the micropores under 2 nm indicating that small additions glycerin appears to cause an increase in the microporosity.

The addition of 15% glycerin affecting the microporous structure increasing the volume thereof and in addition increasing the mesopore volume situated between 2 and 50 nm, so it has influence in strengthening the mesoporous structure. This tendency is reinforced observing the dates for 20% addition to clay, there is hardly microporosity and macroporosity trend (above 50 nm) is to disappear in regard to pore volume.







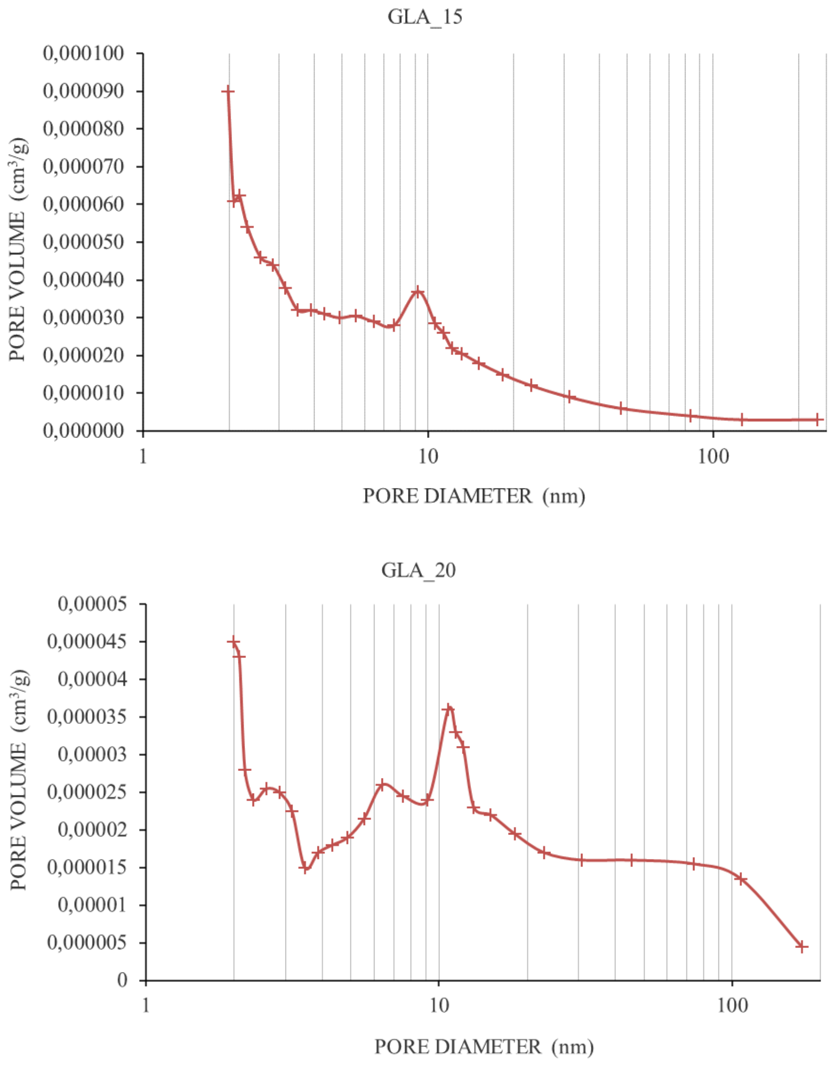


Fig. 6. Pore size distribution determined from adsorption data using the BJH method.

One of the disadvantages resulting from the use of lightening additives, which increase porosity, is the impairment of the mechanical properties of bricks. The impact of glycerine additions in the compressive strength of the fired samples depends on the waste amount (Fig. 7). Compressive strength values of control brick was 86.1 MPa and decreased slightly with the addition of low proportions of glycerine obtaining compressive strength values of 83.3 MPa with the addition of 5 wt % of waste and 50.73 when 12.5 wt% of glycerine is incorporated to the clay. These samples contains lower bulk density and greater total porosity, having less open porosity than brick control based on data from water absorption. However, these bricks present lower compressive strength since in addition to the open porosity that acts as stress concentrators, other factors such as amount of pores, pore distribution, pore size and the new mineral phases that are formed by the addition of glycerine should be considered. However when it is added more than 15 wt % of glycerine the compressive strength decreased to a greater extent due to the increase of the total porosity and open porosity, reducing a 62.8% by the addition of 15 wt % of glycerine and up to 19.2 MPa a 77.7% when the maximum quantity of waste, 20 wt %, was added. Such high porosity level was produced by the combustion of waste organic matter, what is known to have a marked detrimental influence on mechanical strength of ceramic [34]. According to Spanish and corresponding European Standards (UNE-EN 772-1), the minimum strength for building bricks is 10 MPa [26]. In our study, strength values of all samples containing residue were higher.

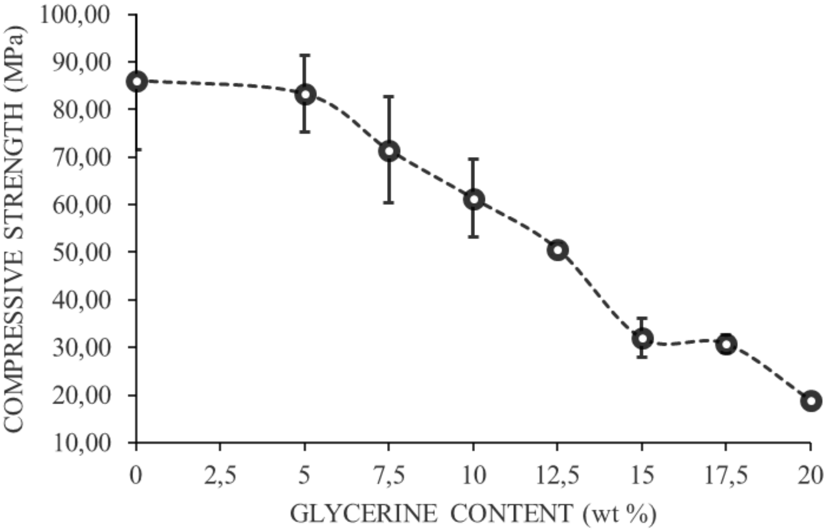


Fig. 7. Compressive strength of the fired bricks as function of glycerine addition.

The microstructure of samples fired at 950 ºC has been studied by SEM on fracture surfaces. Clay porosity (Fig. 8-a), either small sized and closed (micropores), resulting from intergrain porosity, or open (macropores), over the pores placed in the surface, changes due to the presence of glycerine. However, the different impacts of residue amounts on porosity can be observed. While small amounts of glycerine (up to 12.5 wt %) cause an increase in closed porosity, micropores and isolated spherical pores (Fig. 8-d), higher amount (up to 15 wt %) although contain small amount of spherical isolated pores, mainly contains irregular communication pores, increasing open porosity as a result of the macropores connection (Fig. 8-e) leading to increased water absorption and reduced considerably compressive strength.

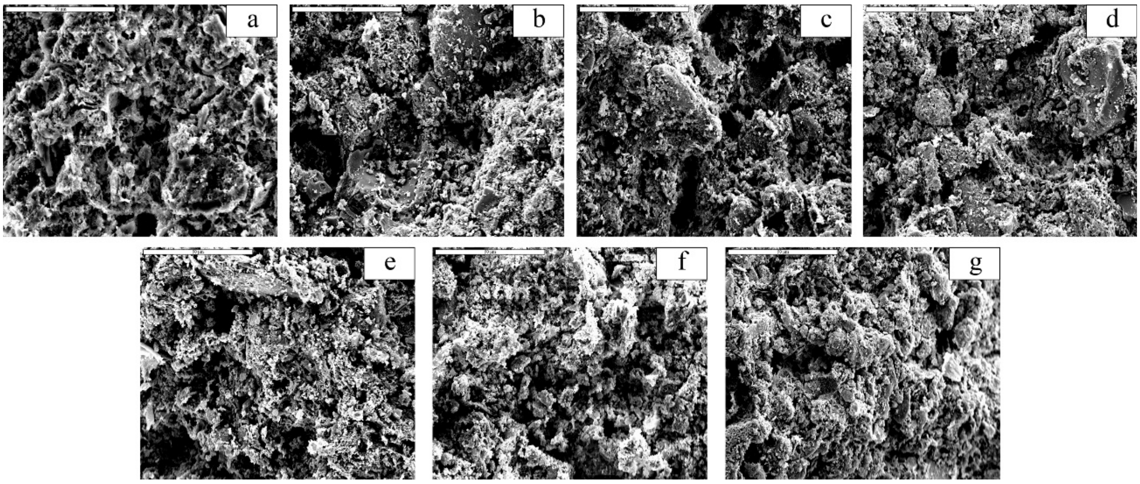


Fig. 8. SEM micrographs of fired bricks (a) with 5 wt % of glycerine; (b) with 7.5 wt % of glycerine; (c) with 10 wt % of glycerine; (d) with 12.5 wt % of glycerine; (e) with 15 wt % of glycerine; (f) with 17.5 wt % of glycerine; (g) with 20 wt % of glycerine.

Frost resistance is an index showing the ability to withstand a series of consecutive freeze–thaw cycles. Frost resistance is characterised by a decrease in compressive strength of samples before and after undergoing a series of 25 freeze–thaw cycles. After a visual examination of the samples, once all 25 cycles were carried out, no exfoliation, fissures or spalls were found. At the firing temperature for the bricks, vitrification by the silicate minerals is insufficient to counteract the reaction of portlandite crystals with other products. During the freeze-thaw assays, the pore water could react with the $Ca(OH)_2$ from calcite decomposition during brick firing [35]. The portlandite's crystallization pressure could cause pressure inside the brick pores, promoting a type of rupturing known as lime blowing [36]. Moreover, the $Ca(OH)_2$ also could react with the CO_2 and recrystallizes the $CaCO_3$, which could contribute to thevolume increase and, therefore, the pressure inside the pores [37]. Following the examination, a comparative trial on compressive strength was implemented. Results showed that mechanical resistance barely varied (Fig. 9).

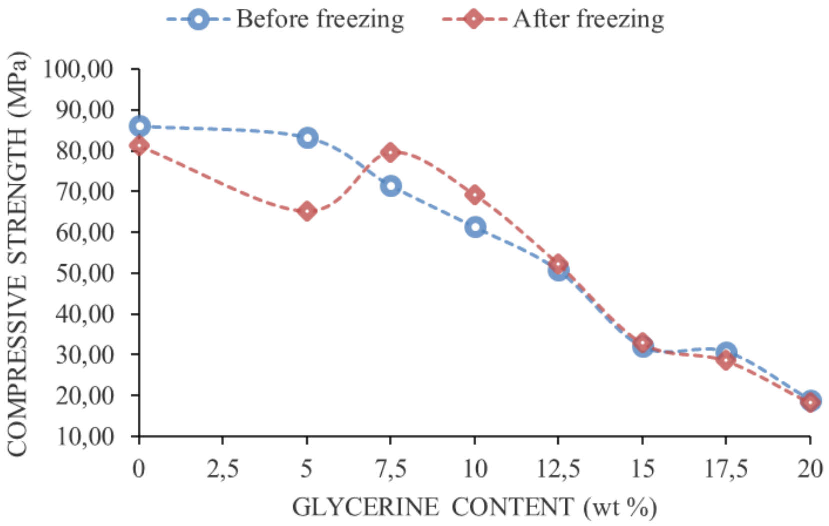


Fig. 9. Compression strength of bricks manufactured before and after 25 freezing-unfreezing cycles.

The thermal conductivity is a decisive factor for the insulation capacity of a building material.

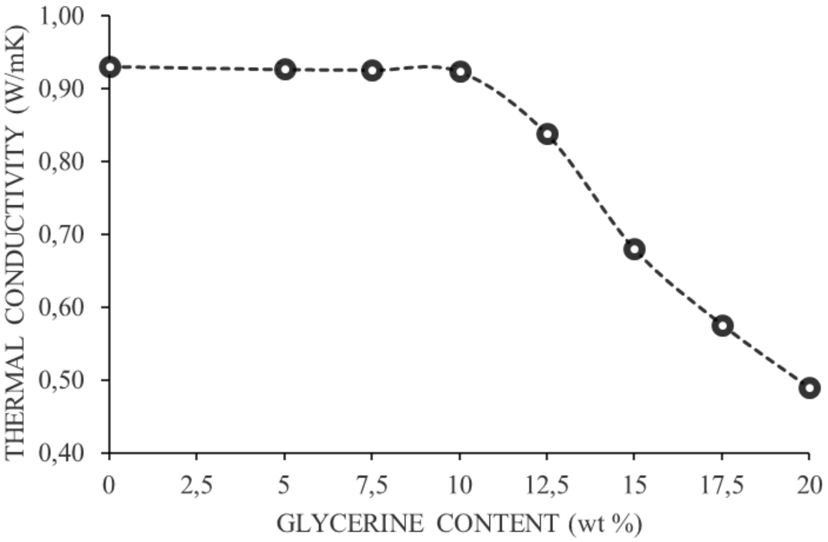


Fig. 10. Effect of glycerine concentration on thermal conductivity of the fired bricks.

The obtained results of the thermal conductivity of the bricks are presented in Fig. 10. The thermal conductivity of control bricks was 0.931 W/m K and decreased after the addition of glycerine. As the residue percentage increases, thermal conductivity decreases by 0.4% (with 5 wt % added glycerine) to 47.5% (with 25 wt % added glycerine). The thermal conductivity of the clay-glycerine bricks varied from 0.927 to 0.489 W/m K. The porosity created by the combustion of glycerine during brick firing provided this insulating quality. Until the addition of 10 wt % of waste, the thermal conductivity hardly varies, showing similar values for samples containing 5, 7.5 and 10 wt % of glycerine, which may be due to these samples presenting similar values of bulk density and total porosity. Above 10 wt % thermal conductivity decreasedmore drastically because the greatest increase in the total porosity of samples. Samples with low bulk density tend to present a higher percentage of air volume filling the voids that act as a useful insulator and decreasing the thermal conductivity of the entire solid matrix. Fig. 11 showed the thermal conductivity versus the bulk density of the fired clay bricks. In fact, considering the data, there seems to be a correlation between the two factors $R^2=0.95$. According with other authors the bulk density is a major factor that governs the thermal conductivity of solids in general and this property in bricks made with organic residue decreases with the bulk density [38,39]. However thermal conductivity could be influenced by other factors, such as mineralogical composition, micro-structure, and not only on the percentage of pores but also on their size and connectivity [40-43].

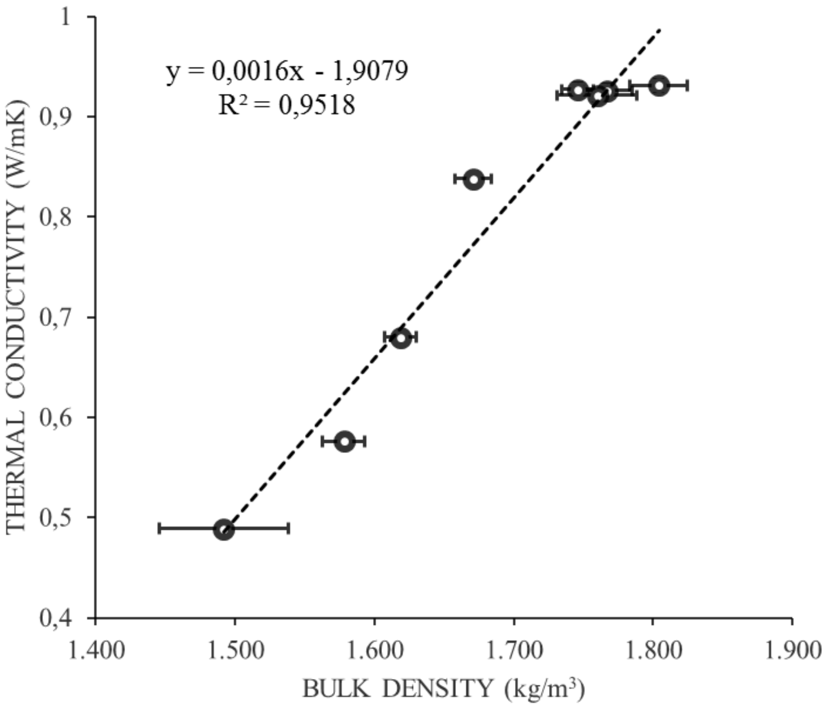


Fig. 11. Relationship between thermal conductivity and bulk density of the fired bricks.

Conclusions

This study proposes the use of glycerine, by-product of biodiesel production, as pore forming in sustainable clay bricks. Glycerine thanks to their organic substances content, during the combustion, bring an energetic support in the firing bricks step reducing heating requirements.

From the technological tests it was observed that to increase the content in glycerine (5-20 wt %) into a brick formulation showed a decreased in bulk density, compressive strength and thermal conductivity confirming the role of pore forming agent.

Technological properties of bricks are not changed significantly when the glycerine addition is equal to 5 wt %. Bulk density decreases 4.5%; compressive strength decrease 3.3% and thermal conductivity decreases 0.4%. Therefore, valorization of glycerine can be achieved at low addition rate as body fuel. However the higher addition of waste (20 wt %) resulted in low density masonry units with a decrease of the bulk density of 17.2%; of the compressive strength of 77.7% and the thermal conductivity of 47.5% compared to control brick. Higher additions of glycerine can be valorizated as body fuel and pore-former agent. Therefore, the addition of glycerine is limited to 10-15 wt % in order to reach an equilibrium between positive (weight decrease and thermal conductivity decrease) and negative (mechanical resistance decrease) effects.

All the values of technological properties of glycerine-bricks fall within the range required by the specific standards for bricks.

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