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Abstract

Lightweight bricks with reduced thermal conductivity and acceptable physical-mechanical properties have become an important trend for green buildings to reduce the building weight and the energy consumption. In this work lightweight bricks were manufactured from wine wastes (stalks, grape seeds and wine less) by controlling the nature and concentration of those additives. The wine wastes (WWs), completely characterized before their use in the matrix, were furnished by a cooperative wine-growers associations located in the Emilia-Romagna Region (Italy). Physico-mechanical properties of fired clay bricks manufactured with different percentages of WWs are reported and discussed. The results showed that the density of fired bricks was reduced up to 13%, depending on the percentage of WWs incorporated into the raw materials. Similarly, the flexural strength of tested bricks decreased according to the percentage of WWs included in the mixture. The best results, in terms of mechanical and physical properties, were obtained with 5wt.% of wine less (WL). The results showed as the lightness of these samples is associated to the porosity increase that directly influences the increase of the thermal insulation making the bricks usable for partitioning walls application.

Keywords: bricks, wine waste, thermal conductivity, mechanical properties.

Introduction

The total amount of biomass in Italy is around 66 million of tons/year, 20 of which produced by the agricultural industry (250 million of tons/year in the whole Europe) [1]. Generally, these residues are still managed with elevated costs of transport and disposal. The major quantity of wastes generated from agricultural sources are sugarcane bagasse, paddy and wheat straw and husk, wastes of vegetables, food products, tea, oil production, jute fiber, groundnut shell, wooden mill waste, coconut husk, cotton stalk, etc. Wine production is one of the most important agricultural activities generating important amounts of residues, which are characterized by high contents of biodegradable compounds and suspended solids [2]. The residues consist of stalks, seeds and grape skins produced during the grape crushing, draining, and pressing procedures. The subsequent fermentation process produces sediments (lees) containing pulp, tartrates and yeasts while clarification process produces bentonite clay and diatomaceous earth [2]. Clearly, the chemical composition of the wine by-products depends on the grape variety. However, the main part of winery solid waste (grape seeds and stalks) have a high content of fibers (lignin and cellulose) and a high percentage of nutritive mineral elements (especially nitrogen and potassium) [3]. The residue deriving from the clarification processes, instead, is mainly composed of silica and silicates, organic residues (as polyphenols), macronutrients (as K salts) and, eventually, heavy metals in low concentrations [2] [4]. According to the European Council Regulation (EC) 479/2008 regarding the common organization of wine market, grape marc and lees must be sent to alcohol distilleries. Anyway, the Italian code D.M. 301 December 2008 (Art. 5) reports a list of cases whereby the wine makers are not obliged to give by-products to the distilleries. On the basis of this legislation, the study of new solutions to recycle and/or valorize winery waste became possible and valuable [5]. In recent years, several researches have demonstrated that winery wastes could be additional sources of income. Indeed, winery wastes can represent an alternative source for obtaining natural

antioxidants, soil conditioner for fertilizer production, or for the recovery of tartaric acid [6][7][8][9]. For example, Molero Gómez et al. [10] and Fiori [11] proposed to use grape marc seeds for oil extraction, Tominaga et al. [12] carried out a lactic acid fermentation of grape marc with lactobacillus to produce anti-allergic substances. Botella et al. [13] and Díaz et al. [14] proposed the use of grape marc to obtain hydrolytic enzymes by solid state fermentation whereas Rodriguez et al. [15] suggested the use of grape marc to obtain bioethanol by solid state fermentation.

Although laboratory scale researches, previously mentioned, have been carried out, the difficulties encountered in developing industrial processes prevented the transfer of obtained findings to commercial processes. Moreover, an efficient and environmentally rational utilization of these wastes and by-products is important to obtain an higher profitability and to minimize the total environmental impact.

In this work, the possibility to use these wastes in the brick industry for the production of lightweight bricks was investigated. Generally, lightweight bricks are manufactured by adding organic and inorganic additives as foaming agents. Sawdust, polystyrene, paper sludge, etc. are some examples of organic pore-forming additives, while perlite, diatamite, calcite and pumice are examples of inorganic materials [16][17][18][19][20][21]. In all these cases, it has been found that both the inorganic and organic materials produce in the fired clay matrix a porosity increase which decrease thermal conductivity and mechanical strength [22][23][24][25][26]. Lightweight bricks can also be obtained by using several types of agro-wastes. This allows obtaining products that are characterized by a unique combination of properties, and at the same time that permit to recycle the growing quantities of agrowastes. Products or by-products of agricultural crops have already been used, as they are abundant and quite cheap. For example, the use of wheat straw, corn cob, several seeds (rape, maize, wheat and sunflower grass) is reported in [5] [27]; the use of olive mill solid residue in [28], sunflower seed shell in [29], rice husks and rice husk ash in [30] [31]. In particular,

several cited works established that the incorporate waste should not exceed 10wt% to produce bricks with an acceptable gain in porosity, thermal conductivity and mechanical resistance [32][33][28]. To the authors' knowledge, only pomace from wine industry has been used, by Muňoz et al, as an additive in bricks production. In that work, the maximum additive concentration to obtain bricks with good properties was 5 wt% [34].

The aim of this study is to evaluate the possibility to use wine by-products, such as grape seeds (GS), wine less (WL) and stalks (S) produced in the Emilia Romagna region (Italy), as foaming agents to produce lightweight bricks.

The project was developed in partnership with a wine cellars of the Emilia Romagna region (Italy), which supplied the agro-wastes, and a brick manufacturer located in Correggio (Reggio Emilia, Italy), which permitted to fire the bricks in industrial conditions. The proposed bricks were tested in the laboratories of the University of Parma (Italy) in order to evaluate the effect of the agrowaste on their physical and mechanical properties.

2. Experimental section

2.1. Characterization of the raw materials

Clay Characterization

The brick clay mixture was kindly provided as dried powders by Fornace Fosdondo (Correggio, RE, Italy). The mixture is mainly composed of quartz (SiO_2), calcite ($CaCO_3$), kaolinite ($Si_2O_5Al_2(OH)_4$), and minor amounts of illite ($(K,H_3O)\ Al_2Si_3AlO_{10}(OH)_2$) and chlorite ($Mg\text{-}SiO_2\text{-}OH$). Table 1 shows the chemical analysis of the mixture, performed by Inductively Coupled Plasma (ICP) technique, which is in good agreement with the mineralogical composition reported in Table 2. The particle size distribution of clay (Figure 1), obtained by laser granulometry, indicates that the as-received clay has a very broad distribution with an average particle size (d_{50}) of approximately 15 μm.

The thermal analysis (TG-DTA) of the clay shows (Fig. 2), after the weight loss of almost 10 wt% due to humidity evaporation (100°C), the dehydroxylation of clays (550°C), the endothermal decomposition of calcite (750°C), an finally an exothermic peak at 920°C due to the formation of new crystalline phases.

Wine wastes characterization

The grape seeds (GS), wine less (WL) and stalks (S) were supplied by Terre Cevico cooperative (Lugo, RA, Italy). In general, the main steps in wine production are harvest, stemming, crushing, pressing, fermentation and clarification. Initially, the grapes are crushed, and stalks (S) removed. Then, the grapes are pressed, and seeds (GS) separated from the *must* by filters or centrifuges before the *must* undergoes fermentation. Then, after fermentation, maceration and clarification of the grapes, wine less (WL) is generated. In order to remove all the residual moisture, the wine wastes, furnished as obtained during the wine production, were dried at maximum temperature of 80 °C in an electric oven for 8 h to avoid degradation of polyphenols during drying treatment.

Since the particle size can affect the physical and the mechanical properties of the fired products [33], the wine waste (WW) materials, in particular GS and S were milled with a grinder (IKA A10 model) at 20000 rpm for 30 seconds and passed through a 1 mm sieve to obtain a uniform particle size distribution suitable for subsequent use. WL is not milled because is a clay with fine particle size, used in the clarification process.

The determination of organic content in WW was performed by firing the samples for 7 h at 450°C. The morphology and the chemical composition of WW particles was observed by a scanning electron microscopy (JEOL JSM 6390) coupled with energy dispersion spectroscopy equipment (EDS, INCA 350, OXFORD) used to evaluate the chemical composition of the WW residues at 450°C. The crystalline phases were identified by a conventional Bragg-Brentano powder diffractometer (X'Pert PRO, Panalytical) with Ni-filtered Cu Kα radiation using bracket holder.

The patterns were collected over 2θ intervals ranging from 10 to 70 °2θ, with size step of 0.02° and time step of 25 s.

Figure 3 shows ESEM images of the three wastes samples under study, passed through a 1 mm sieve. Figure 3a reveals that the wine less (WL) are almost regular-shaped with a narrow distribution and a mean diameter of 25 μm (d_{50}), as evidenced by the grain size distribution analysis (Figure 4). This grain size distribution is compatible with the one of clay reported in Figure 1. On the contrary, the other WW are characterised by heteregoneous and irregular particles, both in size and in shape, as showed in Figure 3b and 3c.

The loss on ignition (LoI) data at 450°C, indicative of the organic content, are presented in Table 2 for all the WW used. In accordance with the average data reported in some works [3][33], the LoI of GS and S is around 92-96 wt% while the LoI of WL, obtained from the clarification processes, is about 58%.

The results of the mineralogical analysis of WW ash (Table 2) show that, after the heating step, the three ashes are mainly constituted by kalicinite ($KHCO_3$) and arcanite (K_2SO_4), as the main crystalline phases, and by traces of calcium phosphate ($Ca_4O(PO_4)_2$). More crystalline phases are identified in wine less ash that are also characterized by the presence of potassium silicate ($K_2Si_2O_5$), and traces of calcite ($CaCO_3$). Finally, the diffraction patterns (not reported in this paper) reveal the presence of an amorphous halo in stalks and grape seeds residues.

*2.2 Preparation of fired brick*s

The preparation of the clay brick specimens involves several steps which influence future bricks properties. To guarantee the feasibility of the process, the research was carried out in partnership with Fornace Fosdondo (Correggio, Italy). The clay mixture, as furnished, was oven-dried at 110°C and then mixed with the selected wine wastes treated as previously reported. The ceramic bodies were prepared by extrusion. In particular, the raw materials were blended and homogenized to produce mixtures with 5 and 10 wt% of dried WWs. Waste-free mixtures were also prepared as

reference. The amount of water that was added to obtain good plasticity depended on the type of incorporated waste. In particular, workability is a key factor for brick manufacturers since it influences extrusion and drying process as well as the geometry that may be achieved without clay body cracking. In this study the amount of water was set at 20% (calculated on a dry basis). For this percentage, the plastic limit, determined by the Atterberg [35], was 22%. Since, a higher quantity of water was needed to mix stalks, defected (cracking) brick samples were obtained after the extrusion process. For this reason, the samples obtained with this agro waste were no longer characterized.

The bricks were shaped with soft extrusion technique to obtain specimen dimensions of 140 x 24 x 11mm^3. The shaped specimens were dried at room temperature for 24 h and then, to reduce further the moisture content, were dried in an oven for 2 h at 100 °C.

In the firing step, the dried samples were sintered in an electrical laboratory furnace according to industrial heat treatment suggested by the brick factory. Moreover, taking into account the TG-DTA results, the maximum firing temperature was set to 980, 1000 and 1020°C to study the effect of firing temperature on the final mechanical and physical properties.

The thermal cycle used in the laboratory-scale firing tests is shown in Fig. 5. The specimens were heated at a rate of 5°C/min and held at 600 °C for 30 min to decompose the organic matter. The temperature was then increased to the final firing temperature with a dwell time of 120 min. The cooling stage involved natural cooling inside the furnace for approximately 12 h.

Depending on the quantity and type of the added waste (GS for grape seeds, WL for wine less and MIX for a 1:1:1 mixture of the three agrowastes), the samples were coded xWWy where x and y are the percentages of agrowaste and the temperature of the thermal treatment, respectively.

2.3 Brick samples characterization

After drying, samples were visually checked to find cracks or geometrical defects. The dimensions of the specimens were measured both after drying and firing steps by using a caliper with ±0.01 mm accuracy. Test pieces were also weighted after each step. Linear shrinkage (LS%), water absorption

(WA%) and measurement of weight loss of ignition (LoI%) of the fired samples were determined according to ISO 10545-3 [36] on samples with size of 26 × 14 × 140 mm^3.

Apparent density (ρ_a) was measured by considering the weight and the dimension of the specimens, simply by ratio of mass and apparent volume. The reported results are the mean of at least three measurements on samples of known geometrical shape obtained from original sample and cut by a saw (size 25 × 25 × 10 mm^3) The experimental errors for LS and WA are ± 0.5 and 1 %, respectively. The experimental errors in the ρ_a evaluations is ± 0.03 g/cm^3.

The porosity of the fired samples was also evaluated by means of Scanning Electron Microscopy (ESEM Quanta 200, FEI Company) coupled with energy dispersion spectroscopy equipment (EDS INCA-350, Oxford Instruments, UK). The micrographs were obtained with an accelerating voltage set at 20 kV. All the specimens (size 10 × 10 × 10 mm^3) were sputtered-coated with gold. The total porosity was calculated from ESEM images with SPIP software (Image Metrology AIS, Horshdm, Denmark). An average value was obtained using 3 images for each sample. The standard deviations varied between ±2%.

After firing, samples were milled in an agate mortar and sieved in a 400-mesh sieve to be characterized with X-ray diffraction (Bragg-Brentano diffractometer, mod. X Pert PRO, Panalytical, Eindhoven, the Netherlands) using Cu Kα radiation and a bracket holder. The spectra were collected over 2θ intervals ranging from 5 to 70°, with step size of 0.02° and time step of 25 s. The identification of the crystalline phases was made using the data on the JCPDS files.

To obtain the thermal conductivity of the studied bricks, a parameter estimation procedure already tested by Bozzoli et al. [37] was adopted: this procedure is based on the solution of the inverse heat conduction problem within the sample. A thin copper plate was applied to a surface of the sample, heated up by ohmic effect. On the opposite side of the specimen the thermal transient response was measured through multiple thermocouples. The sample, which dimensions were 100 × 100 × 10 mm^3, was thermally insulated through a rock wool layer with a thickness of 50 mm, in order to

minimize the heat exchange with the environment. Figure 6 reports a sketch of the experimental set up.

The measured temperature is strongly dependent on the thermal properties of the material in contact with the copper plate. Therefore, it is possible to obtain useful data on the thermal conductivity of the material by monitoring its temperature change with time. In particular, the acquired temperature distribution was employed as input data of the inverse heat conduction problem in the wall [38].

To apply the estimation method, a 3-D numerical finite element model of the whole test section (sample, metal plate, thermal insulation) was implemented within the Comsol Multiphysics® environment. A general procedure, suitable to estimate unknown parameters through the comparison between experimental results and the corresponding theoretical model, is based on least squares minimization. In particular, identifying with $\boldsymbol{Y}$ (Y_i = measured temperature at time i, i = 1….n) the temperature data experimentally measured on the sample surface and with $\boldsymbol{T}(k)$ the corresponding simulated temperature obtained from the solution of the numerical problem by imposing a value of thermal conductivity k, the parameter estimation problem is solved by minimizing the function [37]:

$$S = \sum_{i=1}^{n} (Y_i - T_i(k))^2 \tag{1}$$

Following this procedure, through the minimization of the target function S it is possible to find the value of thermal conductivity k that corresponds to the best approximation of the real value that characterize the studied sample. In the present work, the well-known Nelder-Mead algorithm [38] for multidimensional unconstrained optimization was adopted to minimize $\boldsymbol{S}$.

In Fig. 7 is reported, for a representative case, the comparison between the temperature measured experimentally and the restored temperature distribution obtained by adopting the thermal conductivity found with the described procedure.

The flexural strength of bricks was determined by means of three-point-bending tests using a universal testing machine (MTS model 2/M with a 10 kN load cell). The prismatic specimens presented nominal base b = 26 mm, height h = 14 mm, and total length L_{tot} = 140 mm; the span L

was 100 mm. Specimens were previously grinded with sandpaper to regularize their geometry permitting a uniform contact with the steel rollers. Test were performed controlling the displacement of the testing machine with a speed of 0.2 mm/min, observing the loading branch, the crack formation, and the subsequent softening regime. Both the displacement and the corresponding load were recorded during the test. The measured load at crack onset F was used to compute the flexural strength $f_{t,fl}$

$$f_{t,fl} = \frac{3}{2}\frac{FL}{bh^2} \quad (2)$$

The reported results were the average values of 5 samples.

Additional tests, for technological characterization, included the colour determination (CIE L* a*b* chromatic coordinates), using a portable colorimeter (Konica Minolta CM 2600 D). The effect of WW addition on the material color was determined performing color measurements on samples with and without WW particles. According to ASTM E1347 – 06 (2015) [39] colour change ΔE^* between two different samples was defined as:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (3)$$

where in the CIELAB method ΔL^* is the change in lightness, Δa^* and Δb^* the change in huge (a^* is the red (> 0) green (< 0) coordinate and b^* the yellow (> 0) blue (< 0) coordinate). The reported results were the average values of 10 samples.

Results and discussion

3.1 Bricks samples characterization

The linear shrinkage after drying (100°C) and after firing at different temperature is reported in Table 3. For all samples, there is a decrease in the drying LS as WW were added in the mixture, associated to stability of the WW during the drying step. After firing, the behavior is the same and the LS of the samples with WW addition is in general lower with respect to unfilled sample, independently of the

type of added WW. This behavior is very interesting from a technological point of view because it helps to decrease the LS and thus any internal strain that may occur during drying and firing processes. The loss on ignition (LoI), representing the weight loss of the sample after the firing process, was instead strongly influenced by the WW addition [1] [40]. In fact, the reference samples have a loss on ignition of about 14%, which increases to 21% when WW are incorporated into the clay (Table 3). The increase of LoI is more noticeable in series 10GS_*x* and 10Mix_*x* and it is almost independent of the firing temperature. The very high values of LoI are due to the elimination of the high content of organic matter as confirmed by the LoI of the WW reported in Table 2. This constitutes a serious technological problem and it is necessary to underline that only the samples with WL are under the recommended industrial limit value of 15% [41] [42].

The incorporation of WW into the clay matrix leads to a change of other physical properties of bricks: water absorption (WA) and apparent density (Table 3). The results show a clear increase in the WA after the addition of WW in the clay body. Indeed, if the reference sample shows WA values of 15-16%, the samples obtained by WW addition shows values in the range of 24-41%. According to the results reported in Table 3, it can be noticed that the incorporation of 5wt.% of WW induces an increase in the water absorption of about 60-110%. This value increases at 106-173% for the incorporation of 10wt.% of WW, independently of the firing temperature. The results are in accordance with previous works [27] [43], showing the same increasing percentage for water absorption for the same amount of organic waste added. Anyway, all the measured values of water absorption are greater than 20%, which is the standard limit according to ASTM C67-07a:2003 [44]. This standard on bricks indicates, for severe exposure, a maximum water absorption between 17% and 20% and no limit for negligible-weather-resistant bricks. Since, lightweight bricks have been widely applied in the inner walls of “green buildings” the water absorption of the new lightweight bricks of our work is an insignificant factor in considering their application.

As well as, the water absorption increases after the WW addition, the apparent density decreases, leading to a lightening of the material. In fact, compared to the value of the reference sample, the apparent density decreases with the waste content increasing. This expected trend is associated to porosity brought by the organic combustion. This decrease is more noticeable in series 10GS_*x* and is quite independent of the firing temperature. Similar behaviors and values are reported in other previous researches which showed a density decreasing, varying from 13% to 25%, when 10 wt% of waste is added [27] [45]. This property is a key factor for investors and constructors, who consider the economic costs related to transport of the bricks and the lower masonry weight. Since lightweight bricks are widely applied to build the inner walls of green buildings, their high water absorption is an insignificant factor for their application.

Focusing on the nature of the additive, at fixed incorporation amount, it appears that the bricks with WL have lower modifications in terms of water absorption and apparent density.

The results of bricks color (Table 4), an important feature for materials often used in building without a glaze, showed that the color of the fired bricks was slightly modified by the WW addition. In fact, the measured color variations ΔE^* are moderate and acceptable, being always below 5. These results are particularly important since in many industries, and in particular in the building sector, color is often the first impression that influences the consumer choice.

The evolution of the phase composition during heating was studied by means of XRD analysis. Figure 8 reports the XRD patterns of the samples heated at 980°C, chosen as representative. The X-ray patterns confirmed the presence of quartz and albite in all the fired bricks, independently on the type and amount of WW added. Illite, which takes part to vitrification during sintering, is absent indicating that the products underwent vitrification. In particular, the spectra of batches sintered at 980°C present alpha quartz [JCPDF file 01-086-1560] as the main crystalline phase, as well as traces of albite [JCPDF file 01-083-2215] and anorthite [JCPDF file 00-003-0505] deriving from the clay components. At 1000°C and 1020°C, no formation of new crystalline phases was evidenced in all the samples.

Figure 9 shows the difference in texture and porosity degree between reference and brick samples obtained adding 5wt.% of WW and heated at 980°C. Sample 0_980 (Figure9a) shows a dense structure with very low porosity. The sample with 5wt.% of WL (Figure9b) shows a comparatively dense structure with isolated small spherical pores (50-300 micron). On the contrary, 5GS_980 and 5MIX_980 samples (Figure 9c-d) contain both spherical and irregular pores, clearly due to the fiber decomposition. By the total porosity analysis conducted on optical images taken at 40X, it was observed that the porosity of 0_980 sample is 5%, the one of 5WL_980 is 9-10%, whereas 5GS_980 and 5MIX_980 samples have highest porosity values of 17-18%. The as measured total porosity was in agreement with the WW concentration in the clay. Since the increase of porosity is related to water evaporation, carbonates and sulfates decomposition, and organic combustion [45], the lower porosity of 5WL_980 sample can be explained by the lower organic matter content, as confirmed by the LoI results previously reported. Moreover, the formation of small pores in sample 5WL_980, as result of finer organic matter decomposition [46], can be observed while the presence of elongated cavities in 5GS_980 and 5MIX_980 samples are the results of organic matter decomposition of heteregoneous irregular particles sizes.

Mechanical performance of developed bricks

Figure 10 shows the average flexural strengths of the bricks. Considering the bricks after drying at 100°C, a slight increase of flexural strength was obtained after the addition of WW. Instead, the flexural strength of the fired bricks decreases, for a given temperature and additive, with increasing WW concentration, ~~. This behavior is~~ in line with the porosity increase ~~that affects the cohesion and hence reduces the material resistance to failure~~. ~~In particular, the flexural strength decreases as the WW percentage is increased. These results are~~ ~~in agreement with numerous~~ as reported in several works [27];[46];[47]; [48] ~~reporting the effect of porosity on mechanical properties. In fact, it is well known that pores act as a second phase of zero modulus and the Young's modulus depends on pore shape and orientation~~. Regarding the temperature, its increase did not particularly affect the flexural strength which is, probably, more dependent on the porosity of the sample than on the

densification of clay phase [19]. Despite the decrease of the mechanical strength, when compared with the bricks obtained without WW addition, most of the developed compositions have a rather high flexural strength (from 4.8 to 13.2MPa), which fulfills the minimum values prescribed by several code standards. Infact, depending on the countries, there are different standards specifying bricks grades according to the flexural strength values. For instance, withdrawn International standards specify a minimum strength of 10 MPa for clay tiles and 1.5 MPa for bricks [49]. ~~On the other hand, lightweight fired bricks are mainly used for partitioning walls or claddings rather than load bearing walls, therefore the mechanical strength is less important than the thermal behavior, which influences wall thermal transmittance and energy consumption.~~

In conclusion, we can state that the best results in terms of mechanical and physical properties were obtained with sample 5WL_*x* sample, in which 5wt.% of WL was used in the clay body.

Thermal conductivity

Based on the previous discussion, the thermal conductivity was evaluated for bricks sintered at 980°C with 5wt.% of WW. As shown in Figure 11, despite the WW addition provides an increase in porosity and a consequent decrease in mechanical properties of bricks, it helps to increase the thermal insulation of these new building bricks. In particular, the thermal conductivity (TC) of fired bricks was reduced from 0.70 W/m K (sample 0_980) to 0.35 W/m K (sample 5GS_980). These values are lower than the ones reported in literature by Sutcu et al. [24], who recorded TC values in the range from 1.0-0.7 W/m K for the fired clay without additive, to 0.4 W/m K when 30 wt.% of olive will waste was added.

The decrease of thermal conductivity (TC) can be associated with an increase of porosity and a decrease of apparent density, independently of the type of WW added [50]; [51]; [52]; [53]. In fact, the introduction of higher porosity into the microstructure, because air is trapped in the pores, permits to obtain a better thermal insulating behavior [54]. Figure 11 shows the thermal conductivity versus apparent density and total porosity of fired bricks. An almost linear correlation

between TC and both apparent density (R^2=93; see Figure 10a) and total porosity (R^2=82; see Figure 10b) can be observed. TC decreases of 18% for 5WL_*980* sample, 36% for 5MIX_*980* and 45% for 5GS_*980*. This confirms the fact that the pore forming action of the organic material has a positive influence on the thermal insulation. Despite 5MIX_*980* sample is the specimen characterized by the lowest apparent density and the highest total porosity, the best results in terms of thermal insulation are reached with the addition of 5 wt.% of GS. The reason for this behavior could be found in the different type of pores structures that are present in the two samples. For what concerns the 5MIX_980 sample, stalk fibers with irregular particle shape and one orthogonal dimension higher than 1 micron could explain the more irregular size porosity. As reported in the literature, other important factors that influence the thermal conductivity are represented by the type of porosity (open or closed) and by the pore size [50][54]: a more regular and densely distributed porosity can contribute to increase the insulation [54].

Discussion

Lightweight bricks with reduced thermal conductivity and acceptable physical-mechanical properties, have become an important trend for green buildings. This is because lightweight bricks reduce the building weight and energy consumption. Lightweight bricks were manufactured in this research from wine wastes (WWs) by controlling the nature and concentration of these additives. The best results were obtained with 5wt % of wine less (WL).

To assess the sustainability of adding WWs as new additive in the production of bricks and to estimate the expected annual quantities of wine wastes (WWs) at the regional scale, the following indications were employed. Assuming the wine production as a basic calculation unit, a generation rate of approximately 90.000-120.000 tons/years of grape seeds, 28.000-30.000 ton/year of stalks and 2.800-3.000 ton/years of wine less are generated in Emilia-Romagna region for 7 million hl of wine produced in 2016 [55]; [56]. Moreover, because the annual capacity of masonry brick production in Emilia-Romagna is over 46.000 ton/years [57], it can be assumed that the wine less

could be used as a pore-forming agent for building bricks from at least 2 firms. Moreover, the high cost of commercial pore-forming agents, (30-50 €/tons) and the need to reduce our dependence from raw materials, highlight the economic and ecological benefits for Emilia-Romagna in using wine less (WL) as additive.

Moreover, in the stage for the process scaling up, it should be also taking into account that WWs have sulfur components. Because these organic wastes burn into the first stage of tunnel kiln, the gaseous emissions during firing should be considered. It is known that the organic sulphur is sublimated in the colder parts of the furnace especially at the chimney due to the relatively low temperatures [34]. Therefore, the installation of flue gases treatments must be considered if these wine wastes are used in an industrial scale. Moreover, even if chlorine (Cl) and fluorine (F) waste contents have not been determined, the small percentage provided by the clay, mainly through the presence of halite, may generate harmful emissions that must be carefully controlled.

In conclusion, the scale up of the process, that can be considered feasible from a technical and economical point of view, have to be associated to a robust environmental analysis in order to define all the necessary emission controls.

Conclusion

Lightweight bricks with reduced thermal conductivity and acceptable physical-mechanical properties were obtained by using wine wastes (WWs) and controlling the nature and the concentration of additives. The incorporation of WWs is limited due to the increase of water absorption and the decrease of mechanical properties. In particular, the water absorption and the flexural strength of bricks with 5wt.% of WWs are good and sufficiently to satisfy the International Standards. Focusing on the nature of WWs type, it appears that all the waste addition reduces the linear drying shrinkage and also the total one of the whole process, helping to decrease any internal strain that may occurring during the drying and firing process. Among the wine wastes, WL allows to obtain bricks with the lower modification in terms of water absorption, apparent porosity and

weight loss under the recommended industrial values. Then, even if WL addition provides a slightly decrease in mechanical properties of bricks, the increase in porosity helps thermal isolation. In conclusion the use of WL as new pour forming agent in good quality clay bricks is feasible up to a maximum amount of 5wt.%.

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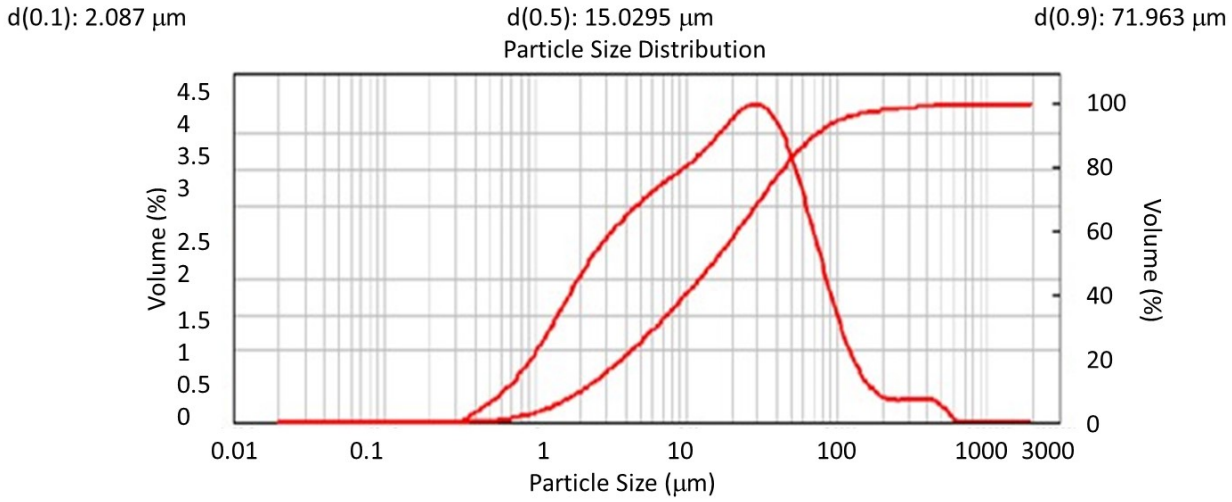


Figure 1. Particle size distribution of clay

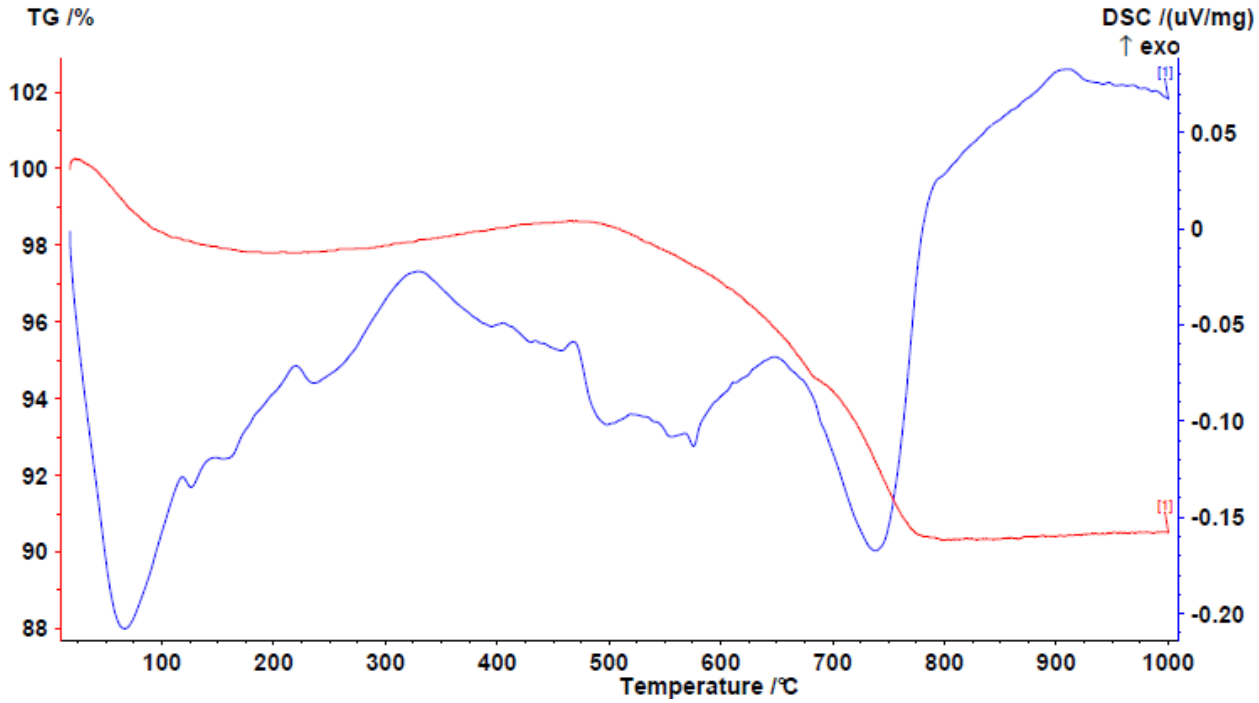


Figure 2. Thermogravimetric and differential thermogravimetric curves of the clay.

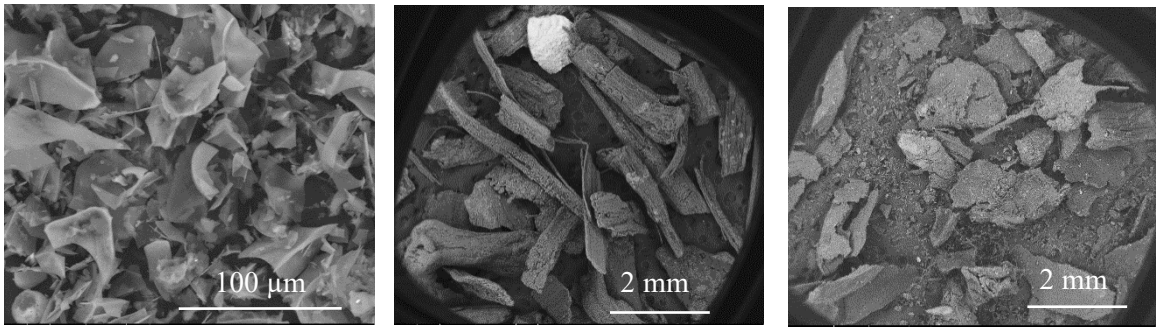


Figure 3. ESEM images of a) wine lees (WL), b) stalks (S) and c) grape seeds (GS

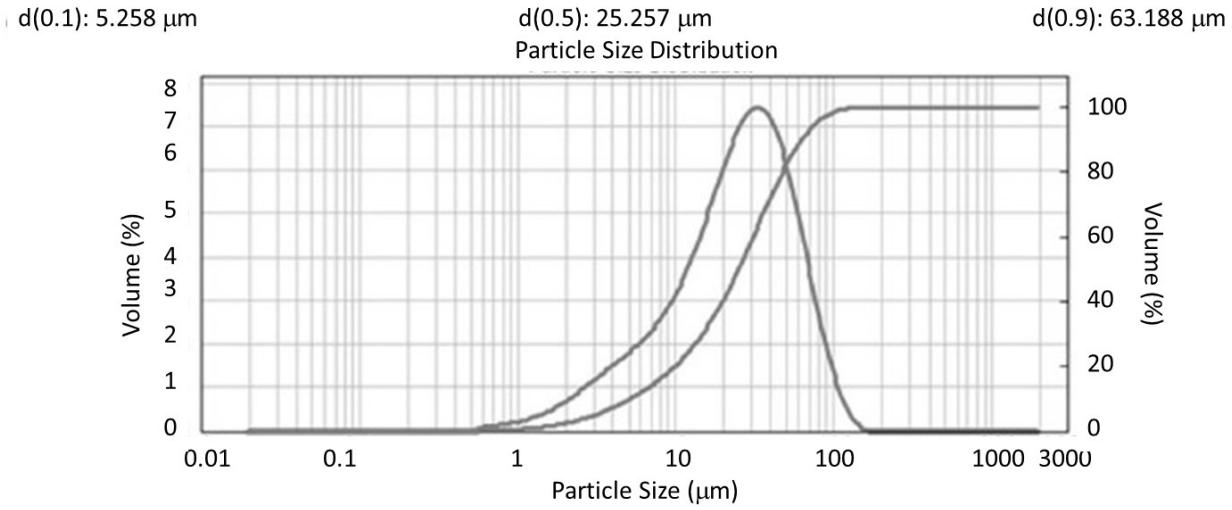


Figure 4. Particle size distribution of wine less (WL)

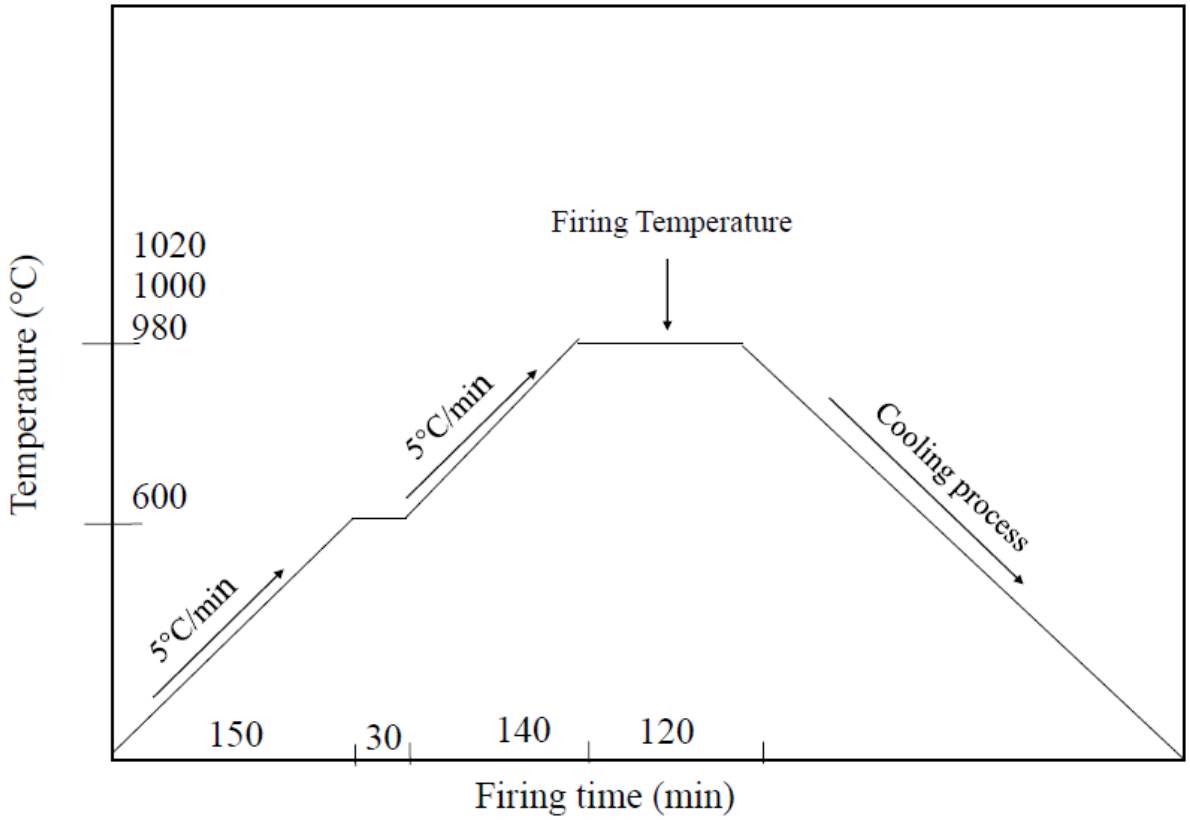


Figure 5. Heating program of the bricks.

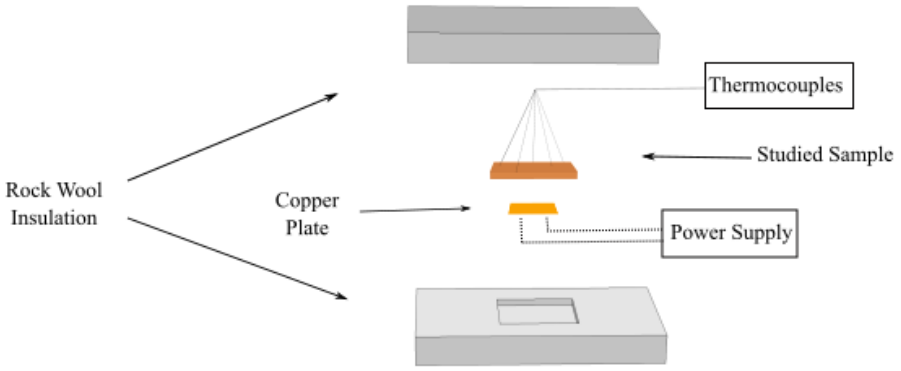


Figure 6. Sketch of the experimental set up for thermal conductivity.

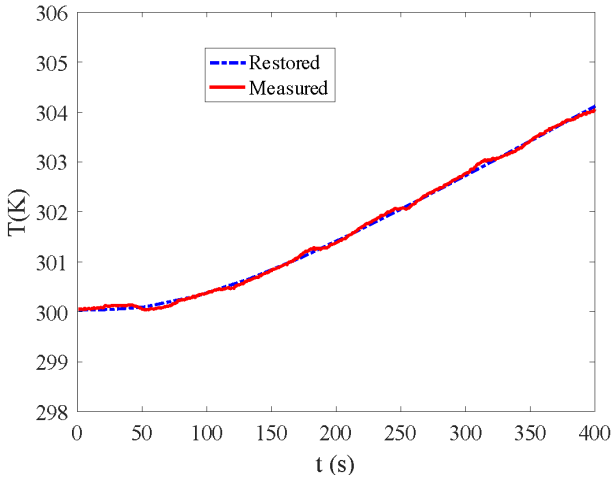


Figure 7. Comparison between measured and restored temperature distribution (5Mix_980 sample)

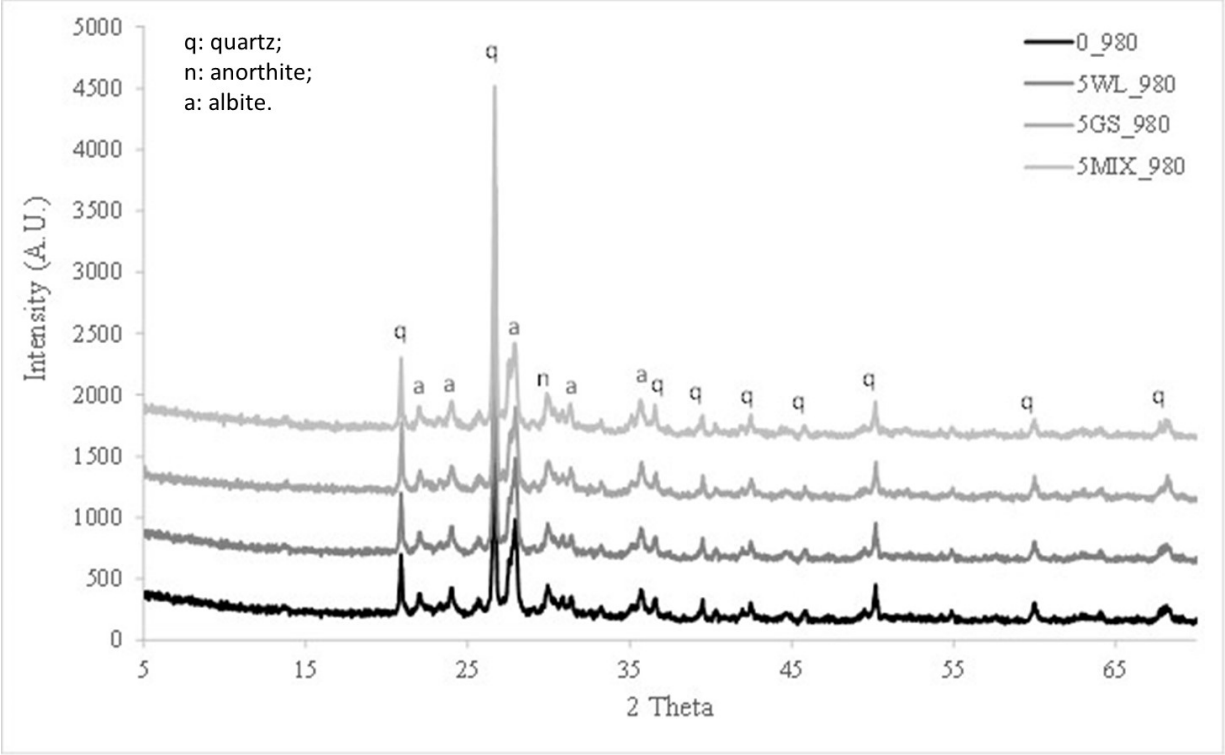
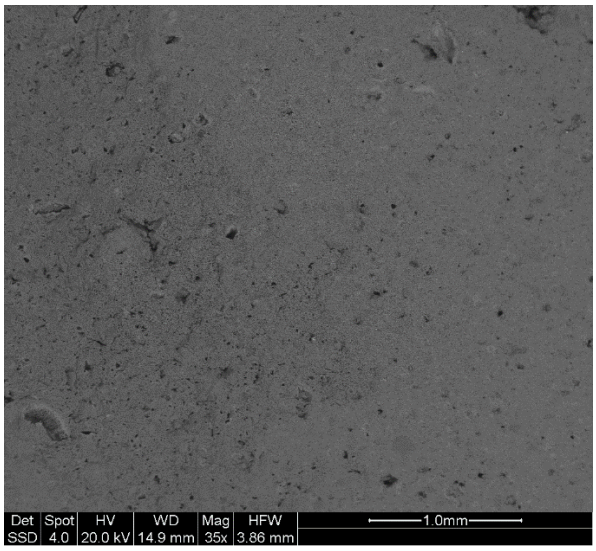
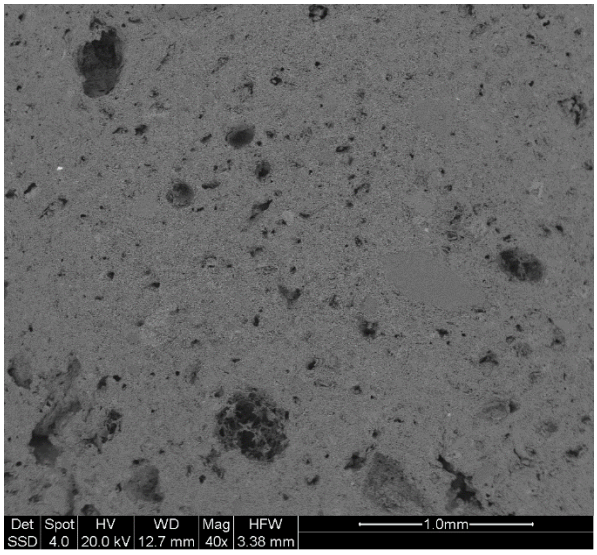


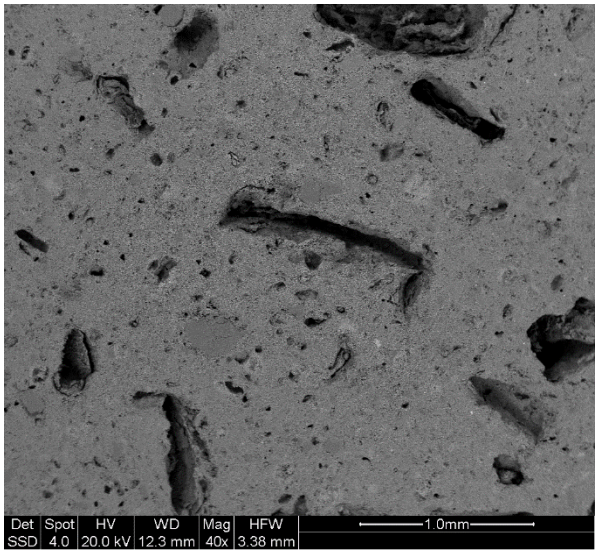
Figure 8. XRD spectra of a) 0_980, b) 5WL_980, c) 5GS_980 and d) 5MIX_980.



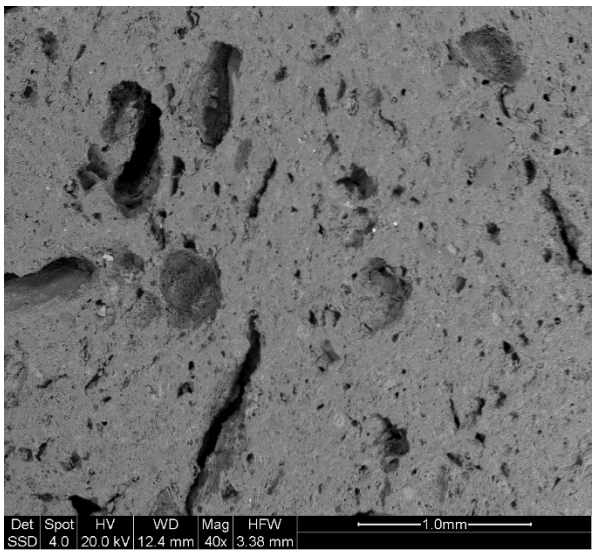
a)



b)



c)



d)

Figure 9. ESEM micrographs at 40X of: a) 0_980, b) 5WL_980, c) 5GS_980, and d) 5MIX_980 bricks.

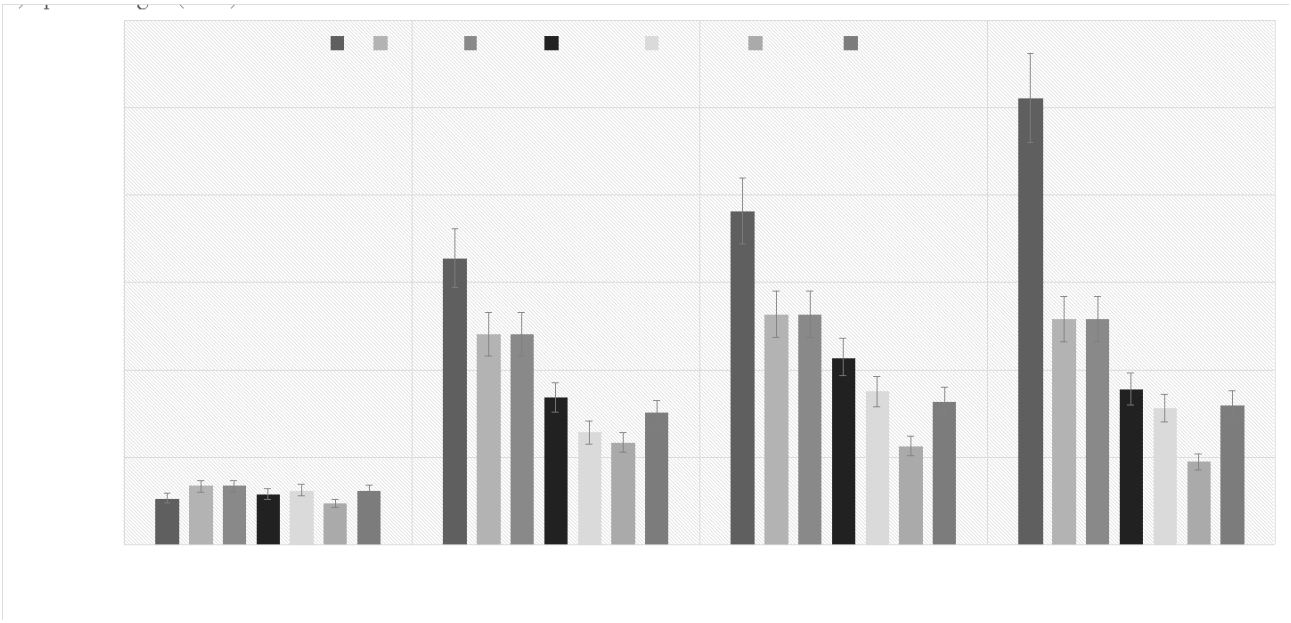
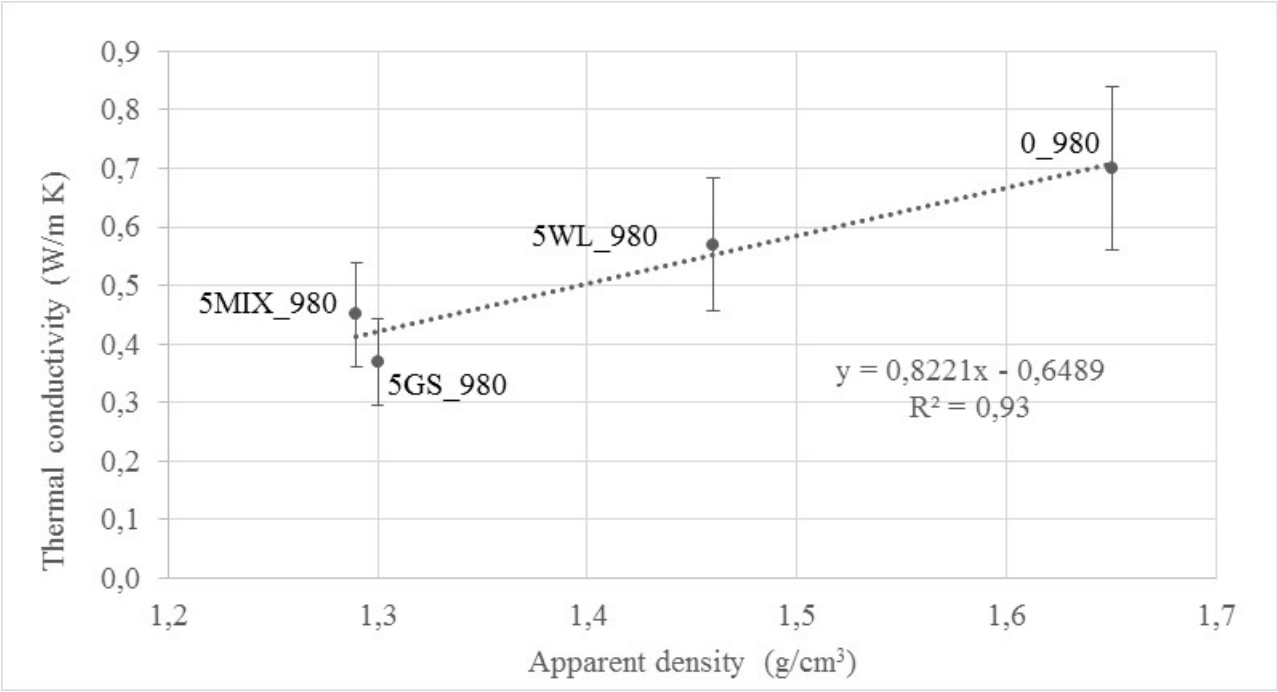
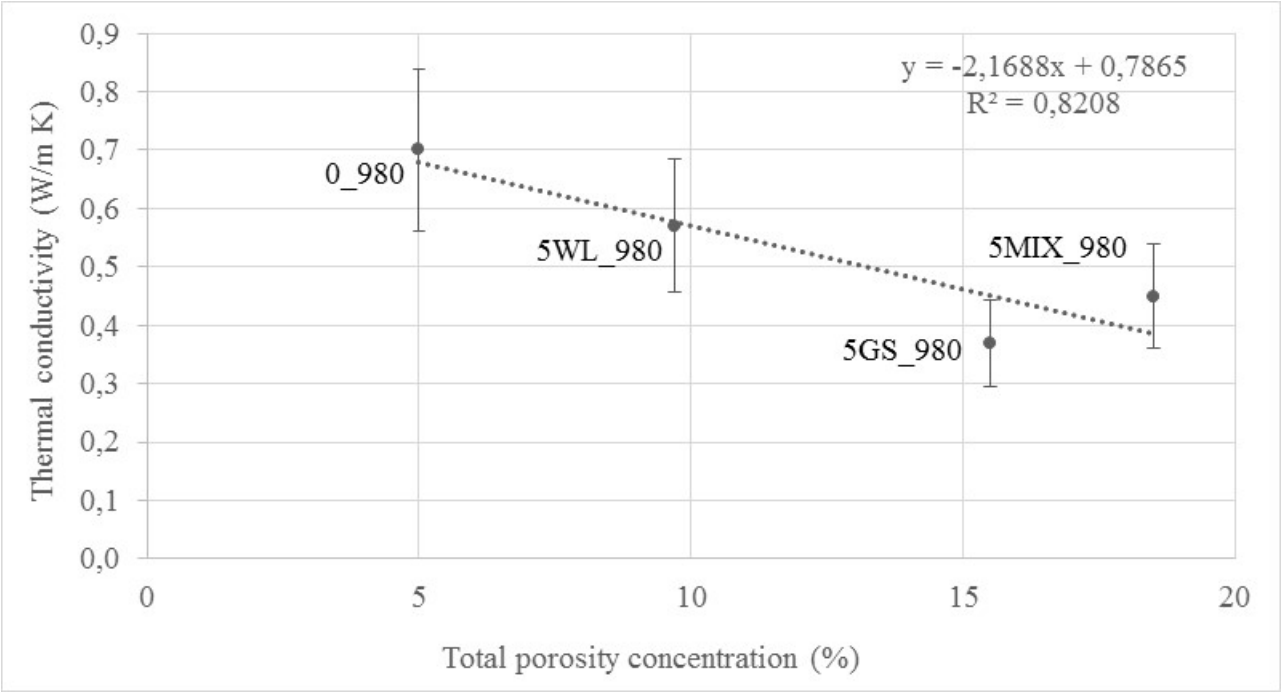


Figure 10. Flexural strength of the samples with dosage of 5wt.% and 10wt.% of wine wastes.


Thermal conductivity (W/m K)
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
1,2
1,3
1,4
1,5
1,6
1,7
Apparent density (g/cm³)
0_980
5WL_980
5MIX_980
5GS_980
y = 0,8221x - 0,6489
R² = 0,93

a)


Thermal conductivity (W/m K)
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
5
10
15
20
Total porosity concentration (%)
y = -2,1688x + 0,7865
R² = 0,8208
0_980
5WL_980
5MIX_980
5GS_980

b)

Figure 11. Thermal conductivity versus apparent density (a) and total porosity (b) of 0_*980*, 5WL_*980*, 5GS_*980,* and 5MIX_*980* samples.

Table 1: Clay major oxides (%) and trace elements (ppm) compositions. (data provided by Fornace Fosdondo, Correggio, RE)

Chemical composition	Results (wt%)	Chemical composition	Results (wt%)
SiO_2	44.5	CaO	12.5
TiO_2	0.5	Na_2O	1
Al_2O_3	12.5	K_2O	3
Fe_2O_3	7.5	P_2O_3	<0.5
MnO	<0.5		
MgO	3.5	Fluorinated compounds (total)	770 ppm

Table 2. Mineralogical analysis and Loss of Ignition (LOI) values of WW ash

Materials	**Crystalline phases [#ICDD]**	**LOI[a] (wt%)**
Clay	Quartz, SiO_2 [01–085–0457] Kaolinite, $Si_2O_5Al_2(OH)_4$ [01–078–1996] Illite, (K,H_3O) $Al_2Si_3AlO_{10}(OH)_2$ [026–0911] Chlorite, Mg-SiO_2-OH [00-002-0025]	10
Stalks (S)	Kalicinite, $KHCO_3$ [01-070-0995] Arcanite, K_2SO_4 [00-044-1414] Calcium Oxide Phosphate, $Ca_4O(PO_4)_2$ [00-025-1137]	92
Grape seeds (GS)	Kalicinite, $KHCO_3$ [01-070-0995] Arcanite, K_2SO_4 [00-044-1414] Calcium Oxide Phosphate, $Ca_4O(PO_4)_2$ [00-025-1137]	96
Wine lees (WL)	Kalicinite, $KHCO_3$ [01-070-0995] Arcanite, K_2SO_4 [00-044-1414] Calcium Oxide Phosphate $Ca_4O(PO_4)_2$ [00-025-1137] Potassium Silicate ($K_2Si_2O_5$)[00-014-0254] Calcite ($CaCO_3$)[00-001-0837]	58

[a]LOI: Loss on Ignition at 450°C.

Table 3. Technological properties of bricks: loss on ignition (LoI), linear shrinkage (LS), water absorption (WA), and apparent density.

Sample code	LoI[a] (%)	LS (%)	WA (%)	Apparent density (g/cm^3)
0_100	-	7.8	nd	1.85
5WL_100	-	7.6	nd	1.65
5GS_100	-	8.1	nd	1.64
5Mix_100	-	6.5	nd	1.59
10WL_100	-	6.0	nd	1.51
10GS_100	-	6.7	nd	1.49
10Mix_100	-	6.3	nd	1.47
0_980	14.0	7.4	16	1.65
0_1000	14.5	7.9	15	1.65
0_1020	14.6	8.1	16	1.68
5WL_980	14.1	7.6	24	1.46
5GS_980	18.2	7.9	27	1.30
5Mix_980	17.1	6.2	31	1.29
5WL_1000	14.4	7.9	24	1.44
5GS_1000	17.8	8.1	29	1.38
5Mix_1000	17.1	6.3	30	1.34
5WL_1020	14.7	7.2	23	1.48
5GS_1020	18.3	7.8	28	1.36
5Mix_1020	17.2	6.1	30	1.39
10WL_980	15.5	5.8	35	1.46
10GS_980	21.5	6.5	41	1.17
10Mix_980	19.5	7.6	36	1.24
10WL_1000	16.9	5.8	35	1.32
10GS_1000	21.3	7.2	40	1.19
10Mix_1000	19.3	7.0	37	1.26
10WL_1020	17.1	6.1	31	1.33

10GS_1020	21.5	7.1	39	1.20
10Mix_1020	19.8	7.5	36	1.25

nd=not detected

Table 4. Chromatic coordinates (L^*, a^*, b^*) and colour change ΔE^* of fired bricks.

Sample code	L^*	a^*	b^*	ΔE^*
0_980	54.62	15.85	23.63	-
0_1000	55.46	15.07	21.52	-
0_1020	56.89	14.56	22.17	-
5WL_980	57.88	14.63	22.95	3.55
5GS_980	51.97	16.66	24.04	2.80
5Mix_980	53.07	13.91	21.67	3.16
5WL_1000	53.06	16.84	23.36	3.50
5GS_1000	53.87	14.96	22.96	2.15
5Mix_1000	55.81	12.75	21.74	2.36
5WL_1020	57.73	13.90	22.78	1.23
5GS_1020	53.53	14.80	22.97	3.46
5Mix_1020	56.95	11.95	21.58	2.68
10WL_980	54.49	16.80	25.80	2.37
10GS_980	53.50	15.19	23.14	1.39
10Mix_980	54.67	13.79	21.69	2.83
10WL_1000	55.87	14.95	24.57	3.08
10GS_1000	53.72	15.25	23.51	2.65
10Mix_1000	5573	13.26	22.44	2.05
10WL_1020	56.07	14.31	23.15	1.3
10GS_1020	54.53	14.19	22.51	2.41
10Mix_1020	54.24	13.84	22.17	2.75