This paper is part of the Proceedings of the 8th International Conference on Waste Management and The Environment (WM 2016)
www.witconferences.com

The characterization of brewing waste and feasibility of its use for the production of porous ceramics

N. Quaranta[1,2], M. Caligaris[1], G. Pelozo[1], M. Unsen[1] & A. Cristóbal[3]
[1]*Environmental Studies Group, San Nicolás Regional Faculty, National Technological University, Argentina*
[2]*CIC, La Plata, Argentina*
[3]*INTEMA-CONICET, Mar del Plata National University, Argentina*

Abstract

During brewing large amounts of organic solid waste, including bagasse, yeast, malt and hops residues, among others are formed. The objective of this work is to study this waste and analyse the feasibility of its use as pore-forming material in the manufacture of porous ceramics. The residues from the production of craft beer consist of wet solid waste resulting from the separation by filtration after the mixtures maceration. This material was dried and then characterized using various techniques. Porous ceramic pieces were obtained from green bodies manufactured with mixtures of commercial clay with 10% in volume of residue, formed by uniaxial pressure of 25MPa, with the addition of 6% in weight of water. After a drying period, the samples were heat treated at 950°C following curves similar to those used in the ceramic industry. The compacts were characterized with different techniques. The obtained products have good physical and mechanical properties, with values of porosity, modulus of rupture, permanent volumetric variation and weight loss on ignition, within the range required in the market. The study of the feasibility of using this waste as a porosity former in ceramic tiles indicates that it is possible to use them without modifying the usual conditions of the industry, since the organic material incorporated combusted leaving a very low proportion of inorganic material that does not modify the diagrams with major oxides which remain being those of the clay used as main raw material, and these combustions are slow enough to allow sintering without deformation of the samples.
Keywords: waste, biomass, ceramics materials.

WIT Transactions on Ecology and The Environment, Vol 202, © 2016 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/WM160271

1 Introduction

In order to take advantage of biomass as an energy source for the production of heat, synthetic gas, bio-fuel, etc., different methods of thermal conversion have been used. In the last decade a large number of studies have been conducted in order to analyse physical, chemical and thermal processes that lead to the use of a wide variety of biomass with the highest efficiency [1–3].

As in any complex or multicomponent system, it is important to know how each compound behaves. In this sense the biomass is composed mainly of cellulose, hemicellulose and lignin. These are organic compounds differing in composition and structure, as well as in their thermal behaviour, which has been extensively studied [4, 5]. The proportion of these components change in different biomasses, being in most of them the cellulose which is in higher proportion (38–50%), followed by hemicellulose (23–32%) and lignin (15–25%) [6]. The thermal behaviour of these organic compounds is closely related to their structures. Hemicellulose is the one with the easiest combustion, due to its linear polymeric structure, with short side chains. Meanwhile, cellulose chains present arrangements associated one with each other that make combustion occur at higher temperatures, and lignin, with a closed aromatic polymer structure, is stronger and a heat resistant material. Temperature ranges cited in literature for the reactive decomposition of these compounds are between 200°C and 350°C for hemicellulose, 305°C to 375°C for cellulose, and lignin with the broadest range, between 250°C and 500°C [5, 7]. However, some authors have reported temperatures up to 900°C for heavier volatiles of lignin, considering these as more thermally stable than the other compounds [7]. Temperatures of 510°C, 590°C and 700°C for hemicellulose, cellulose and lignin respectively, have been reported in studies by Peters [8] on pistachio shells pyrolysis depending on the heating rates, concluding that ranges of reactivity temperature of these species move to higher values, as the heating rate increases.

In the brewing a large amount of organic solid waste, including bagasse, yeast, malt and hops are formed. The main destination of this waste is the feeding of cattle. However, several studies have sought more useful destinations for these waste materials. Barbosa-Pereira *et al*. [9, 10] for example have studied the antioxidant properties of extracts obtained from brewery waste stream. Other authors [11, 12] have reported studies on the use of these industrial discards as possible substrates for adsorption of heavy metals.

There are precedents on the incorporation of biomass waste in clay matrices. This addition becomes pore former, because at the operating temperatures its combustion within the brick produces gases and inorganic compounds, resulting in the so called lightweight bricks. In this way, the residue from the production of olive oil [13], wheat straw, sunflower seeds and olive pits [14], grape seeds and cherry pits [15], chipped branches of the vine [16] and rice hulls [17] have been studied.

The objective of this work is to exhaustively study brewing discards and perform a first analysis of the feasibility of their use as pore-forming material in the manufacture of lightweight ceramic materials. To do so, an addition of 10%

waste is studied. Also, the ashes of this waste are characterized since this material will remain in the final product.

2 Materials and methods

The brewing waste are formed for wet solid discards, resulting from the separation by filtration after the maceration of the mixtures. The dried residual material and the commercial clay were characterized by various techniques: optical microscopy (OM) and scanning electron microscopy (SEM) with X-ray electron dispersive analysis (EDS), X-ray diffraction (XRD), differential and thermogravimetric thermal analysis (DTA-TGA) and weight loss on ignition (LOI). The biomass was also characterized by Fourier transform infrared spectroscopy (FTIR), determination of conductivity, pH, and calorific value, and analysis of ecotoxicity.

Optical microscopy observations were made with a Zeiss-Axiotech equipment with a Donpisha 3CCD camera and image scanner. SEM analyses were performed with Philips SEM 515, with an X-ray detector (EDAX-Phoenix).

The TGA-DTA essays were conducted on a Shimadzu DTA-50 analyzer TGA-50 with YC-50 WSI.

The conductivity and pH were measured with SPER SCIENTIFIC Model 860,032 and Altronix TPX-III equipment, respectively, using 10 g of waste in 100 ml of demineralized water, stirring for 2 hours at room temperature.

X-ray diffraction diagram of the powder waste material was obtained with Philips PW 3710 equipment, for values 2θ between 0° and 80°, with radiation CuKα (λ = 1.5406 nm) and Ni filter. The operating conditions were 40 kV and 20 mA. The patterns were analysed by ASTM files (pcpdfwin files).

The calorific value of the waste material was determined by a bomb calorimeter LECO AC-350, following ASTM D-5865 standard.

The FTIR spectra were obtained with a Nicolet 6700, Thermo Electron Corp. equipment, in attenuated total reflectance – ATR mode.

Ecotoxicity tests were carried out by adapting the standard IRAM 29114: 2008. Dilutions were prepared with waste and distilled water in a wastewater ratio of 1:4 and were stirred for 2 hours, then the aqueous extract was filtered to be used in ecotoxicity tests, in concentrations of 25%, 50% and 100%. Filter papers that are saturated with 3.5 ml of the dilution to be tested and 20 seeds of the species rye grass, are placed in a Petri dish and covered. A sample with undiluted residue is also prepared. The seeds were incubated for 120 hours at 24°C, performing 3 repetitions for each concentration. Reference controls were carried out with distilled water. When the test was finished, the percent inhibition of the average elongation of the radicle regarding the average elongation of control (IR) was measured.

Porous ceramic pieces were obtained from green bodies made with mixtures of 10% in volume of residue in commercial clay. The decision to begin the study adding this percentage of residue is based on previous experiences with other biomass waste.

The pieces have been formed by uniaxial pressure of 25MPa, with addition of 6% in weight of water, into moulds of 70mm x 40mm x 18mm. After a drying

period, the samples were thermally treated at 950°C with a heating rate of 1ºC/min. The compact bodies were characterized with different techniques: porosity, permanent volumetric variation (PVV), weight loss on ignition (LOI) and mechanical properties, among others.

The porosity of samples was determined according to Standard IRAM 12510. The modulus of rupture (MOR) was performed on specimens to scale according to the aspect ratio set in the standard ASTM C67-03a in a Digimess machine, TG 100L model, in conditions of 500kg, 10 mm/min.

3 Results and discussion

Table 1 shows the semi-quantitative chemical analysis by EDS of brewery residues, ashes and clay used, expressed as percentage of the elements without considering the content of carbon and oxygen in samples. The C content is 60.6% and 24.9% in the residue and the clay, respectively.

Table 1: EDS semi-quantitative chemical analysis.

Elements [wt%]	Al	Ca	K	Fe	Mg	Na	Si	P
Residue	–	7.5	–	–	4.5	–	50.9	37.1
Ash	–	6.6	11.0	–	8.0	6.3	38.3	29.8
Clay	17.2	1.3	6.2	15.9	2.9	2.4	54.1	–

Although these semi-quantitative tests do not show Na, K and Fe in the residue, these elements were detected in the ash by EDS and XRD, because their proportions in the sample after calcinations are higher.

The results of differential thermal analysis and thermogravimetric analysis are presented in Figure 1. DTA-TGA analysis of the residue shows a wide exothermic peak at 318°C and then other wide peak with two maximum values at 451 and 470°C. The first one has been assigned to the combustion-decomposition of hemicellulose and the other to the co-combustion reaction of cellulose and lignin. The TGA curve shows three weight loss stages, one up to 200°C which corresponds to water and gases adsorbed, a second weight loss assigned to hemicellulose, and a final weight loss up to 600°C corresponding to cellulose and lignin. Although this has a small change in slope, it is not possible to determine from this curve different ranges of reaction for these two compounds. A composition of 11.5% moisture and gases, 45.8% hemicellulose, 37.9% cellulose and lignin and 4.8% of material remaining as inorganic ash is estimated. These results are very important because they indicate that in the bricks, the incorporated biomass burns into a wide temperature range, and not abruptly at a fixed temperature, which allows the slow diffusion of the gaseous products, avoiding cracking in the bricks.

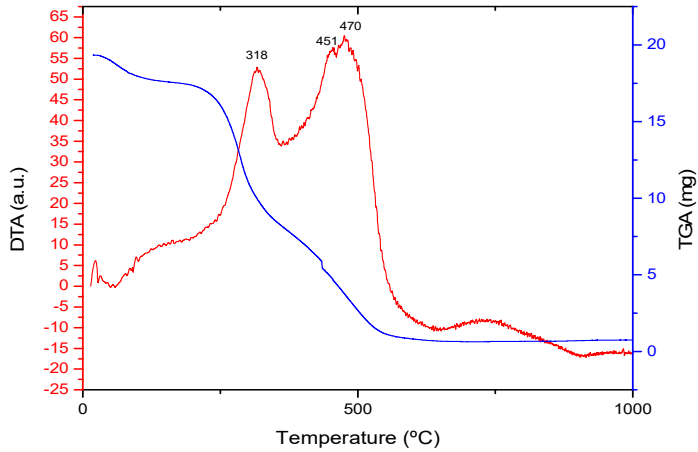

Figure 1: DTA-TGA analysis of the residue.

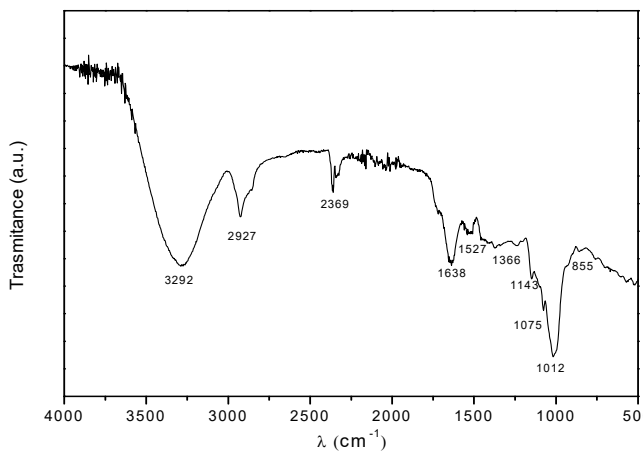

Figure 2: Waste FTIR analysis.

Figure 2 shows FTIR analysis of biomass. The bands have been assigned to the functional groups according to Table 2, wherein the associated polymers present in the biomass are also expressed [18–20].

The calorific value determined for the residual material was 4422 kcal/kg. This caloric contribution during the firing of bricks does not modify the temperatures at laboratory scale due to the material proportions used in these samples.

pH and conductivity were measured for this residue at room temperature and after 2 hours under stirring, obtaining values of conductivity of 1876 µS and pH 4.5 showing that this is an acidic residue, which cannot be deposited uncontrollably in all kinds of soils.

Table 2: Analysis of FTIR. C: cellulose, H: hemicellulose, L: lignin.

$\lambda[cm^{-1}]$	Functional group	Polymer – Compound
855	Glycosidic linkage	C – H
1012	C-O, C=C and C-C-O stretching	C – H – L
1075	C-OH and C-H stretching	C – L
1143	C-O-C asymmetrical stretching	C – H
1366	C-H methyl group bending	C – H – L
1527	Aromatic ring vibration	L
1638	C=O, C-N and C-N-H stretching (amides)	C – L
2359	O=C=O asymmetric stretching	CO_2
2927	C-H aromatic methoxy group stretching	L
3292	O-H and N-H stretching	L

On the other hand, the ecotoxicity test shows that the presence of these residues inhibits the normal development of sensitive species, which is directly related to acidic property.

These three determinations, pH, conductivity and ecotoxicity, are important in order to know the characteristics of this biomass waste in those cases in which it is deposited and maintained in industries directly on the ground in the open.

Figures 3 to 5 show the SEM images of the clay employed in this study, the residue analysed and its ashes, respectively. In these figures, it is possible to observe the fibrous structure of biomass residual grains, and the ashes that maintain the original shape of the grain, although they disintegrate very easily when handling.

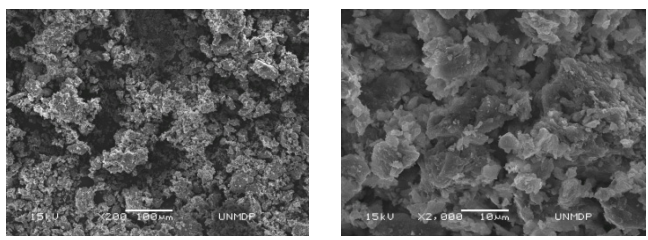

Figure 3: SEM images of the clay.

The X-ray diffraction diagram of the residue (Figure 6), shows the typical structure of this type of biomass, with a single broad peak between 15° and 28° in 2θ, with overlapping small peaks at angles 15.2°; 19.9°; 22.3° and 32.0°. Several authors have identified peaks in this spectra region, studying other biomass, as belonging to low crystalline cellulose. Thus Mtibe *et al*. [21], in their studies on

cellulose from corn, have determined the presence of peaks 2θ at 15.7°, 22.6° and 34.9°. On the other hand, Benitez-Guerrero *et al*. [2] have obtained diffraction peak values in their work with natural sisal cellulose fibres (hemp plant) in 2θ 15°, 16.5°, 20.5°, 22.5° and 34.5°.

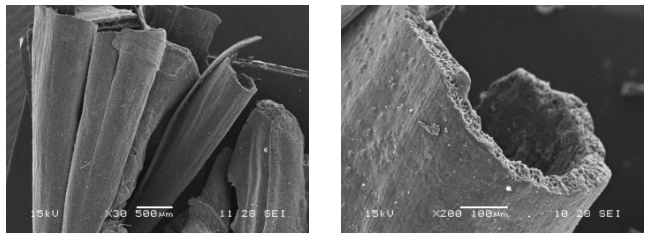

Figure 4: SEM photographs of the brewing waste.

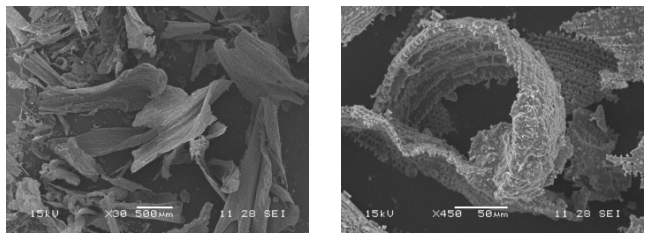

Figure 5: SEM photographs of the residue's ashes.

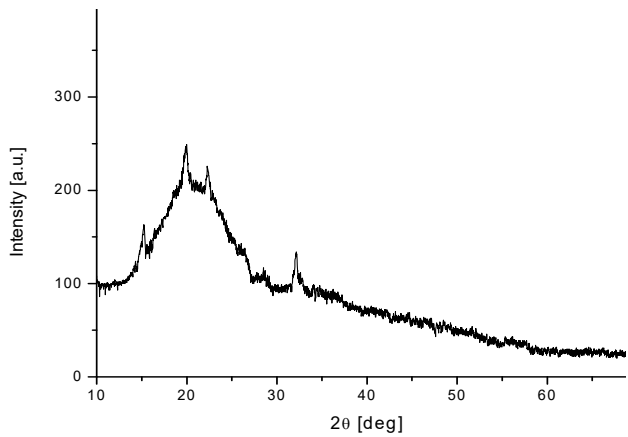

Figure 6: XRD of the brewing residue.

Cellulose samples from sugarcane studied by Rollin *et al*. [22], show the presence of peaks at angles 2θ 15.1°, 22.2° and 34.3°, that these authors assigned to different planes of the unit cell.

The XRD pattern obtained from the ashes of this residue (Figure 7), shows the presence of diffraction peaks assigned to cristobalite phase (SiO_2, pdf 82-0512), calcium phosphate (Ca_2P2O_7, pdf 45-1061), calcium magnesium phosphate ($(CaMg)_3(PO_4)_2$, pdf 13-0404) and iron oxide (Fe_3O_4, pdf 88-0315). These compounds remain in the brick after the heat treatment.

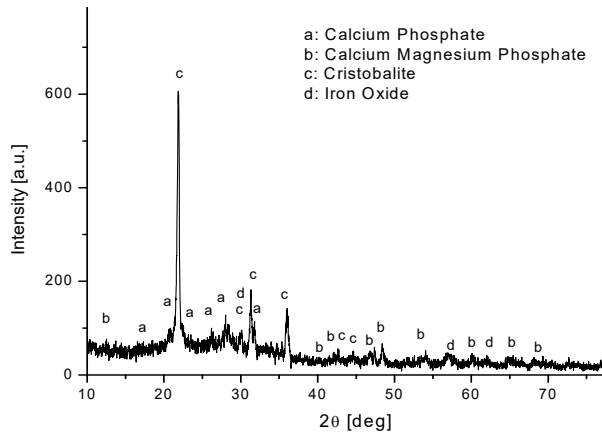

Figure 7: XRD of the biomass ashes.

Figure 8 shows the macroscopic appearance of the bricks obtained with commercial clay and with mixtures of clay and 10% in volume of brewing residue.

The obtained pieces are compact, with intense reddish colour due to the Fe content of the commercial clay, and a greater open porosity in the brick obtained with the residue addition is observed.

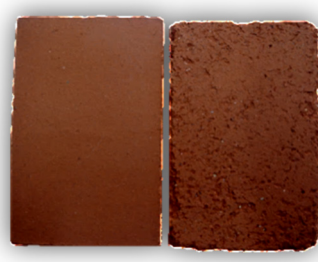

Figure 8: Bricks with clay alone (left) and with 10% of residue (right).

Figure 9 shows optical micrographs of the bricks. The upper images show the bricks without addition of residue, in which the structure is very homogeneous, with internal pores of small size. Lower images correspond to bricks with 10% of waste. In these bricks it is possible to see the presence of numerous pores of various sizes, larger than those in the clay bricks, distributed evenly throughout the structure. These result from the combustion of organic biomass material during the sintering process.

These pores are seen as white areas because they are covered with resin due to sample preparation for observation by OM, that is, the brick pieces are embedded in resin and polished. In the latter micrographs, at higher magnification, the edges of these pores are observed.

Table 3 shows the results of the properties characterization of the obtained bricks.

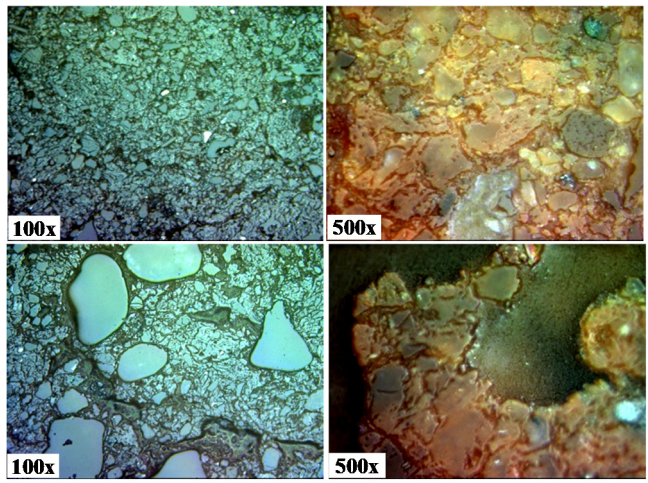

Figure 9: Optical micrographs of bricks. Upper images correspond to bricks without addition of residue and lower images correspond to bricks with 10% of waste.

Table 3: Bricks' properties.

	PVV [%]	LOI [%]	Porosity [%]	MOR [MPa]
RC0	- 4.3	5.3	24.2	10.2
RC10	- 4.7	9.8	30.2	7.7

It is observed that the values of permanent volumetric variation (PVV), loss on ignition (LOI) and porosity of the samples with addition of 10% residue (sample RC10), are higher than those obtained for samples of clay without addition (sample RC0). This result is expected due to the combustion of organic material.

The mechanical resistance measured in this case by the flexural strength (MOR) is lower for the RC10. However, this brick still has a MOR value suitable for market requirements for this kind of materials.

4 Conclusions

In this paper the feasibility of using brewing waste as porosity former in ceramic pieces was analysed. The results show that it is possible to use this residue without modifying the conditions of usual heat treatment in industry, since in the conditions tested the organic material burn leaving a very low proportion of inorganic substances. In addition, the reactions of this biomass with temperature are slow enough to allow the sintering without deformation of the pieces. The products obtained from mixtures of clay and 10% biomass, exhibit good physical and mechanical properties, with values of porosity, modulus of rupture, permanent volumetric variation and weight loss, within the range required in the market for these kinds of products.

Acknowledgements

The authors offer thanks to the Scientific Investigations Commission of Buenos Aires Province (CICPBA), National Technological University (UTN) and National Agency for Scientific and Technological Promotion (ANPCyT) of Argentina, for the financial support.

References

[1] Abdullah, S., Yusup, S., Ahmad, M.M., Ramli, A. & Ismail, L. Thermogravimetry study on pyrolysis of various lignocellulosic biomass for potential hydrogen production. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, **4(12)**, pp. 137–141, 2010.

[2] Benitez-Guerrero, M., López-Beceiro, J., Sánchez-Jiménez, P.E. & Cosp, J.P. Comparison of thermal behavior of natural and hot washed sisal fibers based on their main components: cellulose, xylan and lignin. TG-FTIR analysis of volatile products. *Thermochimica Acta*, **581**, pp. 70–86, 2014.

[3] Acikalin, K., Karaca, F. & Bolat, E. Pyrolysis of pistachio Shell: Effects of pyrolysis conditions and analysis of products. *Fuel,* **95**, pp. 169–177, 2012.

[4] Gang, W., Wen, L., Baoqing, L. & Chen, H. TG study on pyrolysis of biomass and its three components under syngas. *Fuel*, **87**, pp. 552–558, 2008.

[5] Wu, H., Zhao, Z., Li, H. & He, F. Low temperature pyrolysis characteristics of major components of biomass. *Journal of Fuel Chemistry and Technology*, **37**, pp. 427–432, 2009.
[6] J. Mac Millan. Biotechnological routes to biomass conversion. Biomass & Solar Energy 2004: S10 and 11. www.slideshare.net/Biorefinery/biotechnological-routes-to-biomass-conversion
[7] Uslu, A., Faaij, A. & Bergman P. Pretreatment technologies and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. *Energy*, **33**, pp. 1206–1223, 2008.
[8] Peters, B. Prediction of pyrolysis of pistachio shells based on its components hemicellulose, cellulose and lignin. *Fuel Processing Technology*, **92**, pp. 1993–1998, 2011.
[9] Barbosa-Pereira, L.A., Angulo, I., Paseiro-Losada, P. & M. Cruz, J. Phenolic profile and antioxidant properties of a crude extract obtained from a brewery waste stream. *Food Research International*, **51**, pp. 663–669, 2013.
[10] Barbosa-Pereira, L., Bilbao, A., Vilches, P., Angulo, I., Lluis J., Fité, B., Paseiro-Losada, P. & Cruz J. M. Brewery waste as a potential source of phenolic compounds: Optimisation of the extraction process and evaluation of antioxidant and antimicrobial activities. *Food Chemistry*, **145**, pp. 191–197, 2014.
[11] Chen, C. & Wang, J. Removal of Pb+, Ag+, Cs+ and Sr+ from aqueous solution by brewery´s waste biomass. *Journal of Hazardous Materials*, **151**, pp. 65–70, 2008.
[12] Marques, P., Pinheiro, H. M. & Rosa, M. F. Cd(II) removal from aqueous solution by immobilised waste brewery yeast in fixed-bed and airlift reactors. *Desalination*, **214**, pp. 343–351, 2007.
[13] de la Casa, J.A., Romero I., Jiménez, J. & Castro, E. Fired clay masonry units production incorporating two-phase olive mill waste (alperujo). *Ceramics International*, **38(6)**, pp. 5027–5037, 2012.
[14] Bories, C., Aouba, L., Vedrenne, E. & Vilarem, G. Fired clay bricks using agricultural biomass wastes: Study and characterization. *Construction and Building Materials*, **91**, pp. 158–163, 2015.
[15] Barbieri, L., Andreola, F., Lancellotti I. & Taurino R. Management of agricultural biomass wastes: Preliminary study on characterization and valorisation in clay matrix bricks. *Waste Management*, **33(11)**, pp. 2307–2315, 2013.
[16] Velasco, P.M., Ortiz, M.P.M., Giró, M.A.M., Melia, D.M. & Rehbein, J.H. Development of sustainable fired clay bricks by adding kindling from vine shoot: Study of thermal and mechanical properties. *Applied Clay Science*, **107**, pp. 156–164, 2015.
[17] Mohanta, K., Kumar, A., Parkash, O. & Kumar, D. Processing and properties of low cost macroporous alumina ceramics with tailored porosity and pore size fabricated using rice husk and sucrose. *Journal of the European Ceramic Society*, **34(10)**, pp. 2401–2412, 2014.

[18] Xu, F., Yu, J., Tesso, T., Dowell, F. & Wang, D. Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review. *Applied Energy*, **104**, pp. 801–809, 2013.
[19] Gholizadeh, H., Naserian, A.A., Xin, H., Valizadeh, R., Tahmasbi, A.M. & Yu, P. Detecting carbohydrate molecular structural makeup in different types of cereal grains and different cultivars within each type of grain grown in semi-arid area using FTIR spectroscopy with uni- and multi-variate molecular spectral analyses. *Animal Feed Science and Technology*, **194**, pp. 136–144, 2014.
[20] Strassberger, Z., Prinsen, P., van der Klis, F., van Es, D.S., Tanase, S. & Rothenberg, G. Lignin solubilisation and gente fractionation in liquid ammonia. *Green Chemistry*, **17**, pp. 325–334, 2015.
[21] Mtibe, A., Linganiso, L., Mathew, A., Oksman, K., John, M. & Anandijiwala, R. A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibers. *Carbohydrate Polymers*, **118**, pp. 1–8, 2015.
[22] Rollin, J., Zhu, Z., Sathitsuksanoh, N. & Zhang, Y.H.P. Increasing cellulose accessibility is more important than removing lignin: a comparison of cellulose solvent-based lignocelluloses fractionation and soaking in aqueous ammonia. *Biotechnology and Bioengineering*, **108(1)**, pp. 20–30, 2011.